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(54) STEEL MATERIAL

(57) A steel material, comprising, in terms of percentage by mass: from 0.01 to 0.20% of C, from 0.01 to 1.00% of Si, from 0.05 to 3.00% of Mn, from 0 to 0.050% of P, from 0 to 0.0100% of S, from 0.05 to 0.25% of Sn, from 0 to 0.100% of Al, from 0.0005 to 0.0100% of N, from 0.0001 to 0.0100% of O, from 0 to 0.050% of Ti, from 0 to 0.050% of Nb, from 0 to 0.050% of V, from 0 to 0.050% of W, from 0 to 0.050% of Mo, from 0 to 0.10% of Cu, Ni: from 0 to 0.05% of Ni, from 0 to 0.10% of Cr, from 0 to 0.05% of Sb, from 0 to 0.0010% of B, from 0 to 0.0100% of Ca, from 0 to 0.0100% of Mg, from 0 to 0.0100% of REM, and a balance consisting of Fe and impurities, wherein an Sn ratio of an Sn concentration, a, at a crystal grain boundary to an Sn concentration, b, inside a crystal grain, expressed by a/b, is 1.2 or less.

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Description

Technical Field

[0001] The present disclosure relates to steel material.

Background Art

[0002] In recent years, demand has urgently increased for improvement of the material properties of various steel materials, such as thick steel plates to be used for large structures such as offshore structures built in ice-bound seas, or bridges, and in addition to the improvement of corrosion resistance, there is high demand for the improvement of low-temperature toughness and fatigue characteristics.

[0003] Conventionally, an Sn-alloyed steel has been proposed in order to improve corrosion resistance in a seawater environment.

[0004] For example, Japanese Patent Application Laid-Open (JP-A) No. 2010-064110, JP-A No. 2012-057236, and JP-A No. 2012-255184 disclose steel materials in which corrosion resistance in an environment containing chloride ions (Cl^- ions) is improved by the inclusion of Sn in amounts of from 0.005 to 0.3 mass%, from 0.02 to 0.40 mass%, and from 0.01 to 0.50 mass%, respectively.

[0005] Further, JP-A No. 2012-144799 discloses a steel material for an offshore structure containing Sn in amount of from 0.03 to 0.5 mass%, and composed of ferrite and a hard second phase.

[0006] Further, Japanese Patent No. 5839151 discloses a technique for improving the corrosion resistance of steel by regulating the Sn concentration ratio between a soft structure and a hard structure by dividing water cooling into two stages.

SUMMARY OF INVENTION

Technical Problem

[0007] As described above, in order to improve corrosion resistance in a seawater environment or the like, an Sn-alloyed steel has been proposed. However, in addition to improvement of corrosion resistance by the addition of Sn, further improvement of mechanical properties, especially toughness and fatigue characteristics, is required.

[0008] For example, with respect to the inventions of JP-A Nos. 2010-064110, 2012-057236, and 2012-255184, which disclose improvement of corrosion resistance by the addition of Sn, there remains room for further improvement in terms of toughness and fatigue characteristics, and a technique that satisfies all of the demands regarding corrosion resistance, toughness, and fatigue characteristics is still required.

[0009] In the invention described in JP-A No. 2012-144799, while both corrosion resistance and low-temperature toughness can be improved, there remains room for further improvement with respect to fatigue characteristics.

[0010] Further, according to Japanese Patent No. 5839151, the corrosion resistance of steel is improved by regulating the Sn concentration ratio between the soft structure and the hard structure by dividing water cooling into two stages; however, there remains room for further improvement with respect to low-temperature toughness and fatigue characteristics.

[0011] An object of the present disclosure is to provide a steel material which has excellent corrosion resistance as well as low-temperature toughness and fatigue characteristics. Solution to Problem

[0012] The present disclosure was made to achieve the above object with a steel material which essentials were as follows.

(1) A steel material includes, in terms of percentage by mass:

from 0.01 to 0.20% of C,
from 0.01 to 1.00% of Si,
from 0.05 to 3.00% of Mn,
from 0 to 0.050% of P,
from 0 to 0.0100% of S,
from 0.05 to 0.25% of Sn,
from 0 to 0.100% of Al,
from 0.0005 to 0.0100% of N,
from 0.0001 to 0.0100% of O,
from 0 to 0.050% of Ti,

from 0 to 0.050% of Nb,
from 0 to 0.050% of V,
from 0 to 0.050% of W,
from 0 to 0.050% of Mo,
from 0 to 0.10% of Cu,
from 0 to 0.05% of Ni,
from 0 to 0.10% of Cr,
from 0 to 0.05% of Sb,
from 0 to 0.0010% of B,
from 0 to 0.0100% of Ca,
from 0 to 0.0100% of Mg,
from 0 to 0.0100% of REM, and
a balance consisting of Fe and impurities,
in which the Sn ratio of the Sn concentration, a, at a crystal grain boundary to the Sn concentration, b, inside a crystal grain, expressed by a/b, is 1.2 or less.

(2) The steel material according to (1) above in a form of steel plate with a plate thickness of from 6 to 100 mm.

Advantageous Effects of Invention

[0013] According to the present disclosure, it is possible to obtain a steel material with excellent corrosion resistance, low-temperature toughness, and fatigue characteristics.

DESCRIPTION OF EMBODIMENTS

[0014] A steel material according to the present embodiments will be described in detail.

[0015] A numerical range expressed by "from x to y" or "between x and y" includes herein the values of x and y in the range as the minimum and maximum values, respectively.

[0016] A steel material according to the embodiment, comprising in terms of percentage by mass, from 0.01 to 0.20% of C, from 0.01 to 1.00% of Si, from 0.05 to 3.00% of Mn, from 0 to 0.050% of P, from 0 to 0.0100% of S, from 0.05 to 0.25% of Sn, from 0 to 0.100% of Al, from 0.0005 to 0.0100% of N, from 0.0001 to 0.0100% of O, from 0 to 0.050% of Ti, from 0 to 0.050% of Nb, from 0 to 0.050% of V, from 0 to 0.050% of W, from 0 to 0.050% of Mo, from 0 to 0.10% of Cu, from 0 to 0.05% of Ni, from 0 to 0.10% of Cr, from 0 to 0.05% of Sb, from 0 to 0.0010% of B, from 0 to 0.0100% of Ca, from 0 to 0.0100% of Mg, from 0 to 0.0100% of REM, and a balance consisting of Fe and impurities, in which the Sn ratio of the Sn concentration, a, at a crystal grain boundary to the Sn concentration, b, inside a crystal grain, expressed by a/b, is 1.2 or less.

[0017] When a steel material of the embodiment has the above composition, it can be a steel material excellent in corrosion resistance and also in low-temperature toughness and fatigue characteristics. Although the reason therefor is not very clear, it is presumed as follows.

[0018] The present inventors prepared various steel plates with different Sn contents, and investigated the relationship between corrosion resistance and toughness. As a result, it has been found that as the Sn content increases, the corrosion resistance improves, but the absorbed energy (low temperature toughness) at 0°C in the Charpy impact test may deteriorate in some cases. For example, when the threshold of corrosion resistance in a SAE J 2334 test is set at 0.6 mm or less, and the threshold of absorbed energy at 0°C is set at 150 J or more, it has been found that not both can be easily satisfied stably.

[0019] Therefore, further investigations on corrosion resistance and absorbed energy were conducted, and as a result the composition of steel material, with which excellent absorbed energy could be obtained even at high Sn content, was found.

[0020] Further, detailed investigation on the steel material with improved absorbed energy was conducted, and as a result it was found that the ratio between the Sn at the crystal grain boundary and the Sn inside the crystal grain strongly influences the low-temperature toughness of a steel. Also, it was found that the ratio between the Sn at the crystal grain boundary and the Sn inside the crystal grain also influences the fatigue characteristic of a steel. Furthermore, it was found that the same influences the corrosion resistance.

[0021] The inventors further studied diligently about a steel material excellent in all of corrosion resistance, low-temperature toughness, and fatigue characteristics, and as a result, the following findings were obtained.

[0022] Since the melting point of Sn is low, when Sn is added to a steel material, Sn diffuses within a crystal grain during cooling after rolling and reheating, and segregates at the crystal grain boundary. Then, when Sn segregation at the crystal grain boundary occurs, the toughness of the steel decreases markedly.

[0023] In this regard, when segregation of Sn at a crystal grain boundary of Sn in a steel material is suppressed, in particular, when the Sn ratio of the Sn concentration [a] at a crystal grain boundary to the Sn concentration [b] inside a crystal grain, expressed by [a/b] (hereinafter also simply referred to as "the ratio between the Sn at the crystal grain boundary and the Sn inside the crystal grain") is 1.2 or less, it has been found that the low-temperature toughness and the fatigue characteristics are improved, while maintaining excellent corrosion resistance.

[0024] There is no particular restriction on the means for regulating the ratio between the Sn at the crystal grain boundary and the Sn inside the crystal grain to 1.2 or less, and for example, when an Sn-containing steel is produced under appropriate conditions, it is possible to suppress segregation of Sn at a grain boundary. Specifically, a steel after the finish rolling is slowly cooled first, then held at a predetermined temperature for a certain period of time allowing recuperation. Thereafter by conducting strong-cooling to a temperature of 550°C or less, segregation of Sn at a grain boundary can be suppressed, and the Sn ratio can be regulated within the above range.

[0025] This embodiment was devised based on the above findings. Each requirement of the embodiment will be described in detail below.

(A) Chemical Composition

[0026] The reasons for defining the respective elements are as follows. In the following description, "%" for a content means "mass%".

C: 0.01 to 0.20%

[0027] C is an element for improving the strength of a steel material. However, when the C content is excessive, the weldability is remarkably deteriorated. Further, as the C content increases, the formation amount of cementite that acts as a cathode to promote corrosion in a low pH environment increases, and the corrosion resistance of a steel material decreases. Therefore, the C content is defined in a range of from 0.01 to 0.20%. The C content is preferably 0.02% or more, and more preferably 0.03% or more. The lower limit of the C content may be 0.05%, 0.07%, or 0.09%. Further, the C content is preferably 0.18% or less, and more preferably 0.16% or less. The upper limit of the C content may be 0.15%, or 0.13%.

Si: 0.01 to 1.00%

[0028] Si is an element necessary for deoxidation. In order to obtain a sufficient deoxidation effect, it is necessary to contain it 0.01% or more. On the other hand, when the Si content is excessive, the toughness of a steel material, especially when welding is performed, the toughness of a base metal and a weld heat affected zone is impaired. Therefore, the Si content is defined in a range of from 0.01 to 1.00%. The Si content is preferably 0.03% or more, and more preferably 0.05% or more. The lower limit of the Si content may be 0.10%, 0.15%, or 0.20%. Also, the Si content is preferably 0.80% or less, and more preferably 0.60% or less. The upper limit of the Si content may be 0.50%, 0.40%, or 0.30%.

Mn: 0.05 to 3.00%

[0029] Mn is an element having an action of increasing the strength of a steel material at low cost. However, when the Mn content is excessive, the Mn segregation increases, and the toughness deteriorates. Therefore, the Mn content is defined in a range of from 0.05 to 3.00%. The Mn content is preferably 0.50% or more, and more preferably 0.80% or more. Further, the Mn content is preferably 2.50% or less, and more preferably 2.00% or less.

P: 0 to 0.050%

[0030] P is an element existing as an impurity in a steel material. P is an element that lowers acid resistance of a steel material, and lowers the corrosion resistance of a steel material in a chloride corrosion environment where the pH at a corrosion interface decreases. P also deteriorates the weldability and toughness of a steel material. Therefore, the P content is limited to 0.050% or less. The P content is preferably 0.040% or less, and more preferably 0.030% or less. For improving the toughness, the upper limit of the P content may be 0.020%, 0.015%, or 0.010%. Although it is not easy to completely remove P, it is not necessary to exclude it, and the lower limit of the P content is 0%. Since the desulfurization cost for dephosphorization to ultra-low concentration is high, the lower limit of the P content may be 0.0005%, 0.001%, or 0.003%.

S: 0 to 0.0100%

[0031] S is an element existing as an impurity in a steel material. S forms MnS as a starting point of corrosion in a steel material. When the S content exceeds 0.0100%, the decrease in corrosion resistance of a steel material becomes conspicuous. Therefore, the S content is limited to 0.0100% or less. The S content is preferably 0.0080% or less, more preferably 0.0060% or less, and even more preferably 0.0040% or less. Although it is not easy to remove S completely, it is not necessary to exclude it, and the lower limit of the S content is 0%. Since the refining cost for desulphurization to ultra-low concentration is high, the lower limit of the S content may be 0.0005%, or 0.0010%.

Sn: 0.05 to 0.25%

[0032] Since Sn significantly suppresses an anode dissolution reaction of a steel material in a low pH chloride environment, it greatly improves corrosion resistance of a steel material in a chloride corrosion environment. However, when the Sn content becomes excessive, not only the above effect is saturated, but also the toughness of a steel material, and especially when welding is performed, the toughness of a base material, and a high-heat-input welded joint deteriorates. Therefore, the Sn content is defined in a range of from 0.05 to 0.25%. The Sn content is preferably 0.07% or more, more preferably 0.09% or more, and further preferably 0.10% or more. Further, the Sn content is preferably 0.20% or less, more preferably 0.18% or less, and further preferably 0.016% or less.

Al: 0 to 0.100%

[0033] Al is an element effective for deoxidizing a steel material. Since Si is contained in a steel material in this embodiment, deoxidation is performed by Si. Therefore, a deoxidation treatment with Al is not absolutely necessary, and the lower limit of the Al content is 0%. However, deoxidation with Al may be performed in addition to the same with Si. Meanwhile, when the Al content exceeds 0.100%, the corrosion resistance of a steel material in a low pH environment is lowered, so that the corrosion resistance of the steel material in a chloride corrosion environment is lowered. Further, when the Al content exceeds 0.100%, a nitride becomes coarse and the toughness of a steel material decreases. Therefore, the Al content is defined in a range of from 0 to 0.100%. In order to obtain the deoxidation effect with Al, the Al content is preferably 0.005% or more, more preferably 0.010% or more, further preferably 0.015% or more, still further preferably 0.020% or more, and particularly preferably 0.025% or more. Further, the Al content is preferably 0.060% or less, and more preferably 0.045% or less.

N: 0.0005 to 0.0100%

[0034] N dissolves in the form of ammonia and has an effect of improving the corrosion resistance of a steel plate in a saline environment by suppressing the pH decrease due to the hydrolysis of Fe^{3+} in an environment where the amount of air borne salt particle is high. On the other hand, when the N content is excessive, not only the effect is saturated, but also the toughness of a steel plate is deteriorated. Therefore, the N content is regulated in a range of from 0.0005 to 0.0100%. Since it is not easy to lower the lower limit of N below 0.0005%, and it is also costly, the lower limit is set at 0.0005%. The lower limit of the N content may be set at 0.0010% or 0.0020%, according to need. When the content of N exceeds 0.0100%, there arises a risk that coarse AlN is formed and the toughness is apt to decrease, so the upper limit is set at 0.0100%. In order to further increase the toughness, the upper limit of the N content may be set at 0.0080% or 0.0060%.

O: 0.0001 to 0.0100%

[0035] When a steel material contains a trace amount of O (oxygen), the toughness of the same is improved, and especially when welding is applied, the toughness of a welded joint is improved. Meanwhile, O forms an oxide, such as SnO and SnO_2. Therefore, when the O content becomes excessive, when the O content becomes excessive, the Sn concentration in the steel cannot be sufficiently secured. In addition, since the above oxide acts as a starting point of corrosion, the corrosion resistance of a steel material decreases. Therefore, the O content is regulated in a range of from 0.0001 to 0.0100%. The content of O is preferably 0.0002% or more, and more preferably 0.0003% or more. The lower limit of the O content may be 0.0005%, 0.0010%, 0.0015%, or 0.0019%. Also, the O content is preferably 0.0090% or less, and more preferably 0.0080% or less. The upper limit of the O content may be 0.0060%, 0.0040%, or 0.0030%.

Ti: 0 to 0.050%

Nb: 0 to 0.050%

V: 0 to 0.050%

[0036] All of Ti, Nb, and V are elements which form precipitates to enhance the strength of a steel material, and may be contained according to need. It is not prerequisite to contain the elements, and the lower limits of their contents are all 0%. On the other hand, when Ti, Nb, or V are excessively contained, the toughness is apt to decrease. Therefore, each content should be 0.050% or less. Each content is preferably 0.0030% or less, and more preferably 0.020% or less. In order to obtain the above effect, one or more kinds selected from Ti, Nb, and V may be contained at 0.001% or more.

W: 0 to 0.050%

Mo: 0 to 0.050%

[0037] When the content of W or Mo exceeds 0.050%, the corrosion resistance decreases. Therefore, the contents of W and Mo should be respectively 0.050% or less. It is preferable that both the contents are 0.040% or less. The upper limit of each of the W content and the Mo content may be 0.030%, 0.020%, 0.010%, or 0.005%. In order to improve the corrosion resistance, it is preferable that the W content and the Mo content are as small as possible, and the lower limits of their contents are 0%. However, in order to improve such properties as strength or toughness (especially low-temperature toughness), W and Mo may be contained, and the lower limits of their contents may be 0.010%, or 0.020%.

Cu: 0 to 0.10%

[0038] It is generally believed that Cu is an element that improves the corrosion resistance of a steel material. However, the present inventors have found that the corrosion resistance of a steel material decreases in a corrosive environment containing a chloride as assumed in this embodiment, when it contains Cu. The Cu content is preferably as low as possible, and the lower limit of the Cu content should be 0%. Meanwhile, considering possibility of contamination as an impurity, the Cu content is set at 0.10% or less. For the sake of enhancement of the corrosion resistance, the Cu content is preferably 0.07% or less, more preferably 0.05% or less, further preferably 0.03% or less, and still further preferably 0.02% or less. The Cu content is particularly preferably 0.01% or less.

Ni: 0 to 0.05%

[0039] It is generally believed that Ni improves, similarly to Cu, the corrosion resistance of a steel material. However, the present inventors have found that the corrosion resistance of a steel material decreases in a corrosive environment containing a chloride as assumed in this embodiment, when it contains Ni. The Ni content is preferably as low as possible, and the lower limit of the Ni content should be 0%. Meanwhile, even when it is mixed in as an impurity, so long as the Ni content is 0.05% or less, the corrosion resistance decrease is only slight. Therefore, the Ni content is set at 0.05% or less. For the sake of enhancement of the corrosion resistance, the Ni content is preferably 0.03% or less, more preferably 0.02% or less, and further preferably 0.01% or less.

Cr: 0 to 0.10%

[0040] It is generally believed that Cr is an element that improves corrosion resistance of steel material. However, the present inventors have found that the corrosion resistance of a steel material is deteriorated in a corrosive environment containing a chloride as assumed in this embodiment, when it contains Cr. The Cr content is preferably as low as possible, and the lower limit of the Cr content should be 0%. Meanwhile, considering possibility of contamination as an impurity, the Cr content is set at 0.10% or less. For the sake of enhancement of the corrosion resistance, the Cr content is preferably 0.07% or less, more preferably less than 0.05%, further preferably 0.03% or less, and still further preferably 0.02% or less. The Cr content is particularly preferably 0.01% or less.

Sb: 0 to 0.05%

[0041] Since Sb is an element that improves the acid resistance, Sb may be contained as necessary. It is not indispensable to contain Sb, and the lower limit of its content is 0%. Incidentally, even when Sb is contained in an amount exceeding 0.05%, not only the effect is saturated, but also the toughness and the like of the steel material are deteriorated.

Therefore, the Sb content is set at 0.05% or less. The upper limit of the Sb content may be 0.04% or less, or 0.03% or less. In order to obtain the above effect, the Sb content is preferably 0.005% or more, more preferably 0.010% or more, and further preferably 0.015% or more. When it is not necessary to obtain the above effect, the upper limit of the Sb content may be 0.015%, 0.010%, or 0.005% according to need.

B: 0 to 0.0010%

[0042] B is an element for increasing the strength of a steel material by addition of a trace amount thereof, so it may be added optionally. It is not indispensable to contain B, and the lower limit of its content is 0%. When B is added in an amount exceeding 0.0010%, the toughness may be deteriorated, so the B content is set at 0.0010% or less. In order to obtain the above effect, the B content is preferably 0.0003% or more, and more preferably 0.0005% or more. When it is not necessary to obtain the above effect, the upper limit of the B content may be 0.0005%, or 0.0003%, according to need.

Ca: 0 to 0.0100%

[0043] Ca is present in the form of an oxide in a steel material, and has an action of suppressing decrease in pH at the interface in a corrosion reaction zone to prevent corrosion, and therefore Ca may be included if necessary. It is not indispensable to contain Ca, and the lower limit of its content is 0%. When the Ca content exceeds 0.0100%, the above effect is saturated. Accordingly, the Ca content is set at 0.0100% or less. The Ca content is preferably 0.0050% or less, and more preferably 0.0040% or less. In order to obtain the above effect, the Ca content is preferably 0.0002% or more, and more preferably 0.0005% or more. When it is not necessary to obtain the above effect, the upper limit of the Ca content may be 0.0030%, 0.0005%, or 0.0002% or less, according to need.

Mg: 0 to 0.0100%

[0044] Similar to Ca, Mg has an action of suppressing decrease in pH at the interface in a corrosion reaction zone to prevent corrosion of a steel material, and therefore Mg may be included according to need. It is not indispensable to contain Mg, and the lower limit of its content is 0%. When the Mg content exceeds 0.0100%, the above effect is saturated. Therefore, the Mg content is set at 0.0100% or less. The Mg content is preferably 0.0050% or less, and more preferably 0.0040% or less. In order to obtain the above effect, the Mg content is preferably 0.0002% or more, and more preferably 0.0005% or more. When it is not necessary to obtain the above effect, the upper limit of the Mg content may be set at 0.0030%, 0.0005%, or 0.0002%, according to need.

REM: 0 to 0.0100%

[0045] Since REM (rare earth element) is an element that improves the weldability of a steel material, it may be included as necessary. It is not indispensable to contain REM, and the lower limit of its content is 0%. When the REM content exceeds 0.0100%, the above effect is saturated. Therefore, the REM content should be 0.0100% or less. The REM content is preferably 0.0050% or less, and more preferably 0.0040% or less. In order to obtain the above effect, the REM content is preferably 0.0002% or more, and more preferably 0.0005% or more. When it is not necessary to obtain the above effect, the upper limit of the Mg content may be set at 0.0030%, 0.0005%, or 0.0002%, according to need.

[0046] In this regard, REM is a collective term of 17 elements including 15 elements of lanthanoid, as well as Y and Sc. One or more of these 17 elements may be included in a steel material, and the REM content means the sum of the contents of such elements.

[0047] The balance of the chemical composition of a steel material of the embodiment is Fe and impurities.

[0048] In this regard, "impurity" means a component which is mixed in when a steel material is produced industrially due to various factors related to the raw material, such as ore, and scrap, or a production process, and which is tolerable so long as the embodiment is not adversely affected.

(B) Sn Ratio

The Sn ratio of the Sn concentration [a] at a crystal grain boundary to the Sn concentration [b] inside a crystal grain, expressed by [a/b]: 1.2 or less

[0049] As described above, the Sn ratio between the crystal grain boundary and the crystal grain inside affects the low-temperature toughness, the fatigue characteristics and the corrosion resistance of a steel. When Sn is segregated at the crystal grain boundary and the Sn ratio between the crystal grain boundary and the crystal grain inside exceeds 1.2, the improvement effect on the low-temperature toughness and the fatigue characteristics cannot be expected.

Therefore, the Sn ratio between the crystal grain boundary and the crystal grain inside is set at 1.2 or less. The Sn ratio is preferably 1.1 or less, and more preferably 1.05 or less. Although the lower limit of the Sn ratio need not be particularly determined, the lower limit may be set at 0.7, 0.8, 0.9, or 1.0.

[0050] There is no precipitate of Sn in a steel material of the embodiment, and the extraction residue is 0%. That is, all of Sn is dissolved as a solid solution in a steel material.

[0051] An Sn ratio between the crystal grain boundary and the crystal grain inside of the embodiment may be determined by the following method. Firstly, a cylindrical specimen having a diameter of 3 mm and a length of 10 mm is prepared from a steel material at a position of 1/4 t (t represents plate thickness or wall thickness). Then, the specimen was subjected to an ultra-high vacuum impact fracture mechanism attached to an Auger spectroscopic analyzer (Model 670i, manufactured by ULVAC-PHI, Inc.), and the fracture surface, which is formed by fracture in vacuum ($1.0E^{-9}$ Torr or less) in an atmosphere at the liquid nitrogen temperature (-150°C), is observed. The fracture surface is mostly occupied by cleavage fracture surfaces having a river pattern, and dimple fracture surfaces, and sparse intergranular fractured surfaces are also recognized. The crystal grain boundary and the crystal grain inside of the fracture surface are discriminated by a macro-fractographic method, and Auger spectra are measured at 10 positions in each crystal grain boundary and crystal grain inside. To verify the discrimination between the crystal grain boundary and the crystal grain inside, the fracture surface examined by the macro-fractographic method is analyzed by Auger spectroscopy with respect to C, which is apt to segregate at a crystal grain boundary, to confirm discrimination between the crystal grain boundary and the crystal grain inside. The Sn ratio is calculated by measuring the ratio of the concentrations (atom%) of Sn between the crystal grain boundary and the crystal grain inside. In this regard, the relative sensitivity coefficient is calibrated with Au.

(C) Dimensions

[0052] There is no particular restriction on the dimensions such as the thickness of a steel material of the embodiment. However, the effect of improving the corrosion resistance, the low-temperature toughness, and the fatigue resistance is more remarkably obtained when a steel material is used in a form of a steel plate having a thickness of from 6 to 100 mm. The thickness (plate thickness) of a steel plate is preferably from 10 to 40 mm. A steel material may be a steel pipe or a section steel, and its thickness or wall thickness may be from about 3 to 50 mm.

(D) Production Method

[0053] A steel material according to the embodiment can be produced using, for example, the production method described below.

[0054] Namely a method of producing a steel material including:

a step of preparing a slab whose chemical composition is the same as the above composition,
a heating step of heating the slab from 1000 to 1150°C,
a rough rolling step of applying rough rolling to the slab,
a finish rolling step of applying finish rolling to the slab having undergone rough rolling such that the finishing temperature of the surface becomes from 900 to 750°C while keeping the rolling reduction rate from 950°C at 50% or higher,
a first accelerated cooling step of performing accelerated cooling of the finish-rolled slab (steel material) at a cooling rate of from 5 to 10°C/s until the surface temperature reaches 630°C or less,
a recuperation step of suspending accelerated cooling of the slab (steel material) after the first accelerated cooling step and allowing cooling in the air for 30 to 120 sec (suspension of accelerated cooling and cooling in the air is hereinafter referred to as "holding"), and further allowing recuperation by the heat from the inside of the slab (steel material) until the surface temperature reaches a range of from 650 to 700°C
a second accelerated cooling step of performing accelerated cooling of the slab (steel material) after the recuperation step at a cooling rate of from 10 to 60°C/s until the surface temperature reaches 550°C or less, and
an air cooling step of performing cooling in the air after the second accelerated cooling step.

[0055] The heating temperature in the heating step is from 1000 to 1150°C. When the temperature is within the above range, the austenite grain size at the time of heating can be kept small, so that grain refining of the rolled structure can be achieved. When the heating temperature is 1150°C or lower, coarsening of austenite grains is suppressed and coarsening of the structure after cooling transformation is also suppressed, so that excellent low-temperature toughness can be achieved. On the other hand, when the heating temperature is 1000°C or higher, the alloy elements are sufficiently solutionized, so that the deterioration of the internal quality of the steel is suppressed, and the finishing temperature in rolling is not excessively lowered, so that the enhancement of low-temperature toughness can be expected.

[0056] Further, when the finishing temperature at the surface in the rolling step is 900°C or lower, the growth of recrystallized austenite grains is suppressed, and grain refining thereof is promoted. Further, when the finishing temperature is 750°C or higher, the ferrite structure becomes less susceptible to processing, so that the low-temperature toughness is improved. Consequently, the finishing temperature is set from 900 to 750°C.

[0057] Furthermore, when the rolling reduction rate from 950°C is 50% or more, partial recrystallization of austenite hardly occurs, so that a duplex grain structure is suppressed to enhance the low-temperature toughness. Consequently, the rolling reduction rate from 950°C is set at 50% or more.

[0058] Regarding cooling after rolling, water cooling is carried out under the following conditions.

<Slow Cooling After Completion of Rolling (First Accelerated Cooling Step)>

[0059] After finish rolling, accelerated cooling is immediately performed at a cooling rate of from 5 to 10°C/s until the surface temperature of a steel material becomes 630°C or lower. With the cooling rate within the above range, grain boundary segregation of Sn can be suppressed. When the cooling rate is 5°C/s or more, Sn diffusion is suppressed. When it is 10°C/s or less, the Sn ratio between the crystal grain boundary and the crystal grain inside is reduced, although the reason therefor is not very clear. As a result, in both cases, the low-temperature toughness and the fatigue characteristics are improved.

<Recuperation by Holding before Accelerated Cooling (Recuperation Step)>

[0060] After slow cooling, the accelerated cooling is suspended allowing cooling in the air (holding) for recuperation until the surface temperature of the cooled steel material rises again due to the internal temperature of the steel material and the surface temperature is equalized in a temperature range of from 650 to 700°C. The holding time (this time is the accelerated cooling suspension time corresponding to the recuperation time) is 30 to 120 sec. Owing to the recuperation step, it is possible to segregate elements that are apt to segregate, such as S, P, and C, into the crystal grain boundary, and to suppress diffusion of Sn. When the holding time is 30 sec or more, uniform recuperation deep into the inside of a steel material becomes possible. When the holding time is 120 seconds or less, elevation of the surface temperature of a steel material up to a temperature range exceeding 700°C may be suppressed more easily so that diffusion of Sn may be reduced to suppress segregation.

<Accelerated Cooling (Second Accelerated Cooling Step)>

[0061] Thereafter, cooling is resumed at a cooling rate of from 10 to 60°C/s until the surface temperature reaches 550°C or less. By accelerated cooling under the above conditions, it is possible to suppress segregation of Sn at the crystal grain boundary, and to refine the steel structure. When the cooling rate is 10°C/s or more, diffusion of Sn is suppressed, and segregation at the grain boundary is suppressed. Meanwhile, when the cooling rate is 60°C/s or less, an increase in the strength of a steel material plate is suppressed, and the fatigue resistance is improved.

[0062] After the second accelerated cooling step, cooling in the air is performed.

[0063] In a case where a steel material of the embodiment is used for a large structure, such as a bridge and an offshore structure, the tensile strength should preferably be in a range of from 400 to 650 MPa. The tensile strength may be also from 480 to 580 MPa.

EXAMPLES

[0064] The present disclosure will be described more specifically below by way of Examples, provided that the present disclosure is not limited to the Examples.

[0065] A steel having the chemical composition shown in Table 1 was melted in a furnace and then cast in to a slab with a thickness of 300 mm. The slab was heated, subjected to rough rolling and finish rolling, and then quickly cooled to a steel plate having a plate thickness of 20 mm. The production conditions are shown in Table 2.

[Table 1]

Steel grade	Chemical composition (mass%, balance: Fe and impurities)										
	C	Si	Mn	P	S	Sn	Al	N	O	Ti	Nb
A	0.13	0.33	1.41	0.010	0.0030	0.18	0.033	0.0041	0.0050		
B	0.12	0.31	1.33	0.001	0.0010	0.12	0.020	0.0028	0.0010		
c	0.10	0.31	1.30	0.003	0.0100	0.11	0.040	0.0038	0.0030		

(continued)

Steel grade	Chemical composition (mass%, balance: Fe and impurities)										
	C	Si	Mn	P	S	Sn	Al	N	O	Ti	Nb
D	0.14	0.36	1.22	0.010	0.0080	0.09	0.027	0.0024	0.0030		
E	0.11	0.34	1.13	0.050	0.0050	0.20	0.036	0.0033	0.0050		
F	0.12	0.38	1.62	0.005	0.0010	0.17	0.023	0.0020	0.0002	0.011	0.024
G	0.13	0.31	1.13	0.003	0.0060	0.09	0.023	0.0036	0.0080		
H	0.08	0.21	1.90	0.010	0.0005	0.12	0.025	0.0045	0.0050		
I	0.08	0.28	1.02	0.005	0.0030	0.19	0.031	0.0034	0.0050		0.016
J	0.12	0.21	1.94	0.001	0.0010	0.05	0.023	0.0026	0.0030	0.015	0.008
K	0.08	0.21	1.02	0.003	0.0030	0.05	0.020	0.0030	0.0020		
L	0.13	0.31	1.13	0.005	0.0010	0.12	0.020	0.0030	0.0030		
M	0.08	0.28	1.02	0.050	0.0050	0.19	0.031	0.0034	0.0050		
N	0.10	0.25	1.13	0.003	0.0050	0.12	0.030	0.0020	0.0030		
O	0.13	0.32	1.25	0.005	0.0050	-	0.030	0.0036	0.0030		
P	0.10	0.22	1.17	0.010	0.0030	0.02	0.030	0.0040	0.0030		
Q	0.14	0.25	1.61	0.005	0.0080	0.30	0.028	0.0034	0.0050		
	V	W	Mo	Cu	Ni	Cr	Sb	B	Ca	Mg	REM
A			0.030		0.01						
B											
C					0.01						
D											
E			0.020								
F		0.011		0.07	0.03			0.0003			
G	0.009								0.0004		
H			0.010					0.0002		0.0033	
I						0.01					0.0019
J	0.007			0.03			0.01				
K				0.12							
L			0.070		0.02						
M					0.07						
N						1.10					
O			0.030		0.03						
P			0.010								
Q					0.01						

[Table 2]

Test No.	Steel grade	Rolling step			1st accelerated cooling step		Recuperation step		2nd accelerated cooling step	
		Heating temperature (°C)	Finishing temperature (°C)	Reduction rate at 950°C or higher (%)	Slow cooling rate (°C/s)	Cooling completion temperature (°C)	Holding time (s)	Holding time completion temperature (°C)	Accelerated cooling rate (°C/s)	Cooling completion temperature (°C)
1	A	1150	850	52	7	600	60	680	30	500
2	B	1150	800	55	6	580	30	650	10	520
3	C	1120	750	55	7	620	30	650	40	450
4	D	1150	840	50	7	600	60	660	50	400
5	E	1120	890	52	6	630	90	700	20	520
6	F	1150	900	55	5	580	120	700	20	500
7	G	1000	810	58	10	600	60	650	20	550
8	H	1150	880	55	6	600	60	690	40	500
9	I	1150	750	55	7	620	30	660	20	520
10	J	1120	860	50	5	630	30	670	30	480
11	K	1150	860	52	6	600	60	660	30	450
12	L	1120	860	55	5	600	30	660	20	400
13	M	1150	890	50	7	580	60	700	40	520
14	N	1150	890	55	6	620	90	700	30	500
15	O	1120	890	55	6	620	60	700	30	520
16	P	1120	850	55	5	600	60	680	30	500
17	Q	1120	850	52	5	580	60	650	30	520
18	A	1150	850	50	2	650	90	680	30	500
19	A	1150	850	50	30	520	30	600	30	520
20	A	1150	850	50	6	600	120	720	30	520
21	A	1150	850	55	6	620	0	-	30	500
22	A	1150	850	50	10	600	30	650	8	560

(continued)

Test No.	Steel grade	Rolling step			1st accelerated cooling step		Recuperation step		2nd accelerated cooling step	
		Heating temperature (°C)	Finishing temperature (°C)	Reduction rate at 950°C or higher (%)	Slow cooling rate (°C/s)	Cooling completion temperature (°C)	Holding time (s)	Holding time completion temperature (°C)	Accelerated cooling rate (°C/s)	Cooling completion temperature (°C)
23	A	1150	850	50	6	620	30	650	65	380

[0066] Subsequently, a cylindrical specimen having a diameter of 3 mm and a length of 10 mm was cut out from each steel plate, and subjected to an ultra-high vacuum impact fracture mechanism attached to an Auger spectroscopic analyzer (Model 670i, manufactured by Ulvac Inc.), and the fracture surface, which was formed by fracture in vacuum (1.0E-9 Torr or less) in an atmosphere at the liquid nitrogen temperature (-150°C), was observed. The fracture surface was mostly occupied by cleavage fracture surfaces having a river pattern, and dimple fracture surfaces, and sparse intergranular fractured surfaces were also recognized. The crystal grain boundary and the crystal grain inside of the fracture surface were discriminated by a macro-fractographic method, and Auger spectra were measured at 10 positions in each crystal grain boundary and crystal grain inside. To verify the discrimination between the crystal grain boundary and the crystal grain inside, the fracture surface examined by the macro-fractographic method was analyzed by Auger spectroscopy with respect to C, which was apt to segregate at a crystal grain boundary, to confirm discrimination between the crystal grain boundary and the crystal grain inside. The Sn ratio was calculated by measuring the ratio of the concentrations (atom%) of Sn between the crystal grain boundary and the crystal grain inside. In this regard, the relative sensitivity coefficient was calibrated with Au.

[0067] Further, a corrosion resistance test, a toughness test, and a fatigue test were conducted for each steel plate.

<Corrosion Resistance Test>

[0068] A specimen having a length of 60 mm, a width of 100 mm, and a thickness of 3 mm was cut out from each steel plate, and subjected to the SAE J 2334 test. In doing so, two specimens were taken from each steel plate, and on one of them, an anticorrosion coating was formed in advance. The SAE J 2334 test will be described below.

[0069] The SAE J 2334 test is an accelerated deterioration test in which a cycle of humid stage and dry stage (humid → salt application → dry; 24 hours in total) is repeated to simulate a severely corrosive environment where the amount of air borne salt particle exceeds 1 mdd. The SAE J 2334 test was conducted repeating a cycle under the following conditions. The corrosion form under the following conditions is similar to the corrosion form of an atmospheric exposure test.

(Test Conditions)

[0070]

Humid stage: 50°C, 100% RH, 6 hours,
Salt application stage: Immersion in the aqueous solution with 0.5 mass% of NaCl, 0.1 mass% of $CaCl_2$, and 0.075 mass% of $NaHCO_3$ for 0.25 hours,
Dry stage: 60°C, 50% RH, 17.75 hours.

[0071] In addition, a shotblasting treatment was applied to the surface of each specimen. With respect to some specimens, after the shotblasting treatment, an anticorrosion primary coating, an under coating, an intermediate coating, and an over coating were applied one on another to form an anticorrosion coating having a total thickness of 250 μm.

[0072] As the anticorrosion primary coating, an inorganic zinc rich paint ("SHINTO-ZINC #2000" produced by SHINTO PAINT CO., LTD.) was coated to a thickness of 75 μm, and as a mist coating an epoxy resin paint ("NEO-GOSE #2300 MC" produced by SHINTO PAINT CO., LTD.) was applied. As the under coating, an epoxy resin coating ("NEO-GOSE #2300 PS" produced by Shinto Paint Co., Ltd.) was spray-coated to a film thickness of 120 μm. In addition, as the intermediate coating, an intermediate paint for a fluorine resin paint ("SHINTO-FLON #100 intermediate paint" produced by SHINTO PAINT CO., LTD.) was coated to a thickness of 30 μm. Further, as the over coating, a fluorine resin coating ("SHINTO-FLON #100" produced by SHINTO PAINT CO., LTD.) was spray-coated to a film thickness of 25 μm.

[0073] For each specimen having the anticorrosion coating, a cross scratch was formed on the anticorrosion coating to expose part of the steel material. With respect to each of the specimens on which an anticorrosion coating was not formed, rust was formed uniformly over the entire specimen surface after the test, and therefore its corrosion amount was determined. The "corrosion amount" was determined as the average plate thickness decrement of the specimen when a surface rust layer on the surface was removed. Specifically, the plate thickness decrement was calculated using the weight change of the specimen before and after the test, and the surface area of the specimen, and used as the corrosion amount.

[0074] The criteria for pass or fail at a corrosion resistance test were as follows. A SAE J 2334 test was conducted for 120 cycles using a specimen on which an anticorrosion coating was not formed, and one in which the corrosion amount was 0.60 mm or less was judged for passed. Further, a SAE J2334 test was conducted for 200 cycles using a specimen on which an anticorrosion coating was formed, and one in which the detached area at a scratched zone was 20% or less, and the maximum corrosion depth was 0.40 mm or less was judged as pass.

<Low-temperature Toughness Test>

[0075] The low-temperature toughness was evaluated on an impact test specimen taken from a central part in the plate thickness direction of the plate and in the direction perpendicular to the rolling direction, by determining the absorbed energy (vE_0) at 0°C using a V-notch specimen according to JIS Z 2242. A specimen with an absorbed energy of 150 J or more was judged as pass.

<Fatigue Test>

[0076] In a fatigue test, the stress amplitude was changed as a test parameter, and the relationship between the stress amplitude and the fatigue fracture life was represented by a S-N diagram, and a fatigue limit was derived therefrom. In the fatigue test, a No. 2 specimen specified in JIS Z 2275 was used, and the load ratio (the value obtained by dividing the minimum load by the maximum load) was set at 0.1. In this regard, the fatigue fracture life was defined as the time point at which the displacement (the displacement of the cylinder of an actuator that applied the load to a specimen) at the maximum load increased by 1 mm as compared with the start of the test. When the fatigue fracture life was 5.5×10^5 cycles or more, the fatigue resistance was judged as pass.

[0077] The results are summarized in Table 3.

[Table 3]

Test No.	Steel grade	Sn ratio between grain boundary and grain inside	SAE J2334 test without a coating 120CY	SAE J2334 test with a coating 200CY		Absorbed energy (J)	Fatigue characteristics ($\times 10^5$)	
			Corrosion amount (mm)	Detached area (%)	Maximum corrosion depth (mm)			
1	A	1.1	0.50	20	0.38	150	6.2	Example of present disclosure
2	B	1.1	0.40	15	0.35	155	6.0	
3	C	1.1	0.50	20	0.35	162	6.2	
4	D	1.2	0.60	20	0.30	150	6.5	
5	E	1.1	0.50	20	0.38	158	6.0	
6	F	1.1	0.50	20	0.38	155	6.7	
7	G	1.2	0.60	20	0.35	150	6.0	
8	H	1.0	0.40	15	0.35	155	6.8	
9	I	1.1	0.60	15	0.30	162	6.0	
10	J	1.2	0.50	20	0.35	155	6.5	

(continued)

Test No.	Steel grade	Sn ratio between grain boundary and grain inside	SAE J2334 test without a coating 120CY	SAE J2334 test with a coating 200CY		Absorbed energy (J)	Fatigue characteristics (×10^5)	
			Corrosion amount (mm)	Detached area (%)	Maximum corrosion depth (mm)			
11	K	1.1	0.70	50	0.45	140	5.5	Comparative Example
12	L	1.0	0.80	45	0.50	150	6.5	
13	M	1.1	1.10	55	1.20	155	6.0	
14	N	1.1	1.50	60	1.60	165	6.0	
15	O	-	1.50	50	1.10	165	6.0	
16	P	0.7	1.15	20	0.30	145	5.5	
17	Q	1.3	0.40	25	0.30	143	5.8	
18	A	1.7	0.70	35	0.45	146	3.9	
19	A	1.8	0.70	30	0.40	145	5.8	
20	A	1.5	0.80	30	0.42	148	3.7	
21	A	1.6	0.70	25	0.45	146	4.3	
22	A	1.6	0.70	20	0.42	145	5.5	
23	A	1.5	0.70	30	0.45	143	4.5	

[0078] Test Nos. 1 to 10 are Examples of the present disclosure which satisfy all the requirements of the present disclosure. As obvious from Table 3, in the SAE J 2334 test, the corrosion amount of the specimen without a coating was 0.60 mm or less, and in the scratched zone of the specimen with a coating the detached area was 20% or less, and the maximum corrosion depth was 0.40 mm or less. In the toughness test, the Charpy absorbed energy at 0°C was 150 J or more. Further, in the fatigue test, the fatigue fracture life was 5.5×10^5 cycles or more.

[0079] In contrast thereto, in Test Nos. 15 and 16, which were Comparative Examples, the Sn content in the steel material was less than the defined lower limit value, and consequently the corrosion resistance was inferior. Further, in Test No. 17, in which the Sn content in the steel material exceeded the defined upper limit value, the Sn ratio between the crystal grain boundary and the crystal grain inside exceeded 1.2, and as a result the low-temperature toughness and the fatigue resistance were inferior.

[0080] Further, in Test Nos. 18 to 23, the Sn ratio between the crystal grain boundary and the crystal grain inside exceeded 1.2, and as a result the corrosion resistance slightly decreased, and the low-temperature toughness and the fatigue resistance were also inferior.

[0081] Further, in Test Nos. 11 to 14, which were Comparative Examples, the content of Mo, Cu, Ni, or Cr in the steel material exceeded the defined upper limit value, and as a result the corrosion resistance was inferior.

INDUSTRIAL APPLICABILITY

[0082] According to the present disclosure, it becomes possible to obtain a steel material excellent in corrosion resistance, low-temperature toughness, and fatigue characteristics. Therefore, a steel material according to the present disclosure is suitable for use as a material for a large structure, such as an offshore structure used in a cold district, and a bridge.

Claims

1. A steel material, comprising in terms of percentage by mass:

from 0.01 to 0.20% of C,
from 0.01 to 1.00% of Si,
from 0.05 to 3.00% of Mn,
from 0 to 0.050% of P,
from 0 to 0.0100% of S,
from 0.05 to 0.25% of Sn,
from 0 to 0.100% of Al,
from 0.0005 to 0.0100% of N,
from 0.0001 to 0.0100% of O,
from 0 to 0.050% of Ti,
from 0 to 0.050% of Nb,
from 0 to 0.050% of V,
from 0 to 0.050% of W,
from 0 to 0.050% of Mo,
from 0 to 0.10% of Cu,
from 0 to 0.05% of Ni,
from 0 to 0.10% of Cr,
from 0 to 0.05% of Sb,
from 0 to 0.0010% of B,
from 0 to 0.0100% of Ca,
from 0 to 0.0100% of Mg,
from 0 to 0.0100% of REM, and
a balance consisting of Fe and impurities,
wherein an Sn ratio of an Sn concentration, a, at a crystal grain boundary to an Sn concentration, b, inside a crystal grain, expressed by a/b, is 1.2 or less.

2. The steel material according to claim 1 in a form of steel plate with a plate thickness of from 6 to 100 mm.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/044984

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C22C38/00(2006.01)i, C21D8/02(2006.01)i, C22C38/60(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)
Int.Cl. C22C38/00, C21D8/02, C22C38/60

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2018
Registered utility model specifications of Japan	1996-2018
Published registered utility model applications of Japan	1994-2018

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 2010-007109 A (SUMITOMO METAL INDUSTRIES, LTD.) 14 January 2010 (Family: none)	1-2
A	WO 2012/161241 A1 (NIPPON STEEL & SUMITOMO METAL CORPORATION) 29 November 2012 & US 2014/0087208 A1 & EP 2716782 A1 & KR 10-2013-0140207 A & CN 103562428 A	1-2

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

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/133563 A1 (NIPPON STEEL CORPORATION) 04 October 2012 & US 2014/0000765 A1 & EP 2692895 A1 & CN 103476960 A & KR 10-2013-0123460 A	1-2
A	WO 2011/102244 A1 (SUMITOMO METAL INDUSTRIES, LTD.) 25 August 2011 & KR 10-2011-0117669 A & CN 102639737 A	1-2
A	JP 2012-122103 A (SUMITOMO METAL INDUSTRIES, LTD.) 28 June 2012 (Family: none)	1-2
A	JP 2012-255184 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 27 December 2012 (Family: none)	1-2
A	JP 2014-001450 A (JFE STEEL CORPORATION) 09 January 2014 (Family: none)	1-2

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- JP 2012057236 A **[0004] [0008]**
- JP 2012255184 A **[0004] [0008]**
- JP 2012144799 A **[0005] [0009]**
- JP 5839151 B **[0006] [0010]**