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(54) STEEL MATERIAL HAVING SUPERIOR TOUGHNESS AT WELDING HEAT AFFECTED ZONE

(57) In this steel material satisfying a predetermined chemical composition and having a remainder comprising iron and unavoidable impurities, a complex oxide is contained containing REM, Zr, Ti, Al, Ca, and S, the complex oxide has no greater than 5.0/mm^2 of oxides having a circular-equivalent diameter of greater than 3 μm, and with respect to complex oxides having a circular-equivalent diameter of 0.1-3 μm, there are at least 100/mm^2 of complex oxides satisfying formula (1), and furthermore the average composition of the complex oxides that are 0.1-3 μm satisfying formula (1) is such that there is no greater than 20% of Al_2O_3, 3-20% of TiO_2, 5-50% of ZrO_2, 5-50 of REM oxide, 5-50% of CaO, and 1-15% of S.

$$0.008 \leq (1/d) \times \{\text{mass\% } S/(\text{mass\% } CaO + \text{mass\% } REM_2O_3)\} \leq 0.289 \ldots (1)$$

(where d is the circular·equivalent
diameter of each complex oxide, and is 0.1-·3 μm).

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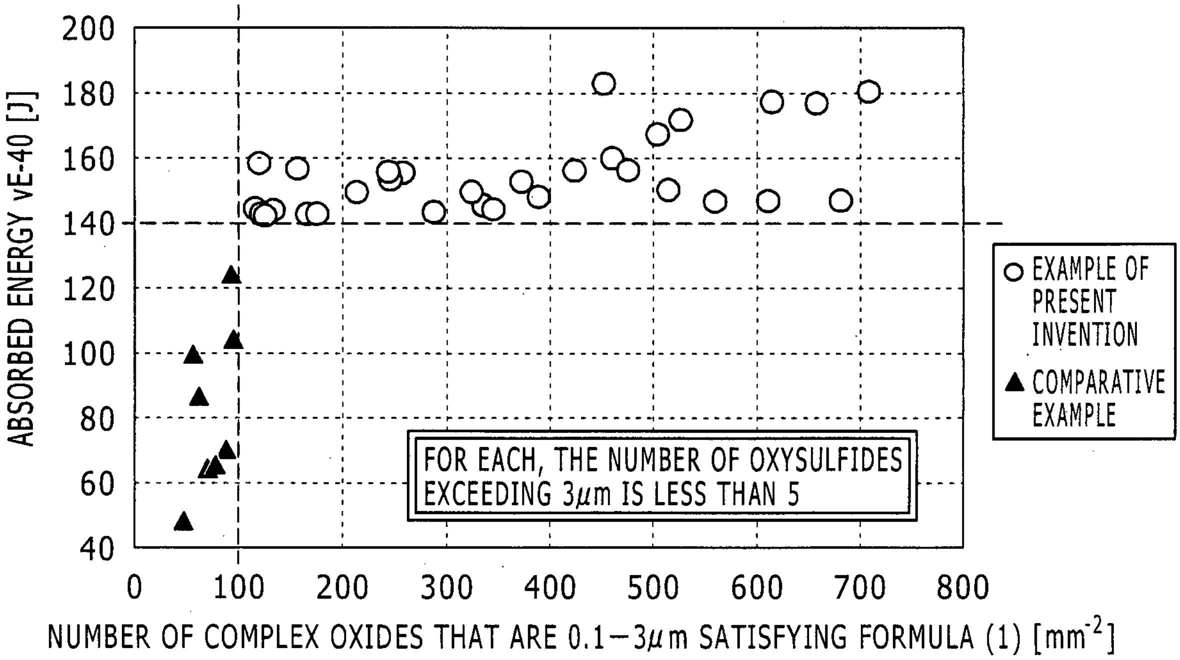
FIG. 1


ABSORBED ENERGY vE-40 [J]
200
180
160
140
120
100
80
60
40
0
100
200
300
400
500
600
700
800
NUMBER OF COMPLEX OXIDES THAT ARE 0.1−3μm SATISFYING FORMULA (1) [mm⁻²]
FOR EACH, THE NUMBER OF OXYSULFIDES EXCEEDING 3μm IS LESS THAN 5
○ EXAMPLE OF PRESENT INVENTION
▲ COMPARATIVE EXAMPLE

Description

Technical Field

[0001] The present invention relates to a thick steel plates suitable to be used in welded structures such as ships, constructions, and bridges, and in particular, to a steel material that achieves superior HAZ toughness even for high heat input welding.

Background Art

[0002] In recent years, there is the tendency that structures using steel materials, such as bridges, high-rise buildings, and large ships, grow in size, and there is a need for steel materials with high strength and large thicknesses in order to achieve these large structures. In addition to that, there is a need for improving welding efficiencies in welding steel materials with high strength and large thicknesses in order to improve construction efficiencies of large structures and to reduce construction cost. In order to improve a welding efficiency of a steel material, it is effective to reduce the number of welding times for the same portion, and high heat input welding with a high efficiency is selected, in which welding is completed at one time by performing high heat input welding in which a large amount of heat (welding heat) is applied to a steel material, rather than the welding in which small amounts of heat (welding heat) are applied multiple times to a steel material.

[0003] However, the temperature of a welding heat affected zone (hereinafter, also referred to as a HAZ) exposed to welding heat generally becomes high while welding is being performed, regardless of whether the amount of heat of the welding is large or small, and hence the crystal grain of the steel material is likely to coarsen. In addition, as the amount of heat put into a steel material is larger, the temperature of a HAZ becomes higher, thereby causing a cooling time to be longer. It is already known that, because a long cooling time in a high temperature causes the formation of a brittle upper bainite structure or the formation of an embrittlement structure, such as island martensite, in a HAZ to be promoted, the HAZ toughness of a steel material may be decreased.

[0004] In order to deal with the aforementioned decrease in HAZ toughness occurring due to welding heat, the techniques disclosed in Patent Documents 1-5 are presented. Patent Document 1 is intended to provide a steel material having superior HAZ toughness and a production method thereof. Specifically, the production method disclosed in Patent Document 1 is said that, fine sulfides are dispersed and the particles in a HAZ structure heated to no lower than 1400°C are made fine by adding Mg and/or REM in addition to Ca having a strong sulfide formation ability in molten steel, so that fine oxides are formed, thereby allowing the HAZ toughness good even for high heat input welding of no less than 200 kJ/cm to be achieved.

[0005] Patent Document 2 is intended to provide steel for high strength welded structure, the steel having superior base plate toughness and superior welded zone HAZ toughness, and a production method thereof. Specifically, the production method disclosed in Patent Document 2 is intended to cause heated γ particles in a base plate to be fine and further to cause heated γ particles in a HAZ to be fine regardless of welding heat input, by adding one or more of Mg, Ca, and REM after Ti is added or simultaneously when Ti is added such that oxides and sulfides are finely dispersed. The production method of Patent Document 2 is said that steel for high strength welded structure, the steel having good base plate toughness and good welded zone HAZ toughness, can be produced as an effect created by these two particle refinements.

[0006] Patent Document 3 is intended to provide a thick steel plate having superior HAZ toughness for super-high heat input welding and a production method thereof. Specifically, in the production method of Patent Document 3, the form of the dendrite formed in a solidification process is further controlled in addition to an adjustment in which the particle compositions of oxides and sulfides, etc., in molten steel are adjusted. Thereby, the production method of Patent Document 3 is said that, austenite particles can be made fine even in a HAZ for super-high heat input welding of no less than 300 kJ/cm by dispersing the dispersed particles in a steel plate more uniformly and finely than related art, thereby allowing HAZ toughness to be remarkably improved.

[0007] Patent Document 4 is intended to provide a high-strength steel plate having a strength of X100 or more in the API standards, the steel plate having good HAZ toughness. Specifically, the high-strength steel plate of Patent Document 4 contains (1) TiN-based fine precipitates containing Mg-based oxides having a size of no greater than 0.1 μm by limiting the amounts of Ti, Mg, REM, Al, S, and N, thereby suppressing the coarsening of γ particles even in the vicinity of a fusion line. Further, this high-strength steel plate is said to allow the structure to be made fine across a HAZ and HAZ toughness to be improved by containing (2) complexes between oxides mainly formed by Ti, Mg, and REM, the oxides having a size of no less than 0.1 μm, and MnS, so that IGF is produced from the insides of relatively small γ particles.

[0008] Patent Document 5 is intended to present a non-heat treated high-tensile steel material having good base plate toughness and having good HAZ toughness. Specifically, the non-heat treated high-tensile steel material of Patent Document 5 is controlled to contain, in units of weight%, 20-90% of Ti oxides, 5-50% of the total of CaO and REM oxides, and no greater than 70% of Al_2O_3 as optimal composition ranges of optimal oxide-based inclusions. It is said that, thereby, the non-heat treated high-tensile steel material can effectively utilize an ability of suppressing the crystal grain coarsening of the inclusions (pinning effect) without causing nozzle clogging or production of a harmful inclusion cluster, and hence HAZ toughness can be improved, and further the toughness and strength of a base plate can be improved by optimally dispersing TiN or further VN.

Prior Art Document

Patent Document

[0009]

[Patent Document 1] Japanese Patent Publication No. 4261968
[Patent Document 2] Japanese Patent Publication No. 4762450
[Patent Document 3] Japanese Patent Publication No. 4039223
[Patent Document 4] Japanese Patent Application Publication No. Hei 11-264048
[Patent Document 5] Japanese Patent Publication No. 4144121

Disclosure of the Invention

Problem to be Solved by the Invention

[0010] As described above, each of Patent Documents 1-5 discloses that a decrease in HAZ toughness, occurring due to welding heat, can be dealt with; however, it is difficult to improve HAZ toughness for further high heat input welding, even when any technique is used. The technique disclosed in each of Patent Documents 1-3 is intended to make a HAZ structure fine by the pinning effect of an oxysulfide, but each of the Patent Documents never refers to an effect of making a structure fine by intra-granular transformation resulting from the oxysulfide, and hence the technique cannot be said as being a technique for dealing with further high heat input welding.

[0011] Patent Document 4 refers to structure transformation originating at an oxide, but a means for a coarse oxide, etc., is not described; and accordingly the possibility that HAZ toughness may be decreased due to the production of a coarse oxide cannot be excluded, and hence the technique thereof cannot be said as being a technique for dealing with further high heat input welding. Additionally, the technique disclosed in Patent Document 5 is one in which a HAZ structure is made fine by the pinning effect of an oxysulfide, but is not one in which the control of the structure transformation originating at an oxysulfide is taken into consideration, and accordingly the technique cannot be said as being a technique for dealing with further high heat input welding.

[0012] The present invention has been made in view of the aforementioned problems, and an object of the invention is to provide a steel material having superior toughness at welding heat affected zone (HAZ toughness) for high heat input welding.

Means for Solving the Problem

[0013] In the present invention, the following means is adopted in order to achieve the above object. That is, a technical means for solving the problems in the invention is a steel material containing, in units of mass%, 0.02-0.13% of C, 0.05-0.5% of Si, 1.0-2.5% of Mn, no greater than 0.03% of P (exclusive of 0%), no greater than 0.01% of S (exclusive of 0%), 0.002-0.040% of Al, 0.005-0.040% of Ti, 0.0003-0.020% of Zr, 0.0003-0.020% of REM, 0.0003-0.0080% of Ca, 0.0030-0.010% of N, and 0.0003-0.0050% of O, the steel material having a remainder comprising iron and unavoidable impurities and having superior toughness at welding heat affected zone, in which: the steel material contains a complex oxide containing REM, Zr, Ti, Al, Ca, and S; the complex oxide in the steel material has no greater than 5.0/mm^2 of oxides having a circular-equivalent diameter of greater than 3 μm; with respect to complex oxides having a circular-equivalent diameter of 0.1-3 μm, there are at least 100/mm^2 of complex oxides satisfying formula (1); and furthermore the average composition of the complex oxides that are 0.1-3 μm satisfying formula (1) contains 20% or less of Al_2O_3, 3-20% of TiO_2, 5-50% of ZrO_2, 5-50% of REM oxide, 5-50% of CaO, and 1-15% of S.

$$0.008 \leq (1/d) \times \{\text{mass\% S}/(\text{mass\% CaO} + \text{mass\% REM}_2\text{O}_3)\} \leq 0.289 \ldots (1)$$

(where d is the circular·equivalent diameter of each complex oxide, and is 0.1-·3 μm).

[0014] Herein, it is better to contain at least one of 0.05-1.50% of Ni, 0.05-1.50% of Cu, 0.05-1.50% of Cr, and 0.05-1.50% of Mo.

[0015] It is also better to contain at least one of 0.002-0.10% of Nb and 0.002-0.10% of V. It is further better to contain 0.0005-0.0050% of B.

Advantage of the Invention

[0016] According to the present invention, a steel material, having superior toughness at welding heat affected zone (HAZ toughness) for high heat input welding, can be obtained.

Brief Description of the Drawings

[0017]

Fig. 1 is a graph showing measurement results of the HAZ toughness of steel materials according to an embodiment of the present invention;

Fig. 2 is a graph showing measurement results of the HAZ toughness of steel materials according to the present embodiment; and

Fig. 3 is a graph showing measurement results of the HAZ toughness of steel materials according to the embodiment.

Modes for Carrying Out the Invention

[0018] Hereinafter, a steel material having superior toughness at welding heat affected zone according to an embodiment of the invention of the present application (hereinafter, simply referred to as a steel material) will be described in detail with reference to the drawings. The steel material according to the present embodiment is a steel material exerting superior toughness of a welding heat affected zone (HAZ, Heat Affected Zone) that has been affected by very large welding energy in which welding heat input exceeds, for example, 60 kJ/mm. In the following description, a welding heat affected zone in the steel material according to the embodiment will be represented by a HAZ, and the toughness of a HAZ will be represented by HAZ toughness.

[0019] The steel material according to the present embodiment can stably achieve good HAZ toughness even for high heat input welding by producing a predetermined amount of complex oxides (oxysulfides containing Al, Ti, Zr, REM, Ca, and S), the complex oxide serving as a nucleus for intra-granular transformation, with the size and S concentration thereof being properly controlled. Specifically, the steel material is characterized as follows: the number of coarse complex oxides having a circular-equivalent diameter of greater than 3 μm, which adversely affect an improvement in HAZ toughness, is significantly controlled; and complex oxides having a circular-equivalent diameter of 0.1-3 μm, which is useful for an improvement in HAZ toughness, and having the composition and particle size thereof properly controlled are contained such that the number of the complex oxides is no less than a predetermined value. By this characteristic, the steel material according to the embodiment can exert stably superior HAZ toughness even for welding with large heat input.

[0020] The steel material according to the present embodiment, having the aforementioned characteristic, can be obtained by adding, for example, in the secondary refining of molten steel, each element so as to have the chemical component composition described below. The steel material according to the embodiment (hereinafter, simply referred to as the present steel material) contains: 0.02-0.13% of Carbon (C), 0.05-0.5% of Silicon (Si), 1.0-2.5% of manganese (Mn), no greater than 0.03% of phosphorus (P) (exclusive of 0%), no greater than 0.01% of sulfur (S) (exclusive of 0%), 0.002-0.040% of aluminum (Al), 0.005-0.040% of titanium (Ti), 0.0003-0.020% of zirconium (Zr), 0.0003-0.020% of rare earth metal (REM), 0.0003-0.0080% of calcium (Ca), 0.0030-0.010% of nitrogen (N), and 0.0003-0.0050% of oxygen (O), with a remainder comprising iron and unavoidable impurities. Furthermore, the present steel material contains complex oxides containing REM, Zr, Ti, Al, Ca, and S, and the complex oxide in the steel material has no greater than 5.0/mm^2 of oxides having a circular-equivalent diameter of greater than 3 μm, and with respect to complex oxides having a circular-equivalent diameter of 0.1-3 μm, there are at least 100/mm^2 of complex oxides satisfying formula (1).

$$0.008 \leq (1/d) \times \{\text{mass\% S}/(\text{mass\% CaO} + \text{mass\% REM}_2\text{O}_3)\} \leq 0.289 \ldots (1)$$

(where d is the circular·equivalent
diameter of each complex oxide, and is 0.1-·3 μm).

[0021] Further, the average composition of the complex oxides that are 0.1-3 μm satisfying formula (1) contains 20% or less of Al_2O_3, 3-20% of TiO_2, 5-50% of ZrO_2, 5-50% of REM, 5-50% of Cao, and 1-15% of S.

[0022] In the present embodiment, the contents of elements and components are represented bv simply using "%", but it is be noted that the "%" is represented by simplifying "mass%". Subsequently, the structure of the aforementioned present steel material will be described in detail.

[Carbon (C): 0.02-0.13%]

[0023] C is an element indispensable for securing the strength of a steel material (base plate). Accordingly, C is added in an amount of no less than 0.02%, and preferably no less than 0.04%. However, if the content of C exceeds 0.13%, many island martensites (MA) are produced in a HAZ, which leads to a decrease in HAZ toughness, and also adversely affects weldability due to the generation of CO gas, etc. Accordingly, the content of C is made no greater than 0.13%, and preferably no greater than 0.1%.

[Silicon (Si): 0.05-0.5%]

[0024] Si is an element having a deacidification action and also contributing to an improvement in the strength of a base plate by solute strengthening. Accordingly, Si is added in an amount of no less than 0.05%, preferably no less than 0.07%, and more preferably no less than 0.1%. However, if the content of Si exceeds 0.5%, the weldability and the toughness of a steel material are decreased, and hence the upper limit of the content thereof is made 0.5%. In order to particularly improve HAZ toughness, it is recommended that the content of Si is made no greater than 0.3%. HAZ toughness is further improved as the content of Si is smaller; however, the strength of a steel material may be conversely decreased. Accordingly, the content of Si is made no greater than 0.5%, preferably no greater than 0.35%, and more preferably no greater than 0.25%.

[Manganese (Mn): 1.0-2.5%]

[0025] Mn is an element contributing to an improvement in the strength of a base plate. However, if the content of Mn is less than 1.0%, the strength is decreased. Accordingly, Mn is added in an amount of no less than 1.0%, and preferably no less than 1.3%. However, if the content of Mn exceeds 2.5%, the weldability of a base plate is decreased. Accordingly, the content of Mn is made no greater than 2.5%, and preferably no greater than 2.0%.

[Phosphorus (P): no greater than 0.03%]

[0026] P is an element likely to segregate, and is an element that segregates particularly in crystal grain boundaries in a steel material such that HAZ toughness is decreased. Because P is normally and unavoidably contained in a base plate in an amount of approximately 0.001%, the content of P is specified to be no greater than 0.03%. The content of P is made preferably no greater than 0.02%, and more preferably 0.01%. In the present embodiment, however, the content of P is not inclusive of 0%.

[Sulfur (S): no greater than 0.01%]

[0027] S is an element that produces a sulfide (MnS) by bonding with Mn, thereby decreasing the toughness or the ductility in the through-thickness of a base plate. For example, if S produces a sulfide of REM (e.g., LaS or CeS) by bonding with REM such as lanthanum La, cerium Ce, or the like, the production of REM oxides is hampered, and hence HAZ toughness is decreased. However, S is normally and unavoidably contained in a base plate in an amount of approximately 0.0005%, and hence the content of S is specified to be no greater than 0.01%. The content of S is preferably no greater than 0.008%, and more preferably no greater than 0.006%. In the present embodiment, however, the content of S is not inclusive of 0%.

[Aluminum (Al): 0.002-0.040%]

[0028] Al is an element acting as a deoxidizing agent. If the content of Al is small, molten steel is likely to be contaminated with oxygen. Accordingly, Al is added in an amount of no less than 0.002%, preferably no less than 0.004%, and more preferably no less than 0.005%. However, if Al is added to a base plate in an excessive amount, the added Al produces coarse Al oxides by reducing the oxides in the base plate, thereby decreasing HAZ toughness. Accordingly, the content of Al is made no greater than 0.040%, preferably no greater than 0.025%, and more preferably no greater than 0.015%.

[Titanium (Ti): 0.005-0.040%]

[0029] Ti is an element contributing to an improvement in HAZ toughness by producing, in a base plate, nitrides, such as TiN, and oxides containing Ti. Accordingly, Al is added in an amount of no less than 0.005%, preferably no less than 0.010%, and more preferably no less than 0.014%. However, if Ti is added to a base plate in an excessive amount, the base plate itself is hardened by the solute strengthening of Ti, which leads to a decrease in HAZ toughness. Accordingly, the content of Ti is made no greater than 0.040%, preferably no greater than 0.030%, and more preferably no greater than 0.025%.

[Zirconium (Zr): 0.0003-0.020%]

[0030] Zr is an element contributing to an improvement in HAZ toughness by producing complex oxides containing Zr. Accordingly, Zr is added in an amount of no less than 0.0003%, preferably no less than 0.0005%, and more preferably no less than 0.0009%. However, if Zr is added to a base plate in an excessive amount, coarse Zr oxides (ZrO_2) are produced, thereby decreasing HAZ toughness. Further, the toughness of the base plate itself is decreased with coarse Zr carbides (ZrC) being produced. Accordingly, the content of Zr is made no greater than 0.020%, preferably no greater than 0.015%, and more preferably no greater than 0.010%.

[Rare Earth Metal (REM): 0.0003-0.020%]

[0031] REM is an element necessary for producing oxides. Oxides including the oxides produced by REM are likely to be finely dispersed in a steel material. These finely dispersed oxides serve as product nuclei of intergranular α in a HAZ, which contributes to an improvement in HAZ toughness. Accordingly, REM is added in an amount of no less than 0.0003%, preferably no less than 0.0005%, and more preferably no less than 0.0009%. However, if REM is added in an excessive amount, solid solution REM is produced and segregate in a base plate, thereby deteriorating the toughness of the base plate itself. Accordingly, the content of REM is made no greater than 0.020%, preferably no greater than 0.015%, and more preferably no greater than 0.010%.

[0032] Specifically, the REM means elements including lanthanoid elements (15 elements ranging from La to Ln), Sc (scandium), and Y (yttrium). In the present embodiment, it is preferable to contain, of these elements, at least one element selected from the group consisting of La, Ce, and Y, and more preferable to contain La and/or Ce.

[Calcium (Ca): 0.0003-0.0080%]

[0033] Ca is an element necessary for producing an oxide. Because Ca also serves as a product nucleus of intergranular α in a HAZ and contributes to an improvement in HAZ toughness, it is better to contain Ca in an amount of no less than 0.0003%, preferably no less than 0.0005%, and more preferably no less than 0.0007%. However, if Ca is added in an excessive amount, coarse Ca sulfides are produced, thereby deteriorating the toughness of a base plate. Accordingly, the content of Ca is made no greater than 0.0080%, preferably no greater than 0.0060%, and more preferably no greater than 0.0030%.

[Nitrogen (N): 0.0030-0.010%]

[0034] N is an element that precipitates nitrides (e.g., ZrN, TiN, etc.). A nitride contributes to an improvement in HAZ toughness by suppressing the coarsening of an austenite particle, which may occur while welding is being performed, by a pinning effect. Because N further promotes an austenite particle to be made fine by forming nitrides as the content of N is larger, N effectively acts to improve HAZ toughness. Accordingly, Al is added in an amount of no less than 0.0030%, preferably no less than 0.0040%, and more preferably no less than 0.0050%. However, if the content of N exceeds 0.010%, the amount of solid solution N is increased, thereby deteriorating the toughness of a base plate itself and also HAZ toughness. Accordingly, the content of N is made no greater than 0.010%, preferably no greater than 0.0090%, and more preferably no greater than 0.0080%.

[Oxygen (O): 0.0003-0.0050%]

[0035] O is an element indispensable for producing an oxide, and if the content thereof is less than 0.0003%, a sufficient amount of oxides cannot be obtained in a base plate. The content thereof is preferably no less than 0.0010%, and more preferably no less than 0.0015%. However, if the content thereof is greater than 0.0050%, HAZ toughness is decreased due to the coarsening of oxides. Accordingly, the content of O is made no greater than 0.0050%, preferably no greater than 0.0040%, and more preferably no greater than 0.0035%.

[0036] Herein, the content of O refers to the amount of total oxygen, which means the total amount of O that forms oxides in a base plate and free O in the form of a solid solution in the base plate. The present steel material contains the aforementioned each element, and a remainder comprises iron and unavoidable impurities. The components of the remainder other than the aforementioned each element are iron and unavoidable impurities (e.g., Mg, As, Se, etc.).

[0037] The present steel material containing the aforementioned elements contains complex oxides (oxides and/or oxysulfides) containing REM, Zr, Ti, Al, Ca, and S. The complex oxide included in the present steel material is an Al-Ti-Zr-REM-Ca-S-based complex oxide containing both oxides of Al, Ti, Zr, REM, and Ca and sulfides; however, the complex oxide may contain, other than these, elements such as, for example, Mn and Si, and other component elements. An Al-Ti-Zr-REM-Ca-based oxide has a good lattice matching performance with a steel material and promotes inter-granular structure transformation (intra-granular transformation) in a HAZ, and hence the oxide is effective in causing the structure of a HAZ to be made fine.

[0038] With respect to the aforementioned complex oxides in the present steel material, the number of oxides having a circular-equivalent diameter of greater than 3 μm is no greater than 5.0/mm^2 in the cross section of the steel material. Because a complex oxide having a circular-equivalent diameter of greater than 3 μm is coarse, the complex oxide conversely decreases HAZ toughness for high heat input welding whose heat input almost reaches 60 kJ/mm. Accordingly, the number of complex oxides having a size of greater than 3 μm should be made no greater than 5.0/mm^2.

[0039] On the other hand, the present steel material contains the aforementioned complex oxides such that, with respect to complex oxides having a circular-equivalent diameter of no less than 0.1 μm and no greater than 3 μm (hereinafter, expressed by 0.1-3 μm) and satisfying formula (1), there are at least 100/mm^2 in the cross section of the steel material.

$$0.008 \leq (1/d) \times \{\text{mass\% S}/(\text{mass\% CaO} + \text{mass\% REM}_2\text{O}_3)\} \leq 0.289 \ldots (1)$$

(where d is the circular·equivalent
diameter of each complex oxide, and is 0.1-3 μm).

[0040] This complex oxide having a circular-equivalent diameter of 0.1-3 μm promotes intra-granular structure transformation (intra-granular transformation) in a HAZ and improves HAZ toughness, and hence a complex oxide having a circular-equivalent diameter of 0.1-3 μm will be examined below. A complex oxide having a circular-equivalent diameter of less than 0.1 μm hardly contributes to an improvement in HAZ toughness, and hence it is not included in the number of the aforementioned complex oxides.

[0041] Hereinafter, the reason why a complex oxide having a circular-equivalent diameter of 0.1-3 μm should satisfy formula (1) will be described. First, REM and Ca are oxysulfide forming elements that can form both an oxide and a sulfide. So, if an S concentration (mass% S) to the concentrations of oxysulfide forming elements (REM_2O_3 and CaO) is too high, excessively produced sulfides hamper the matching between oxides and the matrix, and hence an ability (intra-granular transformation ability), in which a complex oxide contributes to structure control, is decreased. On the other hand, if an S concentration (mass% S) to the concentrations of oxysulfide forming elements (REM_2O_3 and CaO) is too low, the strain energy associated with the production of sulfides cannot be obtained, which becomes disadvantageous for intra-granular transformation and the intra-granular transformation ability is decreased. Furthermore, the strain energy resulting from the size of a complex oxide itself (circular-equivalent diameter d of a complex oxide) affects intra-granular transformation.

[0042] In formula (1), the second term is shown, in which these conditions under which intra-granular transformation is believed to be affected are taken into consideration. In the second term of formula (1), there are optimal ranges both in an S concentration (mass% S) to the concentrations of oxysulfide forming elements (REM_2O_3 and CaO) and in the size of a complex oxide (circular-equivalent diameter d of a complex oxide), for generating the strain energy contributing to intra-granular transformation; and it is inferred that an upper limit and a lower limit may exist in the second term of formula (1). So, the upper limit and the lower limit of the second term of formula (1) were experimentally determined.

[0043] A method for determining the upper limit and the lower limit of the second term of formula (1) will be described. A heat input test, which simulated a HAZ in welding whose heat input was 60 kJ/mm, was first performed on a test material. Thereafter, the test material having subjected to the heat input test was subjected to mirror polishing such that corrosion progressed, and the presence/absence of intra-granular transformation resulting from a complex oxide was examined by revealing the structure with the corrosion. Subsequently, the composition and the size of a complex oxide in the test material were measured by an EPMA (Electron Probe MicroAnalyzer), so that the value of the second term of formula (1) was calculated with respect to a complex oxide having a size of 0.1-3 μm.

[0044] The presence/absence of intra-granular transformation and the calculated values of the second term were summarized as the results shown in Table 1, and the range of the second term was set to be no less than 0.008 and no greater than 0.289 based on the values of the second terms of the steel materials in each of which the presence/absence of intra-granular transformation was shown with O mark (intra-granular transformation occurred).

[Table 1]

Examination results of relationship between second term of formula (1) and presence/absence of intra-granular transformation

Circular-equivalent diameter d	Composition of complex oxide			Second term of formula (1)	Presence/ absence of intra-granular transformation
[μm]	mass%S	mass%CaO	mass%REM_2O_3		
1.9	**1.1**	**39.5**	**42.3**	**0.007**	×
2.0	**1.4**	34.7	**48.5**	**0.008**	○
1.8	**2.1**	**31.1**	**40.5**	**0.016**	○
1.6	**3.4**	**10.7**	**36.3**	**0.045**	○
1.7	**4.8**	**19.6**	**22.7**	**0.067**	○
0.8	**3.2**	**19.5**	**24**	**0.092**	○
0.6	**4.3**	**15.4**	**34.2**	**0.145**	○
0.7	**8.2**	**27.5**	**38.1**	**0.179**	○
0.1	**1.4**	**26.6**	**42.3**	**0.203**	○
1.2	**13.4**	**30.2**	**13.5**	**0.256**	○
1.5	**7.2**	**7.4**	**9.2**	**0.289**	○
1.4	**9.7**	**10.8**	**12**	**0.304**	×
0.5	**4.5**	**8.1**	**19.6**	**0.337**	×

[0045] With respect to complex oxides having a circular-equivalent diameter of 0.1-3 μm and satisfying formula (1), there are at least 100/mm^2 contained, and furthermore the average composition thereof should contain no greater than 20% of Al_2O_3, no less than 3% and no greater than 20% (3-20%) of TiO_2, no less than 5% and no greater than 50% (5-50%) of ZrO_2, no less than 5% and no greater than 50% (5-50%) of REM oxide, no less than 5% and no greater than 50% (5-50%) of CaO, and no less than 1% and no greater than 15% (1-15%) of S.

[0046] This is because oxide compositions affect the lattice matching performance between an oxide and a steel material in a HAZ, and hence if the oxide compositions are not controlled such that the contents thereof fall within the aforementioned ranges, a complex oxide having a circular-equivalent diameter of 0.1-3 μm cannot contribute to the intra-granular transformation in a HAZ, that is, cannot contribute to making a HAZ structure fine. The present steel material having the aforementioned chemical component composition targets a thick steel plate having a thickness of approximately no less than 3.0 mm, and a decrease in HAZ toughness can be prevented for small to middle heat input welding and even for high heat input welding whose heat input is no less than 50 kJ/mm; and accordingly the steel material can be used as a material for large structures such as, for example, brides, high-rise buildings, and ships.

[Nickel (Ni), Copper (Cu), Chromium (Cr), Molybdenum (Mo): 0.05-1.50%]

[0047] In addition to the aforementioned component elements, the steel material according to the present embodiment may contain at least one of Ni, Cu, Cr, and Mo in an amount of no less than 0.05% and no greater than 1.50% (0.05-1.50%). Each of Cu, Ni, Cr, and Mo is an element contributing to increases in the toughness and strength of the present steel material, and each of them can be added alone or in combination thereof. In order to effectively improve the toughness and strength by adding, for example, Cu, it is preferable to contain Cu in an amount of no less than 0.05%. However, if the content of Cu exceeds 1.50%, the strength of a base plate becomes too large and the toughness of the base plate is conversely decreased, and hence HAZ toughness is also decreased. Accordingly, the content of Cu is specified to be no less than 0.05% and no greater than 1.50%.

[0048] It is preferable to contain Ni, Cr, or Mo in an amount of no less than 0.05%, similarly to Cu; however, if the content thereof exceeds 1.50%, the strength of a base plate becomes too large and the toughness of the base plate is conversely decreased, and hence HAZ toughness is also decreased. Accordingly, the content of Ni, Cr, or Mo is also specified to be no less than 0.05% and no greater than 1.50%.

[Niobium (Nb), Vanadium (V): 0.002-0.10%]

[0049] The steel material according to the present embodiment may further contain at least one of Nb and V in an amount of no less than 0.002% and no greater than 0.10% (0.002-0.10%). Each of Nb and V precipitates as a carbonitride. Because this carbonitride exerts a pinning effect, the coarsening of an austenite particle is suppressed while welding is being performed, thereby contributing to an improvement in HAZ toughness. So, in order to effectively improve HAZ toughness by adding Nb, it is preferable to contain Nb in an amount of no less than 0.002%. However, if the content of Nb exceeds 0.10%, the precipitating carbonitride is coarsened, which conversely decreases HAZ toughness. Accordingly, the content of Nb is specified to be no less than 0.002% and no greater than 0.10%.

[0050] It is also preferable to contain V in an amount of no less than 0.002%, similarly to Nb. However, if the content of V exceeds 0.10%, the precipitating carbonitride is coarsened, which conversely decreases HAZ toughness. Accordingly, the content of V is specified to be no less than 0.002% and no greater than 0.10%.

[Boron (B): 0.0005-0.0050%]

[0051] The steel material according to the present embodiment may additionally contain B in an amount of no less than 0.0005% and no greater than 0.0050% (0.0005-0.0050%). B is an element that improves toughness by suppressing the production of grain boundary ferrite. So, in order to improve the toughness of the present steel material by adding B, it is preferable to contain B in an amount of no less than 0.0005%. It is more preferable to contain B in an amount of no less than 0.0010%, and still more preferable to contain B in an amount of no less than 0.0015%. However, if the content of B exceeds 0.0050%, B precipitates as BN in an austenite grain boundary, which leads to a decrease in toughness. Accordingly, the content of B is made no greater than 0.0050%, preferably no greater than 0.0040%, and more preferably no less than 0.0015% and no greater than 0.0030%.

[Production of Steel Material according to the Present Embodiment]

[0052] The steel material according to the present embodiment can be obtained by adding, for example, in the second refining of molten steel, each element so as to have the aforementioned chemical component composition, and a production method (production conditions) of the steel shown in the later-described examples, namely, a method of adding each element will be described as one example of a production method of the present steel material. In the following description, the steel shown in the later-described Examples and Comparative Examples were obtained by melting steel with the use of a vacuum melting furnace (capacity: 150 kg) and then by casting into a 150-kg ingot that is then cooled.

[Adjustment of Dissolved Oxygen Amount]

[0053] Before the elements to form complex oxides (complex oxide forming elements) are added, a dissolved oxygen amount and an S concentration in molten steel melted in the vacuum melting furnace were first adjusted. The dissolved oxygen amount (mass% Of) before the addition of complex oxide forming elements was first adjusted to be no greater than 0.005%. Thereafter, the S concentration (mass% S) in the molten steel was adjusted such that the ratio (mass% Of/mass% S) of the dissolved oxygen concentration (mass% Of) to the S concentration (mass% S) was $0.2 \leq$ mass% Of/mass% S ≤ 9.6.

[0054] Herein, a desulfurization method for adjusting the S concentration (mass% S) is not particularly limited, but molten steel having a low S concentration in advance may be used. The bases of the aforementioned dissolved oxygen amount and S concentration are as follows. If a dissolved oxygen amount exceeds 0.005%, the oxide produced in molten steel is first coarsened. Furthermore, if the value of (mass% Of/mass% S) is large, sulfides that are necessary for oxides are not fully produced. Alternatively, if the value of (mass% Of/mass% S) is small, not only desired oxides cannot be obtained, but also sulfides are produced to a level at which intra-granular transformation is hampered because the S concentration is too high.

[0055] Accordingly, a proper balance exists between the mass% Of and the mass% S, and a proper range exists for the value of (mass% Of/mass% S). The range was experimentally determined such that $0.2 \leq$ mass% Of/mass% S $\leq$ 9.6 was created.

[Addition of Al]

[0056] Subsequently, in order to secure Ti oxides, Al, which is one of oxysulfide forming elements, was added to the molten steel ahead of Ti.

[Addition of Ti]

[0057] Following the addition of Al, Ti was added to the molten steel ahead of REM and Zr. If Ti is added ahead of Al, all of the Ti oxides are reduced by Al in the subsequent steps, and hence Ti should be added after the addition of Al. After the addition of Ti, the molten steel was retained for no shorter than 2 minutes and no longer than 15 minutes without the addition of other elements.

[0058] This is because: if the holding time of the molten steel, after the addition of Ti, is shorter than 2 minutes, complex oxides of Al and Ti are not fully formed even when Al and Ti are added in this order; and if the holding time is conversely longer than 15 minutes, the reduction by Al progresses too much. That is, the order of the addition of Al and Ti affects the aforementioned formula (1).

[Addition of REM and Zr]

[0059] After the molten steel was retained for 2-15 minutes, REM and Zr were added. The order of the addition of REM and Zr is not particularly limited. That is, they may be added in the order of REM and Zr, or Zr and REM, or may be added at the same time.

[0060] With respect to the addition amount of Zr and that of REM, under the present conditions in which the dissolved oxygen amount (mass% Of) is no greater than 0.005% and the value of (mass% Of/mass% S) is $0.2 \leq$ mass% Of/mass% $S \leq 9.6$, it is necessary to make the addition amount of Zr no less than 10 ppm and no greater than 120 ppm and the addition amount of REM no less than 30 ppm and no greater than 150 ppm. This is because: if even either one of Zr and REM is added excessively, a coarse complex oxide having a circular-equivalent diameter of greater than 3 μm may be formed; or if even either one of them is added in a too small amount, the amount of fine complex oxides having a circular-equivalent diameter of 0.1-3 μm may be insufficient. That is, the addition amounts of Zr and REM affect the particle size distribution of complex oxides.

[0061] In addition to these, REM has the characteristic of easily forming both oxides and sulfides, while Zr has the characteristic of forming oxides but not forming sulfides. Accordingly, in order to make the balance between oxides and sulfides proper, it is necessary to add Zr and REM in accordance with the mass% Of and mass% S. So, the ratio of the addition amount of Zr and that of REM (add [Zr]/add [REM]) is determined to satisfy the following formula (2).

$$0.27 \times (\text{mass\% Of}/\text{mass\% S}) + 0.21 \leq \text{add [Zr]}/\text{add [REM]} \leq 0.41 \times (\text{mass\% Of}/\text{mass\% S}) + 0.77 \ldots (2)$$

When the value of (mass% Of/mass% S) is large, namely, when an oxide is likely to be produced and a sulfide is not likely, Zr is added in an amount larger than that of REM (the value of (add [Zr]/add [REM]) is made large) based on formula (2). Alternatively, when the value of (mass% Of/mass% S) is small, namely, when a sulfide is more likely to be produced than an oxide, REM is added in an amount larger than that of Zr (the value of (add [Zr]/add [REM]) is made small). Based on this way of thinking, the upper limit and the lower limit of the value of add [Zr]/add [REM] were experimentally determined, so that formula (2) was obtained.

[Addition of Ca and Forging]

[0062] After the addition of REM and Zr, Ca was added and the molten steel was cast. Ca also forms an oxide and a sulfide, but the forms of the oxide and the sulfide are basically dependent on the forms of the inclusions already present in molten steel, and hence the forms of the inclusions, before the addition of Ca, should be particularly noted. Herein, it is desirable to supply, into the molten steel, each of Al, REM, Zr, and Ca, which are deoxidizing elements, dividedly in two or more times or continuously in small amounts, not to supply all of each of them at one time.

[0063] The forms of REM, Ca, Zr, and Ti, which are to be added to the molten steel, are not particularly limited, and, for example, pure La, pure Ce, or pure Y, as REM; pure Ca, pure Zr, or pure Ti; or further an Fe-Si-La alloy, Fe-Si-Ce alloy, Fe-Si-Ca alloy, Fe-Si-La-Ce alloy, Fe-Ca alloy, or Ni-Ca alloy; or the like, may be added. Alternatively, a misch metal may be added to the molten steel. The misch metal is a mixture of rare earth elements, and specifically it contains approximately 40-50% of Ce and approximately 20-40% of La. However, a misch metal often contains Ca as an impurity, and hence when a misch metal contains Ca, the range of Ca content specified in the present embodiment should be satisfied.

[0064] The compositions (contents) of the component elements, the relational expressions between the contents of the component elements, and the production conditions, etc., which have been described above, are referred to as "conditions specified in the present embodiment".

[Casting and Rolling]

[0065] The molten steel whose components were adjusted as described above was cast into an ingot. The cast ingot was hot-rolled and processed such that a thick steel plate having a thickness of 30-80 mm was produced. In the actual operation, it is sufficient that the molten steel obtained with its components being adjusted is processed into a slab by continuous casting according to a normal method and then hot-rolled according to a normal method.

[Measurement of HAZ Toughness]

[0066] In order to evaluate the toughness of a HAZ in the obtained thick steel plate, the HAZ being affected by welding heat, a test piece for a welded joint was taken from the thick steel plate and was subjected to V-beveling processing, and electrogas arc welding whose heat input was 60 kJ/mm, equivalent to high heat input welding, was then performed. Three test pieces for Charpy impact test (V-notched test pieces according to JIS Z 2202) were taken, in which a HAZ, located near to a weld line (bond) positioned at a depth of t/4 (t: thickness of the test piece) from the surface of the welded test piece, was processed to have a notch. A Charpy impact test was performed at -40°C on each of the three V-notched test pieces to measure absorbed energy (vE-40), so that the average value and the minimum of the measurement results of the three V-notched test pieces were determined.

[0067] In these measurement results, a test piece (thick steel plate) having an average value of vE-40 of greater than 140 J was evaluated as a steel plate having superior HAZ toughness.

[Measuring Method of Composition of Complex Oxide Having Size of 0.1-3 μm]

[0068] A test piece was cut out from a position at a depth of t/4 (t: thickness of the thick steel plate) from the surface of the thick steel plate (the test piece was taken such that the shaft center thereof passed through the position at a depth of t/4), and a cross section parallel to the rolling direction and the thickness direction was subjected to mirror polishing; and with respect to this test piece, the composition of a complex oxide having a size of 0.1-3 μm was measured by using an EPMA (Electron Probe X-ray Microanalyzer made by JEOL Datum (product name: JXA-8500F)). Observation conditions in this case were set such that an acceleration voltage was 20 kV, a sample current was 0.01 μA, a magnification was 5000 times, and an observation area was no less than 0.4 mm^2, and the component composition at the center of the complex oxide was quantitatively analyzed by wavelength dispersive spectroscopy of characteristic X-rays.

[0069] That is, the elements to be the targets of the quantitative determination were set to be Si, Mn, S, Al, Ti, Zr, La, Ce, Ca, and O (oxygen), and the relationship between the X-ray intensity of each element and the concentration of the each element was determined, in advance, as a calibration curve by using a known substance, so that the amount of an element contained in a complex oxide that was an analysis target was quantitatively determined based on the X-ray intensity and the calibration curve obtained from the complex oxide. Each of the aforementioned elements other than S was converted into a simple oxide, so that the composition of the oxide was calculated from the ratio of the X-ray intensity that showed the existence of the each element. The concentration of S was calculated as being present alone. In the present embodiment, the composition of a complex oxide was determined with mass conversion assuming that there were simple oxides and S present alone, as described above, and an average composition of a plurality of complex oxides was determined as the composition of the complex oxide.

[0070] Herein, when REM is represented by the symbol M, the oxides of REM exist in the forms of M_2O_3, M_3O_5, and MO_2, etc., in the steel material; however, all of the oxides thereof were converted into M_2O_3. Similarly, all of the oxides of Ti were converted into TiO_2.

[Measuring Method of Circular-Equivalent Diameter of Complex Oxide and the Number of Complex Oxides]

[0071] In the aforementioned measurement of the composition of a complex oxide using an EPMA, the area of the complex oxide was measured, and the diameter of a circle corresponding to the measured area was calculated as a circular-equivalent diameter, assuming that the shape of the complex oxide was a circle. When the number of complex oxides having a circular-equivalent diameter of greater than 5 μm was measured, observation conditions were set such that a magnification was 200 times, an observation area was no less than 50 mm^2, and the conditions other than these were the same as those under which the number of complex oxides having a circular-equivalent diameter of no greater than 5 μm was measured.

Examples

[0072] Subsequently, examples of the steel material according to the present embodiment will be specifically described. The following Table 2 shows the chemical component compositions of steel materials Nos. 1-31 that are examples of the steel material according to the embodiment. All of the component compositions of the steel materials Nos. 1-31 satisfy the conditions specified in the embodiment.

[Table 2]

No.	Component composition of steel material (mass%)																				
	C	Si	Mn	P	S	Al	N	Ti	Zr	REM			Ca	O	Ni	Cu	Cr	Mo	Nb	V	B
										La	Ce	Total									
	0.02-0.13%	0.05-0.5%	1.0-2.5%	No greater than 0.03%	0.0005-0.01%	0.002-0.040%	0.0030-0.010%	0.005-0.040%	0.0003-0.020%	-	-	0.0003-0.020%	0.0003-0.0080%	0.0003-0.0050%	0.05-1.50%	0.05-1.50%	0.05-1.50%	0.05-1.50%	0.002-0.10%	0.002-0.10%	0.0005-0.0050%
1	0.05	0.18	1.49	0.007	0.003	0.006	0.0065	0.017	0.0024	0.0008	0.0014	0.0022	0.0018	0.0023	0.54	1.14	0.47	0.88	0.068	0.045	0.0021
2	0.06	0.19	1.55	0.008	0.0023	0.01	0.0072	0.019	0.0019	0.0007	0.0017	0.0024	0.0015	0.0018	—	—	0.95	0.08	—	0.031	0.0045
3	0.05	0.05	1.45	0.004	0.0018	0.004	0.0062	0.016	0.0045	0.0007	0.001	0.0017	0.0065	0.0004	—	0.58	0.09	—	—	0.087	—
4	0.05	0.07	1.89	0.005	0.0033	0.01	0.0085	0.02	0.0025	0.0013	0.0006	0.0019	0.0017	0.0035	0.69	0.66	1.02	0.25	0.031	0.002	0.0008
5	0.04	0.07	1.25	0.008	0.0024	0.011	0.0061	0.017	0.001	0	0.0003	0.0003	0.0003	0.0021	—	—	—	—	—	—	—
6	0.06	0.07	1.54	0.007	0.0017	0.014	0.006	0.02	0.0019	0.001	0.0015	0.0025	0.0014	0.002	—	—	—	—	—	—	—
7	0.05	0.16	1.53	0.007	0.0025	0.011	0.0047	0.024	0.0023	0.0016	0.0015	0.0031	0.0013	0.0045	—	0.37	—	0.87	—	—	—
8	0.05	0.05	1.54	0.008	0.0019	0.009	0.0068	0.021	0.001	0.0018	0.0018	0.0036	0.0019	0.0028	1.38	—	—	0.55	0.049	—	0.0016
9	0.05	0.11	1.37	0.006	0.0019	0.008	0.0067	0.021	0.0022	0.0009	0.0011	0.002	0.0025	0.0019	0.66	—	—	—	0.002	—	—
10	0.07	0.46	1.52	0.008	0.0035	0.015	0.0057	0.005	0.0045	0.0002	0.0017	0.0019	0.0022	0.0032	0.34	—	0.5	—	—	—	—
11	0.03	0.09	1.78	0.007	0.0024	0.01	0.0074	0.019	0.0055	0.0012	0.0014	0.0026	0.0018	0.0027	—	—	—	—	—	—	—
12	0.04	0.08	1.64	0.005	0.0014	0.011	0.0059	0.019	0.002	0.001	0.0026	0.0036	0.0013	0.0029	—	—	0.24	1.23	0.07	0.055	—
13	0.05	0.14	1.43	0.007	0.0054	0.009	0.0037	0.024	0.0003	0.001	0.0008	0.0018	0.0011	0.0031	0.58	1.02	—	—	—	—	—
14	0.11	0.08	1.22	0.007	0.0095	0.017	0.0058	0.016	0.0008	0.0011	0.0009	0.002	0.0022	0.0024	0.44	-	0.86	-	-	0.081	0.0005
15	0.06	0.24	1.87	0.009	0.0005	0.011	0.0055	0.015	0.0014	0.0006	0.0011	0.0017	0.0018	0.0025	-	0.58	-	-	0.064	-	0.0012
16	0.04	0.13	1.46	0.015	0.0028	0.039	0.0035	0.007	0.0016	0.0003	0	0.0003	0.0064	0.0014	—	0.49	—	0.75	—	0.061	—
17	0.07	0.07	1.28	0.015	0.0011	0.002	0.0091	0.012	0.0014	0.0008	0.0012	0.002	0.0018	0.0018	0.25	0.74	—	1.46	0.016	—	—
18	0.13	0.06	1.52	0.003	0.0018	0.012	0.0079	0.039	0.004	0.0013	0.0009	0.0022	0.0017	0.0025	1.02	—	—	—	—	—	0.0019
19	0.05	0.08	1.46	0.007	0.002	0.008	0.0078	0.005	0.017	0.0004	0.0005	0.0009	0.0015	0.0026	0.35	1.4	—	—	0.028	—	—
20	0.06	0.07	1.56	0.009	0.0022	0.009	0.0055	0.022	0.0023	0.0069	0.0125	0.0194	0.0013	0.0035	—	0.55	0.75	1.04	—	0.009	0.0036
21	0.02	0.08	1.53	0.008	0.0017	0.021	0.0054	0.013	0.0022	0.0001	0.0002	0.0003	0.0011	0.0039	0.07	—	0.37	—	—	—	0.0007
22	0.07	0.31	1.38	0.006	0.0015	0.039	0.0047	0.021	0.0192	0.0038	0.0072	0.011	0.0017	0.0027	—	0.42	—	—	—	0.016	—
23	0.04	0.08	1.27	0.011	0.0021	0.015	0.0065	0.02	0.0003	0.0006	0.0014	0.002	0.0024	0.0018	0.77	—	—	—	0.025	—	0.0013
24	0.04	0.3	2.45	0.007	0.0036	0.016	0.0045	0.024	0.003	0.0008	0.0016	0.0024	0.0077	0.0026	0.48	0.78	0.67	—	—	—	—
25	0.05	0.07	1.58	0.029	0.0024	0.022	0.0063	0.034	0.0035	0.0015	0.0008	0.0023	0.0003	0.0032	—	—	—	0.45	—	0.092	—
26	0.06	0.15	2.2	0.007	0.0028	0.006	0.0078	0.018	0.0024	0.0015	0.0019	0.0034	0.0024	0.001	—	1.13	1.36	—	0.094	—	—
27	0.08	0.09	1.04	0.008	0.0075	0.014	0.0095	0.025	0.0015	0.0008	0.0005	0.0013	0.0021	0.0018	1.1	0.95	—	—	—	0.027	0.0045
28	0.07	0.11	1.55	0.008	0.0022	0.012	0.0068	0.018	0.0018	0.0055	0.0065	0.012	0.0014	0.0027	—	0.07	0.67	—	0.062	0.039	—
29	0.05	0.06	1.75	0.007	0.0081	0.034	0.0066	0.022	0.0023	0.0019	0.0025	0.0044	0.0013	0.0048	0.28	—	—	0.56	0.024	—	0.0015
30	0.08	0.04	1.66	0.014	0.0093	0.021	0.0066	0.017	0.003	0.001	0.0028	0.0038	0.0018	0.0024	0.34	0.45	1.38	—	—	—	0.0022
31	0.08	0.11	1.23	0.011	0.0007	0.015	0.0057	0.018	0.0018	0.0008	0.0016	0.0024	0.0022	0.0047	0.87	—	0.78	0.3	—	0.042	—

[0073] The following Table 3 shows the production conditions of the steel materials Nos. 1-31 that are examples of the present steel material. All of the production conditions of the steel materials Nos. 1-31 also satisfy the conditions specified in the present embodiment. When there are multiple orders or methods, etc., of adding component elements, the selected addition order or addition method is shown in the remarks column.

[Table 3]

No.	Before addition of complex oxide forming elements				Addition amounts of Zr and REM				Ratio of addition amount of Zr to that of REM				Addition order of complex oxide forming elements	Holding time after addition of Ti [minute]		Remarks
	mass % Of	mass % S	mass % Of/ mass % S		add[Zr] [ppm]		add[REM] [ppm]		Lower limit	Upper limit	Actual value					
	No greater than 0.005 mass%	-	0.2-9.8		10-20ppm		30-150ppm		0.27× (mass%Of/ mass%S) +0.21	0.41 × (mass%Of/ mass%S) +0.77				2-15 minutes		
1	0.0022	0.0033	0.67	○	45	○	80	○	0.39	1.04	0.50	○	○	5.7	○	Each of REM, Zr, and Ca was dividedly added.
2	0.0015	0.0028	0.54	○	50	○	85	○	0.35	0.99	0.59	○	○	3.1	○	
3	0.0004	0.0018	0.22	○	25	○	80	○	0.27	0.86	0.42	○	○	6.6	○	
4	0.0028	0.0038	0.74	○	70	○	70	○	0.41	1.07	1.00	○	○	7	○	
5	0.0019	0.0027	0.70	○	100	○	130		0.40	1.06	0.77	○	○	3.9	○	
6	0.0018	0.0019	0.95	○	60	○	65	○	0.47	1.16	0.92	○	○	12	○	
7	0.0039	0.0027	1.44	○	70	○	60	○	0.60	1.38	1.17	○	○	8.4	○	
8	0.0025	0.0022	1.14	○	35	○	90	○	0.52	1.24	0.70	○	○	7	○	Each of REM and Zr was dividedly added.
9	0.0013	0.0028	0.62	○	40	○	80	○	0.38	1.02	0.50	○	○	3	○	Each of REM, Zr, and Ca was dividedly added.
10	0.003	0.004	0.75	○	20	○	45	○	0.41	1.08	0.44	○	○	4.8	○	Each of

(continued)

No.	Before addition of complex oxide forming elements				Addition amounts of Zr and REM				Ratio of addition amount of Zr to that of REM				Addition order of complex oxide forming elements	Holding time after addition of Ti [minute]		Remarks
	mass % Of	mass % S	mass % Of/ mass % S		add[Zr] [ppm]		add[REM] [ppm]		Lower limit	Upper limit	Actual value					
	No greater than 0.005 mass%	-	0.2-9.8		10-20ppm		30-150ppm		0.27× (mass%Of/ mass%S) +0.21	0.41 × (mass%Of/ mass%S) +0.77				2-15 minutes		
11	0.0024	0.0028	0.66	○	50	○	45	○	0.44	1.12	1.11	○	○	10	○	Ti, REM, Zr, and Ca was dividedly added.
12	0.0026	0.0015	1.73	○	55	○	75	○	0.68	1.48	0.73	○	○	8.3	○	of and added.
13	0.0027	0.0058	0.47	○	70	○	110	○	0.34	0.96	0.64	○	○	4.3	○	Each REM, Zr, Ca was dividedly
14	0.0021	0.0101	0.21	○	75	○	90	○	0.27	0.86	0.83	○	○	5.9	○	Each of Ti, REM, Zr, and Ca was dividedly added.
15	0.0018	0.0005	3.60	○	90	○	50	○	1.18	2.25	1.80	○	○	2.4	○	
16	0.0013	0.003	0.43	○	55	○	80	○	0.33	0.95	0.69	○	○	4.1	○	
17	0.0016	0.0012	1.33	○	65	○	90	○	0.57	1.32	0.72	○	○	3.1	○	
18	0.0022	0.0019	1.16	○	30	○	45	○	0.52	1.24	0.87	○	○	11	○	
19	0.0023	0.0023	1.00	○	35	○	65	○	0.48	1.18	0.54	○	○	12	○	
20	0.0031	0.0025	1.24	○	95	○	145	○	0.54	1.28	0.66	○	○	7.8	○	
21	0.0035	0.0019	1.84	○	35	○	30	○	0.71	1.53	1.17	○	○	5.9	○	

(continued)

No.	Before addition of complex oxide forming elements				Addition amounts of Zr and REM				Ratio of addition amount of Zr to that of REM				Addition order of complex oxide forming elements	Holding time after addition of Ti [minute]		Remarks
	mass % Of	mass % S	mass % Of/ mass % S		add[Zr] [ppm]		add[REM] [ppm]		Lower limit	Upper limit	Actual value					
	No greater than 0.005 mass%	-	0.2-9.8		10-20ppm		30-150ppm		0.27× (mass%Of/ mass%S) +0.21	0.41 × (mass%Of/ mass%S) +0.77				2-15 minutes		
22	0.0035	0.0015	2.33	○	110	○	95	○	0.84	1.73	1.16		○	4.5	○	Each of Ti, REM, Zr, and Ca was dividedly added.
23	0.0013	0.0024	0.54	○	15	○	35	○	0.36	0.99	0.43	○	○	3.3	○	Each of Ti, REM, Zr, and Ca was dividedly added.
24	0.0022	0.0039	0.56	○	60	○	150		0.36	1.00	0.40	○	○	2.6	○	
25	0.0029	0.0024	1.21	○	75	○	70	○	0.54	1.27	1.07	○	○	4.9	○	
28	0.0008	0,003	0.27	○	55	○	145	○	0.28	0.88	0.38	○	○	9	○	
27	0.0015	0.0078	0.20	○	80	○	85	○	0.26	0.85	0.84	○	○	4.4	○	Each of and Ca added.
28	0.0027	0.0024	1.13	○	55	○	85	○	0.51	1.23	0.65	○	○	9.9	○	Ti, REM, Zr, was dividedly
29	0.0044	0.0124	0.35	○	70	○	80	○	0.31	0.92	0.88	○	○	7.5	○	of REM, Zr, and Ca was dividedly added.
30	0.0021	0.0095	0.22	○	65	○	125	○	0.27	0.86	0.52	○	○	5.6	○	Each

(continued)

No.	Before addition of complex oxide forming elements				Addition amounts of Zr and REM				Ratio of addition amount of Zr to that of REM				Addition order of complex oxide forming elements	Holding time after addition of Ti [minute]		Remarks
	mass % Of	mass % S	mass % Of/ mass % S		add[Zr] [ppm]		add[REM] [ppm]		Lower limit	Upper limit	Actual value					
	No greater than 0.005 mass%	-	0.2-9.8		10-20ppm		30-150ppm		0.27× (mass%Of/ mass%S) +0.21	0.41 × (mass%Of/ mass%S) +0.77				2-15 minutes		
31	0.0048	0.0005	9.60	○	105	○	35	○	2.80	4.71	3.00	○	○	3.6	○	

[0074] The following Table 4 shows test results for the particle sizes, the piece-number distributions, and the average compositions of complex oxides, and for the HAZ toughness of the steel materials Nos. 1-31 that are examples of the present steel material. In each of the steel materials Nos. 1-31 that are examples of the present steel material, the number of complex oxides having a circular-equivalent diameter of greater than 3 μm is no greater than 5.0/mm^2, and the number of complex oxides having a circular-equivalent diameter of 0.1-3 μm is at least 100 /mm^2. Furthermore, in each of the steel materials Nos. 1-31, the average composition of complex oxides having a circular-equivalent diameter of 1-3 μm satisfies the conditions specified in the present embodiment. As a result, each of the steel materials Nos. 1-31 has HAZ toughness of no less than 140 J, and hence it can be evaluated as exerting superior HAZ toughness.

[Table 4]

Complex oxides exceeding 3 µm										
No.		Complex oxides that are 0.1-3 µm								HAZ toughness vE-40 [J]
	Piece-number distribution [pieces/mm^2]	Piece-number distribution [pieces/mm^2]	Average composition [mass%]							
			Al2O3	TiO2	REM2O3	ZrO2	CaO	S	Others	
	No greater than 5.0	At least 100	No greater than 20%	3-20%	5-50%	5-50%	5-50%	1-15%		Average value of no less than 140 J
1	0.8	452	8.6	9.5	25.5	19.2	18.6	3.2	15.4	182
2	4.6	476	3	7.1	28.7	32.2	8.2	8.6	12.2	156
3	0.7	118	0.4	12.5	29.1	9.4	14.3	5.1	29.2	144
4	3.2	121	5.1	11.4	37.1	7.2	24.5	4.5	10.2	158
5	1.6	124	7.4	5.2	19.4	8.4	38.3	2.8	18.5	142
6	4.5	611	4.8	6.3	22.5	16.2	18	8	24.2	146
7	2.2	135	2.1	3.3	27.7	18.6	20.5	12.4	15.4	143
8	1.4	615	5.3	5.5	21.4	21	8.2	2.7	35.9	177
9	2.3	528	5.4	6.7	12.7	26.9	19.8	2.5	26	171
10	4.2	334	9.4	17.5	34	14.4	12.8	2.4	9.5	145
11	1.5	658	2.3	11.9	22.1	21.8	15.2	5.6	21.1	176
12	4.2	289	6.5	5.4	21.4	20.7	19	5	22	142
13	2.7	710	5.6	12.8	22.2	17.2	7.4	10.2	24.6	180
14	0.4	460	3.5	6.7	19	28.6	19.9	14.5	7.8	160
15	1.8	372	7	5.4	39.2	31.4	7.7	1.2	8.1	152
16	2.2	326	19.3	5.8	17.6	21.6	8.1	4.5	23.1	149
17	1.3	167	0.2	11.7	31.4	32.2	15.1	5	4.4	142
18	3.9	505	2.1	19.6	21.5	18.9	6.3	5.7	25.9	167
19	2.5	158	3.8	3.2	32	13.5	15.3	8.5	23.7	156

(continued)

Complex oxides exceeding 3 μm										
No.		Complex oxides that are 0.1-3 μm								HAZ toughness vE-40 [J]
	Piece-number distribution [pieces/mm^2]	Piece-number distribution [pieces/mm^2]	Average composition [mass%]							
			Al2O3	TiO2	REM2O3	ZrO2	CaO	S	Others	
	No greater than 5.0	At least 100	No greater than 20%	3-20%	5-50%	5-50%	5-50%	1-15%		Average value of no less than 140 J
20	1.7	260	3.7	6.7	48.2	13.2	23.7	2.5	2	155
21	2.6	248	1.4	8.2	5.4	11.5	36.9	10.4	26.2	153
22	0.3	424	8.5	9.5	13.9	47.9	9.5	3.5	7.2	156
23	1.2	389	2.3	3.6	20	5.3	33.5	10.5	24.8	147
24	4	682	10.5	6.8	18.6	9.1	47.8	3.5	4.7	146
25	2.8	516	3.8	11.7	24.6	22.5	5.7	9.6	22.1	150
26	2.4	215	6.1	3.9	25.7	38.8	10.1	6.2	9.2	149
27	1.9	176	12.5	9.8	14.5	12.3	22.3	5.7	22.9	142
28	1.5	581	1.2	14.5	28.7	9.7	31	2.5	12.4	146
29	0.8	245	14.2	6	24.6	12.9	9.5	7.7	25.1	155
30	3.6	346	5.8	6.7	23.7	29	8.2	8	18.6	143
31	1.7	127	14.4	6.8	19.6	20.2	22.8	3.5	12.7	142

[0075] Herein, the following Table 5 shows the component compositions of steel materials Nos. 32-67 that are examples in which the conditions specified in the present embodiment are not satisfied. In the steel material No. 32, the content of Al does not satisfy the condition specified in the embodiment. In the steel materials Nos. 34 and 35, the contents of Ti do not satisfy the condition specified in the embodiment. In the steel materials Nos. 40 and 41, the contents of REM do not satisfy the condition specified in the embodiment. In the steel materials Nos. 44 and 45, the contents of Zr do not satisfy the condition specified in the embodiment. In the steel materials Nos. 48 and 49, the contents of Ca do not satisfy the condition specified in the embodiment. In the steel materials Nos. 52 and 53, the contents of S do not satisfy the condition specified in the embodiment. The other steel materials satisfy the aforementioned component compositions.

[Table 5]

No greater than 0.03%

No.	Component composition of steel material (mass%)																				
	C	Si	Mn	P	S	Al	N	Ti	Zr	REM			Ca	O	Ni	Cu	Cr	Mo	Nb	V	B
										La	Ce	Total									
	0.02 -0.13%	0.05 -0.5%	1.0 -2.5%		0.0005 -0.01%	0.002 -0.040%	0.0030 -0.010%	0.005 -0.040%	0.0003 -0.020%	-	-	0.0003 -0.020%	0.0003-0.0080%	0.0003-0.0050%	0.05-1.50%	0.05-1.50%	0.05-1.50%	0.05-1.50%	0.002 -0.10%	0.002 -0.10%	0.0005 -0.0050%
32	0.1	0.09	1.45	0.011	0.0055	0.042	0.0066	0.017	0.0024	0.0012	0.0023	0.0035	0.0039	0.0045	—	—	0.75	—	0.072	—	0.0024
33	0.09	0.15	1.16	0.011	0.0034	0.031	0.007	0.008	0.0036	0.0027	0.0025	0.0052	0.0034	0.0024	1.35	—	—	—	0.025	—	—
34	0.09	0.08	1.29	0.005	0.0061	0.008	0.0034	0.041	0.0016	0.0016	0.0025	0.0041	0.0024	0.0028	0.18	0.25	—	0.56	—	—	0.0016
35	0.05	0.26	1.23	0.007	0.0053	0.003	0.0062	0.004	0.0044	0.0039	0.0046	0.0085	0.0018	0.0026	—	—	—	—	—	0.009	—
36	0.05	0.09	1.66	0.018	0.0015	0.008	0.0046	0.031	0.0019	0.0008	0.0009	0.0017	0.0052	0.0022	0.6	0.5	—	—	0.06	—	0.0028
37	0.08	0.18	1.65	0.015	0.0009	0.015	0.008	0.007	0.0052	0.0022	0.002	0.0042	0.0019	0.0017	0.66	—	—	—	0.008	0.032	—
38	0.08	0.11	1.45	0.024	0.0015	0.018	0.0076	0.022	0.0033	0.0013	0.0022	0.0035	0.0015	0.0034	—	0.61	—	—	—	0.024	—
39	0.06	0.16	1.55	0.007	0.0024	0.019	0.0045	0.019	0.0035	0.0011	0.0017	0.0028	0.0018	0.0031	—	—	—	0.46	—	0.055	0.0015
40	0.05	0.28	1.84	0.006	0.0037	0.014	0.0057	0.021	0.0035	0.006	0.0155	0.0215	0.0035	0.0019	0.89	—	—	—	0.011	—	0.0009
41	0.02	0.02	1.04	0.006	0.0022	0.034	0.0059	0.018	0.0024	0.0001	0.0001	0.0002	0.0042	0.0028	—	0.56	0.77	—	—	—	—
42	0.04	0.3	1.29	0.008	0.0031	0.006	0.0054	0.024	0.0031	0.0066	0.0064	0.013	0.0028	0.0009	0.42	0.73	—	1.25	—	—	—
43	0.05	0.16	1.4	0.025	0.0035	0.024	0.0067	0.018	0.0008	0.0002	0.0006	0.0008	0.0015	0.0036	—	0.49	1.24	0.78	0.049	0.075	0.0021
44	0.06	0.14	1.36	0.012	0.0024	0.006	0.0063	0.006	0.022	0.006	0.0095	0.0155	0.0008	0.0024	—	—	—	0.21	—	0.015	0.003
45	0.05	0.05	1.38	0.025	0.0029	0.011	0.0082	0.017	0.0001	0.0013	0.002	0.0033	0.0027	0.0039	1.07	0.58	—	—	—	—	—
46	0.07	0.25	1.65	0.015	0.0055	0.019	0.0045	0.015	0.0014	0.0027	0.0008	0.0035	0.0017	0.0017	—	—	—	0.45	—	0.024	—
47	0.08	0.17	1.29	0.011	0.0038	0.024	0.0058	0.018	0.0025	0.0006	0.0012	0.0018	0.0023	0.0037	0.64	1.44	0.55	0.22	—	—	—
48	0.05	0.14	2.46	0.006	0.008	0.01	0.0089	0.022	0.0052	0.0003	0.0006	0.0009	0.0084	0.003	0.45	—	0.08	—	0.058	0.018	—
49	0.08	0.47	1.85	0.004	0.0012	0.018	0.0073	0.018	0.0023	0.0036	0.0024	0.006	0.0002	0.0027	—	—	0.38	—	—	—	—
50	0.11	0.22	2.31	0.008	0.0041	0.005	0.0052	0.03	0.0014	0.0011	0.0012	0.0023	0.0065	0.0042	—	0.36	—	—	—	—	0.0032
51	0.06	0.12	1.7	0.017	0.0019	0.016	0.0059	0.019	0.0015	0.0019	0.0031	0.005	0.0009	0.0017	1.15	0.28	1.39	0.35		0.032	0.0019
52	0.07	0.01	1.54	0.006	0.0105	0.025	0.0076	0.021	0.0064	0.0008	0.002	0.0028	0.0025	0.0025	0.57	—	—	—	0.044	—	0.0028
53	0.08	0.08	1.57	0.009	0.0004	0.026	0.006	0.018	0.0141	0.0018	0.0018	0.0036	0.0056	0.0018	—	0.5	—	0.56	—	—	0.0015
54	0.04	0.17	1.41	0.012	0.0079	0.011	0.0084	0.018	0.0026	0.0014	0.0015	0.0029	0.0024	0.0021	0.98	—	0.77	—	0.037	0.012	—
55	0.05	0.26	1.88	0.007	0.0010	0.01	0.0076	0.008	0.0076	0.0002	0.0005	0.0007	0.0023	0.0016	—	0.17	—	0.25		—	—
56	0.13	0.08	1.28	0.008	0.0017	0.018	0.0084	0.027	0.0182	0.0013	0.0013	0.0026	0.0075	0.0027	—	1.12	0.78	0.8	—	—	—
57	0.02	0.25	1.24	0.005	0.0088	0.008	0.0076	0.012	0.0008	0.003	0.0075	0.0105	0.0015	0.0034	0.35	—	—	—	0.08	—	—
58	0.07	0.12	1.81	0.017	0.0053	0.017	0.0045	0.02	0.007	0.0008	0.002	0.0028	0.0024	0.0018	—	0.48	—	—	—	0.05	0.0025
59	0.1	0.24	2.05	0.007	0.0021	0.009	0.0064	0.024	0.0055	0.0016	0.0046	0.0062	0.0049	0.0033	—	—	0.2	—	—	—	0.0043
60	0.08	0.23	1.42	0.007	0.0047	0.013	0.0055	0.019	0.0032	0.0029	0.0018	0.0047	0.0019	0.0013	—	—	—	—	—	—	—
61	0.04	0.07	1.68	0.009	0.0033	0.018	0.0068	0.011	0.0151	0.0028	0.0017	0.0045	0.0028	0.0017	0.87	1.12	—	0.76	0.015	—	0.0011
62	0.11	0.22	1.24	0.011	0.0025	0.025	0.0057	0.025	0.0043	0.0005	0.0013	0.0018	0.0016	0.003	—	—	0.34	—	—	0.046	—
63	0.1	0.17	1.55	0.014	0.0018	0.012	0.0071	0.017	0.0035	0.0015	0.0015	0.003	0.0018	0.0025	0.25	0.35	—	—	0.025	—	—
64	0.07	0.12	1.37	0.01	0.0032	0.007	0.0065	0.034	0.0182	0.0022	0.0054	0.0076	0.0037	0.0041	0.66	—	—	1.4	—	0.074	0.0017
65	0.05	0.15	1.88	0.008	0.0028	0.024	0.0054	0.02	0.0184	0.0027	0.0033	0.006	0.0066	0.0029	—	—	0.39	—	—	—	—
66	0.06	0.13	1.75	0.007	0.0083	0.015	0.0034	0.025	0.0039	0.0056	0.0125	0.0181	0.0005	0.0025	—	—	—	—	0.027	0.039	0.0025
67	0.08	0.06	1.44	0.019	0.0013	0.014	0.0076	0.019	0.0066	0.0049	0.0121	0.017	0.0027	0.0036	—	0.96	—	—	—	—	—

[0076] The following Table 6 shows the production conditions of the steel materials Nos. 32-67 that do not satisfy the conditions specified in the present embodiment. In each of the steel materials Nos. 33, 36, 37, 42, 43, 46, 47, 50, and 51, an "x" mark is provided in the "addition order of complex oxide forming elements", which indicates that the complex oxide forming elements (Al and Ti) were added in an order different from the aforementioned one. In each of the steel materials No. 38 and 39, it is shown that a holding time after the addition of Ti does not satisfy the condition specified in the embodiment. In the steel material No. 52, it is shown that the value of (mass% Of/mass% S) does not satisfy the condition specified in the embodiment. In the steel material No. 53, it is shown that the value of mass% Of, the value of (mass% Of/mass% S), and the actual value of (add [Zr]/add [REM]) do not satisfy the conditions specified in the embodiment. In each of the steel materials No. 54 and 55, it is shown that the actual value of (add [Zr]/add [REM]) does not satisfy the condition specified in the embodiment. In each of the steel materials Nos. 56 and 57, it is shown that the value of mass% Of does not satisfy the condition specified in the embodiment. In each of the steel materials Nos. 58 and 59, it is shown that the addition amount of add [Zr] and the actual value of (add [Zr]/add [REM]) do not satisfy the conditions specified in the embodiment. In each of the steel materials Nos. 60 and 61, it is shown that the addition amount of add [REM] and the actual value of (add [Zr]/add [REM]) do not satisfy the conditions specified in the embodiment. In each of the steel materials Nos. 62-67, it is shown that the actual value of (add [Zr]/add [REM]) does not satisfy the condition specified in the embodiment.

[0077] Thus, in each the steel materials Nos. 32-67, either the component composition shown in Table 5 or the production condition shown in Table 6 does not, or both do not satisfy the conditions specified in the embodiment.

[Table 6]

No.	Before addition of complex oxide forming elements				Addition amounts of Zr and REM				Ratio of addition amount of Zr to that of REM: add [Zr] / add [REM]				Addition order of complex oxide forming elements	Holding time after addition of Ti [minute]		Remarks
	mass%Of	mass%Of /	mass%Of / mass%S		add[2r] [ppm]		acid[REM] [ppm]		Lower limit	Upper limit	Actual value					
	No greater than 0.005 mass%	-	0.2-9.5		10-120ppm		30-150ppm		0.27 × (mass50%/ mass%S) +0.21	0.41 × (mass50%/ mas%S) +0.77				2 - 15 minutes		
32	0.0042	0.006	0.70	○	75	○	130	○	0.40	1.06	0.58	○	○	5.8	○	
33	0.0022	0.0042	0.52	○	70	○	90	○	0.35	0.98	0.78	○	×	1.2	○	
34	0.0021	0.007	0.30	○	50	○	105	○	0.29	0.89	0.48	○	○	4.2	○	
35	0.0023	0.0056	0.41	○	65	○	85	○	0.32	0.84	0.76	○	○	8.8	○	
36	0.0018	0.0018	1.00	○	70	○	130	○	0.48	1.18	0.54	○	×	4	○	
37	0.0014	0.0011	1.27	○	100	○	95	○	0.55	1.28	1.05	○	×	7.9	○	
38	0.0029	0.0018	1.61	○	40	○	85	○	0.65	1.43	0.47	○	○	15.8	×	
39	0.0025	0.0031	0.81	○	75	○	85	○	0.43	1.10	0.88	○	○	1.8	×	
40	0.0015	0.0038	0.39	○	55	○	70	○	0.32	0.93	0.78	○	○	13	○	Each of Ti, REM, Zr, and Ca was dividedly added.
41	0.0025	0.0022	1.14	○	20	○	35	○	0.52	1.24	0.57	○	○	3.2	○	
42	0.0008	0.0035	0.23	○	30	○	95	○	0.27	0.66	0.32	○	×	10	○	
43	0.0035	0.0035	1.00	○	45	○	85	○	0.48	1.18	0.53	○	×	7.8	○	
44	0.0024	0.003	0.80	○	90	○	130	○	0.43	1.10	0.69	○	○	12	○	Each of REM, Zr, and Ca was dividedly added.

(continued)

No.	Before addition of complex oxide forming elements				Addition amounts of Zr and REM				Ratio of addition amount of Zr to that of REM: add [Zr] / add [REM]				Addition order of complex oxide forming elements	Holding time after addition of Ti [minute]		Remarks
	mass%Of	mass%Of /	mass%Of / mass%S		add[2r] [ppm]		acid[REM] [ppm]		Lower limit	Upper limit	Actual value					
	No greater than 0.005 mass%	-	0.2-9.5		10-120ppm		30-150ppm		0.27 × (mass50%/ mass%S) +0.21	0.41 × (mass50%/ mas%S) +0.77				2 - 15 minutes		
45	0.0028	0.0031	0.90	○	85	○	85	○	0.45	1.14	1.00	○	○	3.2	○	Each of Ti, REM, Zr, and Ca was dividedly added.
46	0.0016	0.006	0.23	○	60	○	100	○	0.28	0.88	0.60	○	×	6.4	○	
47	0.0033	0.0042	0.79	○	70	○	85	○	0.42	1.09	0.82	○	×	4.9	○	
48	0.0027	0.0085	0.32	○	85	○	100	○	0.30	0.90	0.65	○	○	12	○	Each of Ti, REM, Zr, and Ca was dividedly added.
49	0.0025	0.0013	1.92	○	40	○	85	○	0.73	1.56	0.47	○	○	12	○	
50	0.003	0.0045	0.67	○	30	○	75	○	0.39	1.04	0.40	○	×	6.5	○	
51	0.0013	0.0022	0.59	○	35	○	50	○	0.37	1.01	0.70	○	×	10	○	Each of Ti, REM, Zr, and Ca was dividedly added.
52	0.002	0.0155	0.13	—	50	○	65	○	0.24	0.82	0.77	○	○	11	○	
53	0.0054	0.0005	10.80	—	105	○	120	○	3.13	5.20	0.88	—	○	9.2	○	

(continued)

No.	Before addition of complex oxide forming elements				Addition amounts of Zr and REM				Ratio of addition amount of Zr to that of REM: add [Zr] / add [REM]				Addition order of complex oxide forming elements	Holding time after addition of Ti [minute]		Remarks
	mass%Of	mass%Of /	mass%Of / mass%S		add[2r] [ppm]		acid[REM] [ppm]		Lower limit	Upper limit	Actual value					
	No greater than 0.005 mass%	-	0.2-9.5		10-120ppm		30-150ppm		0.27 × (mass50%/ mass%S) +0.21	0.41 × (mass50%/ mas%S) +0.77				2 - 15 minutes		
54	0.002	0.0068	0.23	○	85	○	95	○	0.27	0.66	0.89	I	○	12	○	Each of REM, Zr, and Ca was dividedly added.
55	0.0015	0.0013	1.15	○	65	○	130	○	0.52	1.24	0.50	I	○	14	○	
56	0.0054	0.0019	2.84	○	45	○	65	○	0.98	1.94	0.69	○	○	9.1	○	
57	0.0057	0.0095	0.60	○	25	○	60	○	0.37	1.02	0.42	○	○	2.9	○	
58	0.0017	0.0058	0.29	○	125	I	55	○	0.29	0.89	2.27	I	○	4.5	○	
59	0.0028	0.0022	1.18	○	5	I	55	○	0.53	1.25	0.08	I	○	6.5	○	
60	0.0011	0.0051	0.22	○	40	○	160	I	0.27	0.86	0.25	I	○	6	○	
61	0.0016	0.0037	0.43	○	45	○	45	I	0.33	0.95	1.00	I	○	11	○	
62	0.0024	0.0028	0.48	○	55	○	45	○	0.44	1.12	1.22	I	○	10	○	
63	0.0023	0.0019	1.21	○	70	○	140	○	0.54	1.27	0.50	I	○	2.2	○	
64	0.0041	0.004	1.03	○	55	○	120	○	0.49	1.19	0.45	I	○	10	○	
65	0.0026	0.0034	0.76	○	50	○	145	○	0.42	1.08	0.41	I	○	4.4	○	
66	0.0024	0.009	0.27	○	35	○	65	○	0.28	0.88	0.54	I	○	5.9	○	
67	0.0035	0.0016	2.19	○	80	○	35		0.80	1.67	1.71	I	○	3.4	○	

[0078] Table 7 shows test results for the particle sizes, the piece-number distributions, and the average compositions of complex oxides, and for the HAZ toughness of the steel materials Nos. 32-67 as comparative examples in which the conditions specified in the present embodiment are not satisfied. In each of the steel materials Nos. 32-55, the average composition of a complex product does not satisfy the condition specified in the embodiment. In each of the steel materials Nos. 56 and 57, the number of complex oxides having a circular-equivalent diameter of greater than 3 μm exceeds 5.0/mm^2. In the steel materials Nos. 58-67, either the number of complex oxides having of a circular-equivalent diameter of greater than 3 μm or the number of complex oxides having a circular-equivalent diameter of 0.1-3 μm does not, or both do not satisfy the conditions specified in the embodiment. In each of the steel materials Nos. 32-55, a condition that does not satisfy the conditions specified in the embodiment is shown in the "remarks column".

[0079] As a result, in each of the steel materials Nos. 32-67, the test result for HAZ toughness was less than 140 J, namely, in a comparative example in which one or more of the conditions specified in the embodiment were not satisfied, a steel material having superior HAZ toughness was not able to be obtained.

[0080] The HAZ toughness of the steel materials according to

[Table 7]

No.	Complex oxides exceeding 3 µm	Complex oxides that are 0.1-3 µm								HAZ toughness vE-40 [J]	Remarks
	Piece-number distribution [pieces/mm²]	Piece-number distribution [pieces/mm²]	Average composition [mass%]								
			Al2O3	TiO2	REM2O3	ZrO2	CaO	S			
	No greater than 5.0	At least 100	No greater than 20%	3-20%	5-50%	5-50%	5-50%	1-15%	Others	Average value of no less than 140 J	
32	2.5	392	21.4 ↑	6.5	17.5	28.9	10.7	10.5	6.5	112	Al concentration of steel material and Al2O3 concentration are out of the ranges.
33	3.1	183	28.3 ↑	7.1	25.8	18.7	10.5	7.3	0.3	91	Al2O3 Concentration is out of the range.
34	2.8	521	8.5	22.5 ↑	32.5	18.2	13	3.1	4.2	94	Ti concentration of steel material and TiO2 concentration are out of the ranges.
35	3.6	154	4.1	2.3 ↓	32.9	14.3	23.9	4.7	17.8	100	Ti concentration of steel material and TiO2 concentration are out of the ranges.
36	1.5	125	10.4	23 ↑	9.5	18.3	16.5	2.8	19.5	77	TiO2 concentration is out of the range.
37	3.8	333	0.8	2.8 ↓	25.3	35.6	10.8	7.8	17.3	95	TiO2 concentration is out of the range.
38	2.4	245	5.4	25 ↑	21.8	19.2	10.2	9.6	8.8	88	TiO2 concentration is out of the range.
39	1.8	187	6.8	1.8 ↓	34	28.8	15.4	6.7	6.5	70	TiO2 concentration is out of the range.
40	2.8	656	5.6	11.5	53.4 ↑	14.6	9.7	1.5	3.7	117	REM concentration of steel material and REM2O3 concentration are out of the ranges.
41	3.3	274	14.3	11.9	4.8 ↓	38.7	16.2	9.5	4.6	94	REM concentration of steel material and REM2O3 concentration are out of the ranges.
42	2.1	296	1.5	6.2	52.8 ↑	13.4	15.5	8.2	3.4	100	Concentration of REM2O3 is out of the range.
43	2.7	213	7.8	8.3	4.5 ↓	39.8	24.1	8.9	8.6	95	Concentration of REM2O3 is out of the range.
44	0.8	418	8.7	2.8	10.2	54.6 ↑	9.9	8.6	5.2	116	Zr concentration of steel material and ZrO2 concentration are out of the ranges.
45	1.3	314	13.6	10.9	23.8	4.6 ↓	17.3	11.3	18.5	106	Zr concentration of steel material and ZrO2 concentration are out of the ranges.
46	2.2	376	10	5.3	19.5	53.9 ↑	7.6	1.4	2.3	85	ZrO2 concentration is out of the range.
47	1.9	152	12.7	16.7	25.1	4.3 ↓	20.4	3.2	17.6	85	ZrO2 concentration is out of the range.
48	0.6	256	4.5	6.4	12.6	12.4	55.5 ↑	3.4	5.2	107	Ca concentration of steel material and CaO concentration are out of the ranges.
49	1.7	301	7.1	6.5	35.3	20.3	4.7 ↓	9.2	16.9	100	Ca concentration of steel material and CaO concentration are out of the ranges.
50	3.4	205	10.4	7.7	9.9	15.4	52.3 ↑	3.6	0.7	68	CaO concentration is out of the range.
51	3	633	11.4	8.2	25.9	29.8	4.1 ↓	12.5	8.1	85	CaO concentration is out of the range.
52	1.9	229	7.3	9.6	15.6	29.5	11.8	16.5 ↑	9.7	86	S concentration of steel material and S concentration of complex oxide are out of the ranges.
53	4.1	271	8.8	15.3	16.8	27.8	18.1	0.6 ↓	12.6	59	S concentration of steel material and S concentration of complex oxide are out of the ranges.
54	2.2	584	8.4	8.8	22.1	21.2	18.8	15.7 ↑	7	80	S concentration of complex oxide is out of the range.
55	1.1	153	11.5	11.7	35.1	15.6	10.6	0.3 ↓	15.2	88	S concentration of complex oxide is out of the range.
56	5.2 ↑	515	9.2	3.9	30.1	18.8	22.5	8.4	7.1	102	The number of complex oxides exceeding 3 µm is large.
57	6.5 ↑	243	8.6	9.7	21.8	19.7	16.6	7.8	15.8	87	The number of complex oxides exceeding 3 µm is large.
58	5.8 ↑	80 ↓	8.1	7.5	18.6	21.5	18.4	9.2	16.7	45	The number of complex oxides exceeding 3 µm is large and that of complex oxides that are 0.1-3 µm is small.
59	3.5	92 ↓	2.1	14	38.7	14.4	9.7	5	18.1	125	The number of complex oxides that are 0.1-3 µm is small.
60	7.4 ↑	85 ↓	6.9	6.7	19.2	26.5	13.4	10.3	17	67	The number of complex oxides exceeding 3 µm is large and that of complex oxides that are 0.1-3 µm is small.
61	1.4	87 ↓	12.5	8.8	21.6	20.5	17.8	4.2	18.6	71	The number of complex oxides that are 0.1-3 µm is small.
62	4.3	69 ↓	9.4	15.4	10.2	33.5	12.6	11.5	7.4	65	The number of complex oxides that are 0.1-3 µm is small.
63	1.8	60 ↓	5.8	6.3	24.8	22.2	12.5	12.9	15.7	87	The number of complex oxides that are 0.1-3 µm is small.
64	0.9	55 ↓	2.3	9.5	16.2	28.4	15.6	10.9	17.1	100	The number of complex oxides that are 0.1-3 µm is small.
65	4.2	48 ↓	7.5	11.4	14.2	13.9	35.6	11.6	5.8	49	The number of complex oxides that are 0.1-3 µm is small.
66	2.7	95 ↓	5	8.4	27.8	25.1	17.7	2.8	13.2	104	The number of complex oxides that are 0.1-3 µm is small.
67	3.5	77 ↓	2.9	14.9	32.5	14.8	9.4	6.2	19.3	68	The number of complex oxides that are 0.1-3 µm is small.

the present embodiment shown in Table 4 will be compared with those of the comparative examples shown in Table 7, with reference to Figs. 1-3. Fig. 1 is a graph showing the HAZ toughness of the steel materials according to the embodiment shown in Table 4 and those of the steel materials Nos. 59 and 61-67 of the comparative examples shown in Table 7. In each of the examples and comparative examples shown in Fig. 1, the number of complex oxides having a circular-equivalent diameter of greater than 3 μm is less than 5.0/mm^2; however, each of the steel materials Nos. 59 and 61-67 of the comparative examples represents an example in which the number of complex oxides having a circular-equivalent diameter of 0.1-3 μm was less than 100, and the test result for the HAZ toughness of each of them was greatly less than 140 J.

[0081] Fig. 2 is a graph showing the HAZ toughness of the steel materials according to the present embodiment shown in Table 4 and those of the steel materials Nos. 32-55 of the comparative examples shown in Table 7. In each of the examples and comparative examples shown in Fig. 1, the number of complex oxides having a circular-equivalent diameter of greater than 3 μm is less than 5.0/mm^2 and the number of complex oxides having a circular-equivalent diameter of 0.1-3 μm is at least 100; however, each of the steel materials Nos. 32-55 of the comparative examples represents an example in which the average composition of a complex oxide does not satisfy the conditions specified in the embodiment, and the test result for HAZ toughness of each of them was greatly less than 140 J.

[0082] Fig. 3 is a graph showing the HAZ toughness of the steel materials according to the present embodiment shown in Table 4 and those of the steel materials Nos. 56 and 57 of the comparative examples shown in Table 7. In each of the examples and comparative examples shown in Fig. 3, the number of complex oxides having a circular-equivalent diameter of 0.1-3 μm is at least 100; however, each of the steel materials Nos. 56 and 57 of the comparative examples represents an example in which the number of complex oxides having a circular-equivalent diameter of greater than 3 μm is no less than 5.0/mm^2, and the test result for the HAZ toughness of each of them was greatly less than 140 J.

[0083] As described above, a steel material, having a structure that satisfies the conditions specified in the present embodiment, can exert superior HAZ toughness even for high heat input welding. The embodiments disclosed herein are to be construed as being exemplary in all respects and not to be construed as being limitative. In the embodiments disclosed herein, in particular, the matters explicitly disclosed herein, such as, for example, running conditions, operating conditions, various parameters, and the size, weight, or volume of a structure, are not deviated from the ranges within which a person skilled in the art usually performs, and the values that a usual person skilled in the art can easily conceive of are adopted.

[0084] It has been described that the present steel material is produced in secondary refining; however, a steel material having similar HAZ toughness can be produced by using, for example, a converter furnace or an electric furnace. Accordingly, a production method of the present steel material using a converter furnace or an electric furnace is also encompassed by the technical scope of the present invention.

[0085] The present application is based on Japanese Patent Application (Patent Application No. 2013-060452), filed March 22, 2013, and the contents are incorporated herein by reference.

Industrial Applicability

[0086] A steel plate according to the present invention achieves superior HAZ toughness even for high heat input welding, and hence is suitable to be used in welded structures, such as ships, constructions, and bridges.

Claims

1. A steel material having superior toughness at welding heat affected zone, the steel material containing, in units of mass%:

0.02-0.13% of C,
0.05-0.5% of Si,
1.0-2.5% of Mn,
no greater than 0.03% of P (exclusive of 0%),
no greater than 0.01% of S (exclusive of 0%),
0.002-0.040% of Al,
0.005-0.040% of Ti,
0.0003-0.020% of Zr,
0.0003-0.020% of REM,
0.0003-0.0080% of Ca,
0.0030-0.010% of N, and
0.0003-0.0050% of O, with a remainder comprising iron and unavoidable impurities, wherein
the steel material contains a complex oxide containing REM, Zr, Ti, Al, Ca, and S, and wherein with respect to the complex oxide in the steel material,
the number of complex oxides having a circular-equivalent diameter of greater than 3 μm is no greater than 5.0/mm^2, and

the number of complex oxides having a circular-equivalent diameter of 0.1-3 μm and satisfying formula (1) is at least 100/mm^2,
and furthermore the average composition of the complex oxides that are 0.1-3 μm satisfying formula (1) contains 20% or less of Al_2O_3, 3-20% of TiO_2, 5-50% of ZrO_2, 5-50% of REM oxide, 5-50% of CaO, and 1-15% of S.

$$0.008 \leq (1/d) \times \{\text{mass\% S}/(\text{mass\% CaO} + \text{mass\% REM}_2\text{O}_3)\} \leq 0.289 \quad \ldots(1)$$

(where d is the circular·equivalent
diameter of each complex oxide, and is 0.1-·3 μm).

2. The steel material having superior toughness at welding heat affected zone according to claim 1 containing at least one of

0.05-1.50% of Ni,
0.05-1.50% of Cu,
0.05-1.50% of Cr,
0.05-1.50% of Mo,
0.002-0.10% of Nb,
0.002-0.10% of V, and
0.0005-0.0050% of B.

FIG. 1

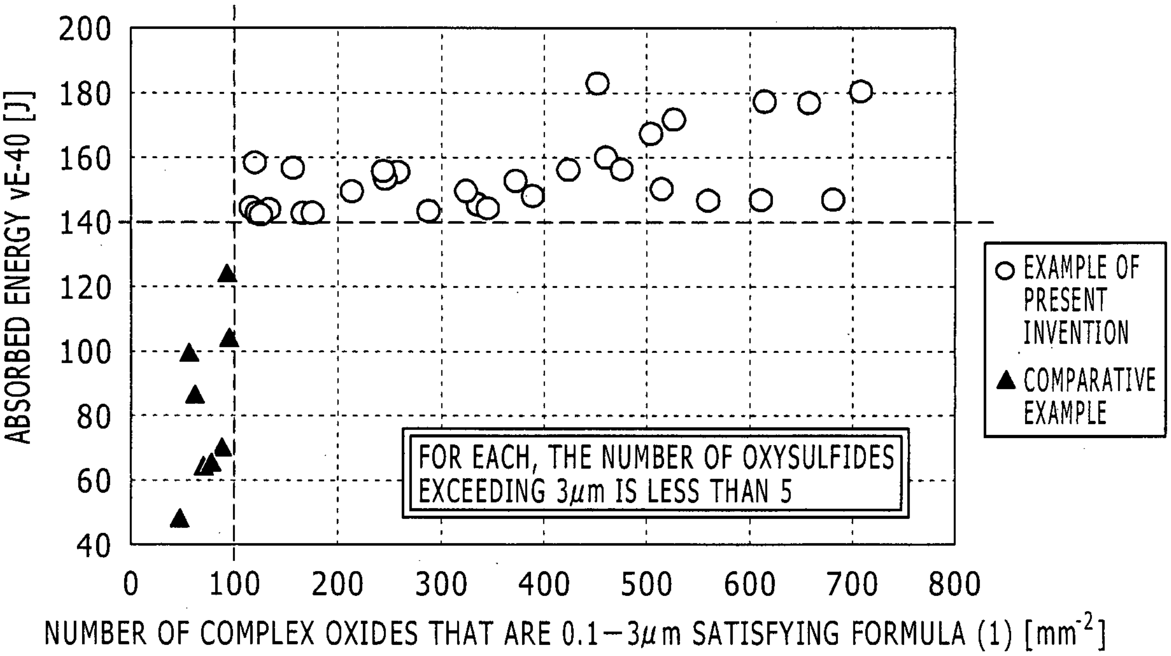

200
180
160
140
120
100
80
60
40
ABSORBED ENERGY vE-40 [J]
0
100
200
300
400
500
600
700
800
NUMBER OF COMPLEX OXIDES THAT ARE 0.1−3μm SATISFYING FORMULA (1) [mm-2]
○ EXAMPLE OF PRESENT INVENTION
▲ COMPARATIVE EXAMPLE
FOR EACH, THE NUMBER OF OXYSULFIDES EXCEEDING 3μm IS LESS THAN 5

FIG. 2

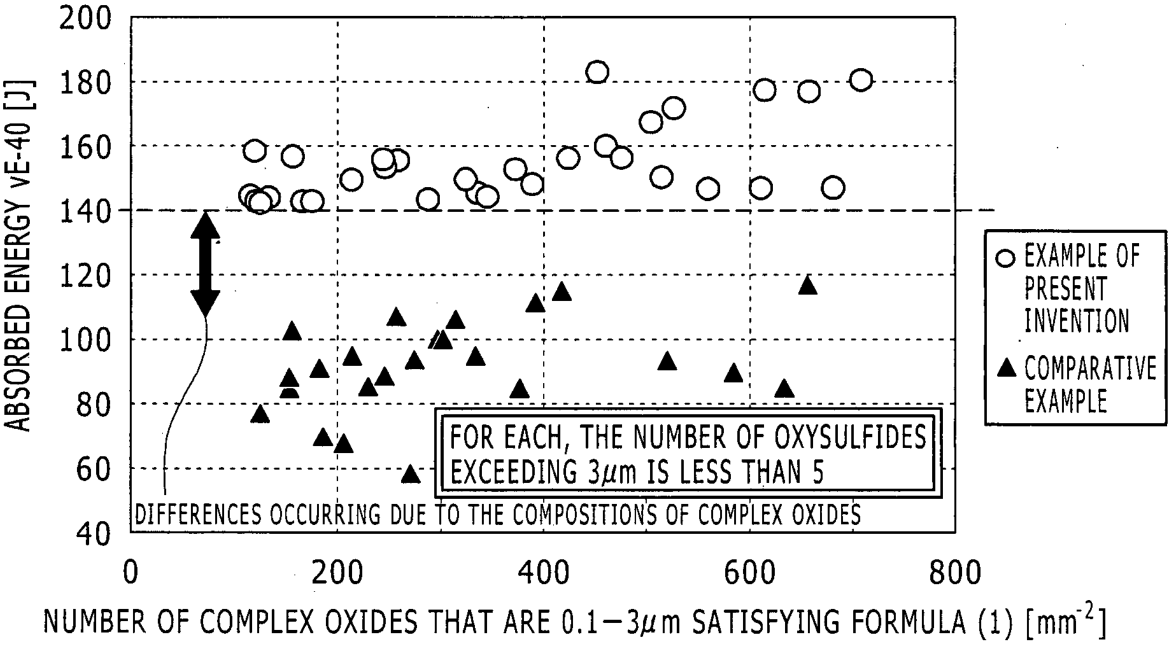
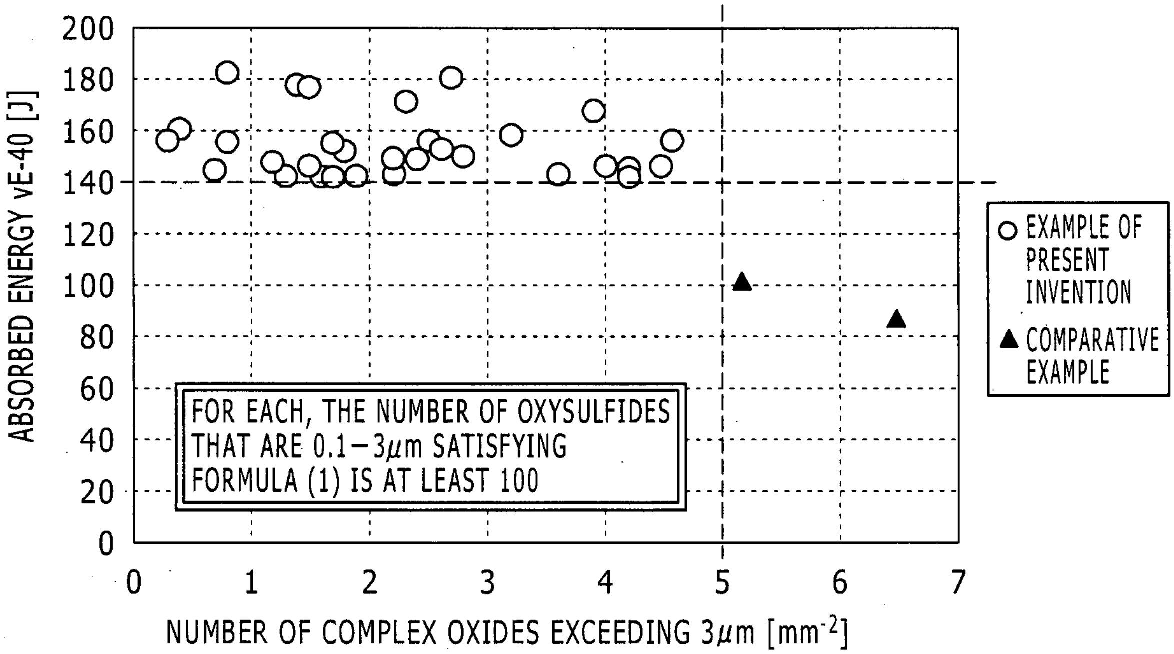

200
180
160
140
120
100
80
60
40
ABSORBED ENERGY vE-40 [J]
0
200
400
600
800
NUMBER OF COMPLEX OXIDES THAT ARE 0.1−3μm SATISFYING FORMULA (1) [mm-2]
○ EXAMPLE OF PRESENT INVENTION
▲ COMPARATIVE EXAMPLE
FOR EACH, THE NUMBER OF OXYSULFIDES EXCEEDING 3μm IS LESS THAN 5
DIFFERENCES OCCURRING DUE TO THE COMPOSITIONS OF COMPLEX OXIDES

FIG. 3


ABSORBED ENERGY vE-40 [J]
200
180
160
140
120
100
80
60
40
20
0
0
1
2
3
4
5
6
7
NUMBER OF COMPLEX OXIDES EXCEEDING 3μm [mm⁻²]
FOR EACH, THE NUMBER OF OXYSULFIDES THAT ARE 0.1–3μm SATISFYING FORMULA (1) IS AT LEAST 100
○ EXAMPLE OF PRESENT INVENTION
▲ COMPARATIVE EXAMPLE

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/057205

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(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, 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	1996-2014
Kokai Jitsuyo Shinan Koho	1971-2014	Toroku Jitsuyo Shinan Koho	1994-2014

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-162797 A (Kobe Steel, Ltd.), 30 August 2012 (30.08.2012), claims; paragraphs [0031] to [0129]; examples & WO 2012/014998 A1	1,2
A	JP 2009-138255 A (Kobe Steel, Ltd.), 25 June 2009 (25.06.2009), claims; paragraphs [0015] to [0047]; examples & KR 10-2009-0049530 A & CN 101435051 A	1,2
A	JP 2011-219797 A (Kobe Steel, Ltd.), 04 November 2011 (04.11.2011), entire text (Family: none)	1,2

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

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance
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"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 22 April, 2014 (22.04.14)	Date of mailing of the international search report 28 April, 2014 (28.04.14)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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

INTERNATIONAL SEARCH REPORT	International application No. PCT/JP2014/057205

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2010-209433 A (Kobe Steel, Ltd.), 24 September 2010 (24.09.2010), entire text & KR 10-2010-0102557 A & CN 101831588 A	1,2
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- JP 4762450 B **[0009]**
- JP 4039223 B **[0009]**
- JP 11264048 A **[0009]**
- JP 4144121 B **[0009]**
- JP 2013060452 A **[0085]**