

DESCRIPTION

ANTI-CORROSION STEEL MATERIAL, MANUFACTURING METHOD THEREOF,
METHOD OF PREVENTING CORROSION OF STEEL MATERIAL, AND BALLAST TANK

5 **Technical Field**

[0001]

The present invention relates to an anti-corrosion steel material and a manufacturing method thereof, a method of preventing corrosion of a steel material, and a ballast tank.

10 **Background Art**

[0002]

When a steel material is used in a corrosive environment including chloride ions over a long period of time, a corrosion prevention measure such as improvement of corrosion resistance
15 by optimizing elements of the steel material or coating is required. In particular, since the inside of a ballast tank of a ship is under a severe corrosive environment which is a cycle of a state of sea water immersion and a moist atmosphere containing salt, coating of the inside thereof is mandated by an international
20 convention.

[0003]

However, a target corrosion resistant life in a coating standard obligated by the international convention is 15 years, and it is shorter than 25 years which is assumed to be a life of

a ship. For this reason, after 15 years, replacement of a corroded steel material or repairing of coating is considered to be required. Therefore, in order to suppress an economic loss such as a maintenance cost or a prolonged docking period (time loss), a new corrosion prevention technique realizing corrosion resistance over a longer period of time is demanded to be developed.

[0004]

Conventionally, in regards to a demand for improving performance of a corrosion resistant steel material having an inorganic zinc coating film, a method such as appropriately controlling the composition or the surface properties of the steel material or appropriately controlling the properties of the inorganic zinc coating film is proposed (for example, see Patent Documents 1 to 12).

15 **Citation List**

Patent Documents

[0005]

[Patent Document 1] JP 1976-028650 B

[Patent Document 2] JP 1976-106134 A

20 [Patent Document 3] JP 1976-123229 A

[Patent Document 4] JP 1984-051951 A

[Patent Document 5] JP 2002-285102 A

[Patent Document 6] JP 2003-531924 A

[Patent Document 7] JP 2005-510584 A

[Patent Document 8] JP 2007-191730 A

[Patent Document 9] JP 2008-144204 A

[Patent Document 10] JP 2010-018846 A

[Patent Document 11] JP 2011-021247 A

5 [Patent Document 12] JP 2011-021248 A

Summary

[0005a]

In one aspect of the present disclosure, there is provided an anti-corrosion steel material comprising:

10 a steel material, and

a coating film having a thickness of 10 μm or larger which is formed on the surface of the steel material; wherein

the steel material contains, in terms of % by mass,

C: 0.001% to 0.20%,

15 Si: 0.01% to 3.0%,

Mn: 0.1% to 3.0%, and

Cr: 0.1% to 9.99%;

the coating film is formed by curing an alkali-silicate inorganic zinc coating composition, the coating film contains a
20 silicon atom, and at least one atom selected from an alkali metal atom and a nitrogen atom, and the molar ratio represented by {the number of moles of silicon atoms Si in the coating film}/{the total number of moles of alkali metal atoms and nitrogen atoms in the coating film} is 2.0 to 125; and

the inorganic zinc coating composition contains alkali silicate and zinc particles, and the mass ratio represented by "the solid content mass of a binder component / the mass of zinc particles" is 0.01 to 0.35.

5 [0005b]

In another aspect of the present disclosure, there is provided a ballast tank constituted by using the anti-corrosion steel material disclosed herein.

[0005c]

10 In a further aspect of the present disclosure, there is provided a manufacturing method of an anti-corrosion steel material comprising

a step of forming a coating film containing a silicon atom, and at least one atom selected from an alkali metal atom and a
15 nitrogen atom, and having a molar ratio represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms and nitrogen atoms in the coating film} of 2.0 to 125,

by applying an alkali-silicate inorganic zinc coating
20 composition containing alkali silicate and zinc particles and having a mass ratio represented by "the solid content mass of a binder component / the mass of zinc particles" of 0.01 to 0.35 on the surface of a steel material containing,

in terms of % by mass,

C: 0.001% to 0.20%,

Si: 0.01% to 3.0%,

Mn: 0.1% to 3.0%, and

Cr: 0.1% to 9.99%

5 such that the thickness of the cured coating film is 10 μm or larger.

[0005d]

In another aspect of the present disclosure, there is provided a method of preventing corrosion of a steel material
10 comprising

a step of forming a coating film containing a silicon atom, and at least one atom selected from an alkali metal atom and a nitrogen atom, and having a molar ratio represented by {the number of moles of silicon atoms Si in the coating film} / {the total
15 number of moles of alkali metal atoms and nitrogen atoms in the coating film} of 2.0 to 125,

by applying an alkali-silicate inorganic zinc coating composition containing alkali silicate and zinc particles and having a mass ratio represented by "the solid content mass of a
20 binder component / the mass of zinc particles" of 0.01 to 0.35 on the surface of a steel material containing,

in terms of % by mass,

C: 0.001% to 0.20%,

Si: 0.01% to 3.0%,

Mn: 0.1% to 3.0%, and

Cr: 0.1% to 9.99%

such that the thickness of the cured coating film is 10 μm or larger.

5 Technical Problem

[0006]

In the corrosion prevention methods described in the Patent Documents or the like, while the composition of a steel material has an influence on corrosion resistance, the performance of a corrosion resistant steel material on which an inorganic zinc coating film is provided is a sacrificial corrosion prevention effect which is mainly due to zinc particles, and it is not assumed that other components or the like contained in the inorganic zinc coating film have influence on the performance of the corrosion resistant steel material on which the inorganic zinc coating film is provided. Therefore, fundamental improvement of the performance of the corrosion resistant steel material on which the inorganic zinc coating film is provided by considering the inorganic zinc coating film and the steel material as one is not attempted.

[0007]

In general, in order to obtain long-term corrosion

resistance of a ballast tank of a ship, a top coating film such as an organic resin layer or the like is further provided on the inorganic zinc coating film. In the corrosion prevention methods described in the Patent Documents or the like, however, long-term corrosion resistance when a top coating film is not provided is still insufficient.

[0008]

Accordingly, the present invention has been made in view of the above described circumstances, and an object of the present invention is to provide an anti-corrosion steel material and a manufacturing method thereof, a method of preventing corrosion of a steel material, and a ballast tank, in which excellent corrosion resistance can be maintained over a long period of time.

Solution to Problem

[0009]

The present invention dramatically improves the performance of a corrosion resistant steel material on which an inorganic zinc coating film is provided, focusing on a synergistic effect between components contained in the inorganic zinc coating film and elements contained in the steel material, and the gist thereof is as follows.

[0010]

[1] An anti-corrosion steel material comprising a steel material, and a coating film having a thickness of 10 μm or larger

which is formed on the surface of the steel material; wherein the steel material contains, in terms of % by mass, C: 0.001% to 0.20%, Si: 0.01% to 3.0%, Mn: 0.1% to 3.0%, and Cr: 0.1% to 9.99%; the coating film is formed by curing an alkali-silicate inorganic zinc coating composition, the coating film contains a silicon atom, and at least one atom selected from an alkali metal atom and a nitrogen atom, and the molar ratio represented by {the number of moles of silicon atoms Si in the coating film}/{the total number of moles of alkali metal atoms and nitrogen atoms in the coating film} is 2.0 to 125; and the inorganic zinc coating composition contains alkali silicate and zinc particles, and the mass ratio represented by "the solid content mass of a binder component / the mass of zinc particles" is 0.01 to 0.35.

[0011]

[2] The anti-corrosion steel material according to the item [1], wherein the Cr content in the steel material and the molar ratio in the coating film satisfy the following conditional expression (1). Conditional expression (1): $[Cr] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\} \times 20 \text{ (}\mu\text{m)} / (\text{the film thickness (}\mu\text{m)})$ of the coating film which is formed on the surface of the steel material) $\times a/b$ [in the conditional expression (1), the [Cr] is the Cr content (% by mass) in the steel material; the molar ratio (Si/M) is represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali

metal atoms and nitrogen atoms in the coating film}; a is 7, and b is 6.]

[3] The anti-corrosion steel material according to the item [1], wherein the Cr content in the steel material and the molar ratio in the coating film satisfy the following conditional expression (1). Conditional expression (1): $[Cr] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\} \times 20 (\mu\text{m}) / (\text{the film thickness } (\mu\text{m}) \text{ of the coating film which is formed on the surface of the steel material}) \times a/b$ [in the conditional expression (1), the [Cr] is the Cr content (% by mass) in the steel material; the molar ratio (Si/M) is represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms and nitrogen atoms in the coating film}; a is 17, b is 6.]

[4] The anti-corrosion steel material according to any one of the items [1] to [3], wherein the coating film contains a silicon atom and an alkali metal atom.

[0012]

[5] The anti-corrosion steel material according to any one of the items [1] to [4], wherein the coating film contains a silicon atom and a nitrogen atom.

[0013]

[6] The anti-corrosion steel material according to any one of the items [1] to [5], wherein the alkali silicate is a

compound represented by $M1_2O \cdot nSiO_2$ [in the formula, M1 is an alkali metal, or an amine component or an ammonium component, and n is a positive number.]

[0014]

5 [7] The anti-corrosion steel material according to any one of the items [1] to [6], wherein the alkali silicate contains at least one selected from lithium silicate, sodium silicate, and potassium silicate.

[0015]

10 [8] The anti-corrosion steel material according to any one of the items [1] to [7], wherein the alkali silicate contains at least one selected from an ammonium silicate composed of a primary amine, a secondary amine, or a tertiary amine and a silicic acid, and a quaternary ammonium silicate composed of a quaternary
15 ammonium and a silicic acid.

[0016]

 [9] The anti-corrosion steel material according to any one of the items [1] to [8], wherein the alkali silicate contains a quaternary ammonium silicate composed of a quaternary ammonium
20 and a silicic acid.

[0017]

 [10] The anti-corrosion steel material according to any one of the items [1] to [9], wherein the inorganic zinc coating composition substantially does not contain alkyl silicate binders

or organic solvents.

[0018]

[11] The anti-corrosion steel material according to any one of the items [1] to [10], wherein the thickness of the coating
5 film is 200 μm or smaller.

[0019]

[12] The anti-corrosion steel material according to any one of the items [1] to [11], which is composed of the steel material and the coating film, which does not comprise a top
10 coating film on the coating film, and which is for a ballast tank.

[0020]

[13] The anti-corrosion steel material according to any one of the items [1] to [12], wherein the steel material contains, in terms of % by mass, Cr: 0.3% to 3.0%.

15 [0021]

[14] The anti-corrosion steel material according to any one of the items [1] to [13], wherein in the steel material, the contents of elements other than C, Si, Mn and Cr, in terms of % by mass, are, Al: 2.0% or smaller, Cu: 1.0% or smaller, Ni: 2.0%
20 or smaller, Mo: 0.5% or smaller, W: 0.5% or smaller, Sn: 0.5% or smaller, Sb: 0.5% or smaller, V: 0.2% or smaller, Nb: 0.08% or smaller, Ti: 0.1% or smaller, Mg: 0.01% or smaller, Zr: 0.05% or smaller, B: 0.0050% or smaller, Ca: 0.02% or smaller, REM: 0.02% or smaller, P: 0.03% or smaller, S: 0.01% or smaller, N: 0.02%

or smaller, and the balance: iron and inevitable impurities.

[0022]

[15] A ballast tank constituted by using the anti-corrosion steel material according to any one of the items [1] to [14].

[0023]

[16] A manufacturing method of an anti-corrosion steel material comprising a step of forming a coating film containing a silicon atom, and at least one atom selected from an alkali metal atom and a nitrogen atom, and having a molar ratio represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms and nitrogen atoms in the coating film} of 2.0 to 125, by applying an alkali-silicate inorganic zinc coating composition containing alkali silicate and zinc particles and having a mass ratio represented by "the solid content mass of a binder component / the mass of zinc particles" of 0.01 to 0.35 on the surface of a steel material containing, in terms of % by mass, C: 0.001% to 0.20%, Si: 0.01% to 3.0%, Mn: 0.1% to 3.0%, and Cr: 0.1% to 9.99% such that the thickness of the cured coating film is 10 μm or larger.

[0024]

[17] The manufacturing method of an anti-corrosion steel material according to the item [16], wherein the Cr content in

the steel material and the molar ratio in the coating film satisfy the following conditional expression (1). Conditional expression (1): $[Cr] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\} \times 20 \text{ (}\mu\text{m)} / (\text{the film thickness (}\mu\text{m) of the coating film which is formed on the surface of the steel material}) \times a/b$ [in the conditional expression (1), the [Cr] is the Cr content (% by mass) in the steel material; the molar ratio (Si/M) is represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms and nitrogen atoms in the coating film}; a is 7, and b is 6.]

[18] The manufacturing method of an anti-corrosion steel material according to the item [16] or [17], wherein a coating film is formed on the surface of the steel material by self-curing the inorganic zinc coating composition.

15 [0025]

[19] A method of preventing corrosion of a steel material comprising a step of forming a coating film containing a silicon atom, and at least one atom selected from an alkali metal atom and a nitrogen atom, and having a molar ratio represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms and nitrogen atoms in the coating film} of 2.0 to 125, by applying an alkali-silicate inorganic zinc coating composition containing alkali silicate and zinc particles and having a mass ratio represented by "the solid

content mass of a binder component / the mass of zinc particles" of 0.01 to 0.35 on the surface of a steel material containing, in terms of % by mass, C: 0.001% to 0.20%, Si: 0.01% to 3.0%, Mn: 0.1% to 3.0%, and Cr: 0.1% to 9.99% such that the thickness of
 5 the cured coating film is 10 μm or larger.

[0026]

[20] The method of preventing corrosion of a steel material according to the item [19], wherein the Cr content in the steel material and the molar ratio in the coating film satisfy the
 10 following conditional expression (1). Conditional expression (1): $[\text{Cr}] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\} \times 20 (\mu\text{m}) / (\text{the film thickness } (\mu\text{m}) \text{ of the coating film which is formed on the surface of the steel material}) \times a/b$ [in the conditional expression (1), the [Cr] is the Cr content (% by mass) in the steel material;
 15 the molar ratio (Si/M) is represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms and nitrogen atoms in the coating film}; a is 7, and b is 6.]

[21] The method of preventing corrosion of steel material
 20 according to the [19] or [20], wherein a coating film is formed on the surface of the steel material by self-curing the inorganic zinc coating composition.

Advantageous Effects of Invention

[0027]

As described above, according to the present invention, excellent corrosion resistance can be maintained over a long period of time by providing a coating film formed by curing an alkali-silicate inorganic zinc coating composition comprising a predetermined component on the surface of a steel material
5 containing a specific component.

Brief Description of Drawings

[0028]

Fig. 1 is a graph in which the Cr content in a steel material
10 is plotted with respect to the atomic molar ratio (Si/M) in a coating film.

Fig. 2 is a graph in which the Cr content in a steel material is plotted with respect to the film thickness of a coating film.

Description of Embodiments

15 [0029]

In the following, a preferred embodiment of the present invention will be described in detail.

[0030]

[Anti-Corrosion Steel Material and Manufacturing Method
20 Thereof]

An anti-corrosion steel material of the present invention is a corrosion resistant steel material having excellent corrosion resistance over a long period of time, which comprises a steel material containing predetermined elements used as a base material

and a coating film formed on the surface of the steel material.
The coating film is formed on a part or the whole of the steel material surface.

[0031]

5 In other words, the anti-corrosion steel material of the present invention is an anti-corrosion steel material comprising a steel material, and a coating film having a thickness of 10 μm or larger which is formed on the surface of the steel material; the steel material containing, in terms of % by mass, Cr: 0.1%
10 to 9.99%; the coating film being formed by curing an alkali-silicate inorganic zinc coating composition, the coating film containing a silicon atom, and at least one atom selected from an alkali metal atom and a nitrogen atom, and the molar ratio represented by {the number of moles of silicon atoms Si in the
15 coating film}/{the total number of moles of alkali metal atoms and nitrogen atoms in the coating film} being 2.0 to 125; and the inorganic zinc coating composition containing alkali silicate and zinc particles, and the mass ratio represented by "the solid content mass of a binder component / the mass of zinc particles"
20 being 0.01 to 0.35.

[0032]

In the following, such a steel material and a coating film will be described in detail.

[0033]

<Elements of Steel Material>

Elements of the steel material used for a base material will be described. In the descriptions of element contained therein, the term "%" means % by mass (or % by weight).

5 [0034]

[C: 0.001 to 0.20%]

C is an element which is effective for improving the strength of the steel material. In the present invention, in order to maintain a needed strength, the amount of C is set to 0.001% or
10 larger. The amount of C is preferably set to 0.005% or larger, and more preferably 0.01% or larger, 0.03% or larger, or 0.05% or larger. On the other hand, when the amount of C is larger than 0.20%, weldability or toughness may be deteriorated, and therefore the upper limit is set to 0.20%. The amount of C is, in
15 consideration of weldability, more preferably 0.16% or smaller, and from the viewpoint of workability, further preferably 0.14% or smaller, or 0.12% or smaller.

[0035]

[Si: 0.01 to 3.0%]

20 Si functions as a deoxidizing agent, and is an element effective for improving the strength. When the amount of Si is smaller than 0.01%, deoxidation may be insufficient, and therefore, in the present invention, the lower limit is set to 0.01%. In order to stably perform deoxidation, the amount of Si is more

preferably 0.05% or larger, or 0.10% or larger. On the other hand, when the amount of Si is larger than 3.0%, the ductility deteriorates, and therefore the upper limit is set to 3.0%. In consideration of the weldability or the toughness of the steel material, the amount of Si is more preferably 0.5% or smaller, or 0.4% or smaller.

[0036]

[Mn: 0.1 to 3.0%]

Mn is an element effective for controlling the structure of a steel, and in the present invention, the amount of Mn is set to 0.1% or larger. In order to stably control the structure, the amount of Mn is more preferably 0.5% or larger. On the other hand, when the amount of Mn is larger than 3.0%, ductility or toughness may deteriorate, the upper limit is set to 3.0%. In order to improve manufacturability such as rolling or weldability, the amount of Mn is more preferably 2.5% or smaller. In order to improve weldability or the like, the upper limit of the amount of Mn may be set to 2.0%, 1.6% or 1.4%. In order to improve ductility or toughness, the lower limit of the amount of Mn may be set to 0.6%, 0.8% or 1.0%.

[0037]

[Cr: 0.1 to 9.99%]

Cr is effective for improving corrosion resistance of the steel material, and is an important element. In the present

invention, in order to obtain a remarkable effect of improving corrosion resistance by an interaction between an alkali-silicate inorganic zinc coating film formed as a coating film and a steel material, the amount of Cr is set to 0.1% or larger. In order
5 to improve corrosion resistance, the amount of Cr is preferably 0.2% or larger, 0.3% or larger, 0.5% or larger, or 0.7% or larger, and more preferably 1% or larger. On the other hand, when the amount of Cr is larger than 9.99%, transformation does not occur in a cooling process of a cast slab, resulting in a ferrite
10 single-phase structure, causing a cast slab crack, and therefore the upper limit is set to 9.99%. The amount of Cr is, for reducing a cost of alloying, preferably 8.0% or smaller, and more preferably 6.5% or smaller. The amount of Cr may, in consideration of weldability or the like, be limited to 5.0% or smaller, 4.0% or
15 smaller, 3.0% or smaller, 2.0% or smaller, 1.5% or smaller, 1.2% or smaller, or 1.0% or smaller.

[0038]

The steel material used in the present invention may contain one or more of Al, Cu, Ni, Mo, W, Sn and Sb in order to further
20 improve corrosion resistance of the steel material. In the following, reasons for limiting the contents of Al, Cu, Ni, Mo, W, Sn and Sb will be described.

[0039]

[Al: 2.0% or smaller]

Al is generally used as a deoxidizing agent, and in the present invention, the steel material may contain Al as needed in order to further improve corrosion resistance of the steel material. On the other hand, when the amount of Al is larger than 2.0%, transformation does not occur in a cooling process of a cast slab, resulting in a ferrite single-phase structure, which may cause a cast slab crack, and therefore the upper limit is preferably set to 2.0%. The amount of Al is more preferably 1.5% or smaller. In order to reduce Al-based inclusion, the upper limit of the amount of Al may be set to 1.0%, 0.5%, 0.2%, 0.1%, or 0.08%. Although the lower limit of the amount of Al does not particularly need to be provided and may be 0%, in order to improve corrosion resistance of the steel material, the lower limit of the amount of Al is preferably 0.002%, and more preferably 0.01%. The amount of Al is further preferably 0.02% or larger.

[0040]

[Cu: 1.0% or smaller]

Cu is an element for improving corrosion resistance of the steel material, and the steel material may contain Cu as needed. On the other hand, when the amount of Cu is larger than 1.0%, the steel material may be embrittled, and therefore the upper limit is preferably set to 1.0%. The amount of Cu is more preferably 0.5% or smaller, and further preferably 0.3% or smaller. Although the lower limit of the amount of Cu does not particularly need

to be provided, and may be 0%, in order to stably improve corrosion resistance of the steel material, the lower limit of the amount of Cu is preferably 0.05%. Since Cu is an element which improves strength and at the same time prevents a cast slab crack, the amount of Cu is more preferably set to 0.10% or larger.

[0041]

[Ni: 2.0% or smaller]

Ni is an element which improves corrosion resistance of the steel material, and when the steel material contains Cu and at the same time contains Ni, deterioration of manufacturability can be prevented. On the other hand, since Ni is an expensive element and the above-described effect saturates when the steel material contains Ni in an amount larger than 2.0%, the upper limit is preferably set to 2.0%. The amount of Ni is more preferably 0.5% or smaller, and further preferably 0.3% or smaller. Although the lower limit of the amount of Ni does not particularly need to be provided, and may be 0%, in order to stably obtain the above-described effect, the lower limit of the amount of Ni is preferably 0.05%, and more preferably 0.10%.

[0042]

[Mo: 0.5% or smaller] [W: 0.5% or smaller]

Mo and W are elements which improve corrosion resistance of the steel material, and the steel material may contain these elements as needed. On the other hand, since the effect saturates

even if the steel material contains Mo and W in amounts larger than 0.5%, the upper limit is preferably set to 0.5%. The amount of Mo and the amount of W are each more preferably 0.1% or smaller. Although the lower limits of the amount of Mo and the amount of W do not particularly need to be provided, and may be 0%, in order to stably improve corrosion resistance of the steel material, the lower limits of the amount of Mo and the amount of W are each preferably 0.01%, and more preferably 0.03%.

[0043]

10 [Sn: 0.5% or smaller]

Sn is an element which improves corrosion resistance of the steel material, and the steel material may contain Sn as needed. On the other hand, since, when the steel material contains an excess amount of Sn, manufacturability or mechanical characteristics may be compromised, the upper limit of the amount of Sn is preferably set to 0.5%. The amount of Sn is more preferably 0.2% or smaller. Although the lower limit of the amount of Sn does not particularly need to be provided, and may be 0%, in order to stably improve corrosion resistance of the steel material, the lower limit of the amount of Sn is preferably 0.01%, and more preferably 0.05%.

[0044]

[Sb: 0.5% or smaller]

Sb is an element which improves corrosion resistance of the

steel material, and the steel material may contain Sb as needed. On the other hand, since, when the steel material contains an excess amount of Sb, manufacturability or mechanical characteristics may be deteriorated, the upper limit of the amount
5 of Sb is preferably set to 0.5%. The amount of Sb is more preferably 0.2% or smaller. Although the lower limit of the amount of Sb does not particularly need to be provided, and may be 0%, in order to stably improve corrosion resistance of the steel material, the lower limit of the amount of Sb is preferably 0.01%,
10 and more preferably 0.05%.

[0045]

The steel material used in the present invention may further contain one or more of V, Nb, Ti, Mg, Zr, B, Ca and REM from the viewpoint of improving mechanical characteristics, usability,
15 manufacturing stability, or the like.

[0046]

[V: 0.2% or smaller]

V is an element which improves mechanical characteristics, usability, and manufacturing stability, and the steel material
20 may contain V as needed. On the other hand, since, when the steel material contains an excess amount of V, anti-rusting properties may be compromised, the upper limit of the amount of V is preferably set to 0.2%. The amount of V is more preferably 0.05% or smaller. Although the lower limit of the amount of V does not particularly

need to be provided, and may be 0%, in order to stably improve various characteristics of the steel material, the lower limit of the amount of V is preferably 0.005%, and more preferably 0.01%.

[0047]

5 [Nb: 0.08% or smaller]

Nb is an element which improves mechanical characteristics, usability, and manufacturing stability, and the steel material may contain Nb as needed. On the other hand, since, when the steel material contains an excess amount of Nb, anti-rusting properties
10 may be compromised, the upper limit of the amount of Nb is preferably set to 0.08%. The amount of Nb is more preferably 0.03% or smaller. Although the lower limit of the amount of Nb does not particularly need to be provided, and may be 0%, in order to stably improve various characteristics of the steel material, the
15 lower limit of the amount of Nb is preferably 0.002%, and more preferably 0.005%.

[0048]

[Ti: 0.1% or smaller]

Ti is an element which improves mechanical characteristics, usability, and manufacturing stability, and the steel material
20 may contain Ti as needed. On the other hand, since, when the steel material contains an excess amount of Ti, anti-rusting properties may be compromised, the upper limit of the amount of Ti is preferably set to 0.1%. The amount of Ti is more preferably 0.03%

or smaller. Although the lower limit of the amount of Ti does not particularly need to be provided, and may be 0%, in order to stably improve various characteristics of the steel material, the lower limit of the amount of Ti is preferably 0.005%, and more preferably 0.01%.

[0049]

[Mg: 0.01% or smaller]

Mg is an element which improves mechanical characteristics, usability, and manufacturing stability, and the steel material may contain Mg as needed. On the other hand, since, when the steel material contains an excess amount of Mg, anti-rusting properties may be compromised, the upper limit of the amount of Mg is preferably set to 0.01%. The amount of Mg is more preferably 0.002% or smaller. Although the lower limit of the amount of Mg does not particularly need to be provided, and may be 0%, in order to stably improve various characteristics of the steel material, the lower limit of the amount of Mg is preferably 0.0001%, and more preferably 0.0005%.

[0050]

[Zr: 0.05% or smaller]

Zr is an element which improves mechanical characteristics, usability, and manufacturing stability, and the steel material may contain Zr as needed. On the other hand, since, when the steel material contains an excess amount of Zr, anti-rusting properties

may be compromised, the upper limit of the amount of Zr is preferably set to 0.05%. The amount of Zr is more preferably 0.02% or smaller. Although the lower limit of the amount of Zr does not particularly need to be provided, and may be 0%, in order to stably improve various characteristics of the steel material, the lower limit of the amount of Zr is preferably 0.003%, and more preferably 0.005%.

[0051]

[B: 0.0050% or smaller]

10 B is an element which improves mechanical characteristics, usability, and manufacturing stability, and the steel material may contain B as needed. On the other hand, since, when the steel material contains an excess amount of B, anti-rusting properties may be compromised, the upper limit of the amount of B is preferably set to 0.0050%. The amount of B is more preferably 0.002% or smaller. Although the lower limit of the amount of B does not particularly need to be provided, and may be 0%, in order to stably improve various characteristics of the steel material, the lower limit of the amount of B is preferably 0.0002%, and more preferably 0.0005%.

[0052]

[Ca: 0.02% or smaller]

Ca is an element which improves mechanical characteristics, usability, and manufacturing stability, and the steel material

may contain Ca as needed. On the other hand, since, when the steel material contains an excess amount of Ca, anti-rusting properties may be compromised, the upper limit of the amount of Ca is preferably set to 0.02%. The amount of Ca is more preferably 5 0.003% or smaller. Although the lower limit of the amount of Ca does not particularly need to be provided, and may be 0%, in order to stably improve various characteristics of the steel material, the lower limit of the amount of Ca is preferably 0.0002%, and more preferably 0.0005%.

10 [0053]

[REM: 0.02% or smaller]

REM is an element which improves mechanical characteristics, usability, and manufacturing stability, and the steel material may contain REM as needed. REM represents Rare Earth Metals, 15 corresponding to so-called lanthanoid elements with atomic number 57, La through atomic number 71. In the present embodiment, the steel material may contain a simple substance or a compound of one kind of element belonging to REM, or may contain a mixture containing a plurality of kinds of REM. Examples of such a mixture 20 include a misch metal composed mainly of Ce, La, Nd, or the like.

[0054]

On the other hand, since, when a steel material contains an excess amount of REM, anti-rusting properties may be compromised, the upper limit of the amount of REM is preferably

set to 0.02%. The amount of REM is more preferably 0.01% or smaller. Although the lower limit of the amount of REM does not particularly need to be provided, and may be 0%, in order to stably improve various characteristics of the steel material, the lower limit
5 of the amount of REM is preferably 0.0002%, and more preferably 0.0005%.

[0055]

The content of the above-described selected elements (Al, Cu, Ni, Mo, W, Sn, Sb, V, Nb, Ti, Mg, Zr, B, Ca and REM) is preferably
10 1.5% or smaller in total, and may be further preferably 1.0% or smaller, 0.8% or smaller, 0.6% or smaller, or 0.4% or smaller.

[0056]

In the steel material used in the present invention, the balance other than the above-described elements is Fe and
15 inevitable impurities. Examples of such inevitable impurities include P, S, and N, and they are accepted without inhibiting improvement of anti-rusting properties of the steel material.

[0057]

[P: 0.03% or smaller]

20 Since, when the amount of P is larger than 0.03%, toughness or ductility may deteriorate, the upper limit is preferably set to 0.03%. A more preferable upper limit of the amount of P is 0.02% or 0.01%. On the other hand, although the lower limit of the amount of P does not particularly need to be provided, and

the lower limit of the amount of P may be set to 0%, the amount of P is preferably 0.001% or larger since, when the amount of P is reduced to smaller than 0.001%, manufacturing cost rises.

[0058]

5 [S: 0.01% or smaller]

Since, when the amount of S is larger than 0.01%, toughness or ductility may deteriorate or hot workability may be compromised, the upper limit is preferably set to 0.01%. A more preferable upper limit of the amount of S is 0.006% or 0.003%. On the other
10 hand, although the lower limit of the amount of S does not particularly need to be provided, and the lower limit of the amount of S may be set to 0%, the amount of S is preferably 0.0001% or larger since, when the amount of S is reduced to smaller than 0.0001%, manufacturing cost rises.

15 [0059]

[N: 0.02% or smaller]

Since, when the amount of N is larger than 0.02%, toughness or ductility may deteriorate, the upper limit is preferably set to 0.02%. A more preferable upper limit of the amount of N is
20 0.01%, and further preferably 0.006%. On the other hand, although the lower limit of the amount of N does not particularly need to be provided, and the lower limit of the amount of N may be set to 0%, the amount of N is preferably 0.001% or larger since, when the amount of N is reduced to smaller than 0.001%, manufacturing

cost rises.

[0060]

The total content of elements other than C, Si, Mn, Cr and Fe may be limited to 2.0% or smaller. As needed, the total may
5 be set to 1.6% or smaller, 1.2% or smaller, 0.9% or smaller, 0.6% or smaller, or 0.4% or smaller. The lower limit of the total does not particularly need to be provided, and the lower limit may be set to 0%.

[0061]

10 The steel material used in the present invention is manufactured through a general manufacturing process (for example, casting, heating and rolling, cold rolling, and as needed, heat treatment). In other words, in the present invention, a steel material which is manufactured through a usual general steel
15 manufacturing process in which molten metal is casted to form a billet, then subjected to hot rolling, cold rolling, or the like, and as needed, a heat treatment can be used in a shape such as a steel plate, a steel strip, a shaped steel, a steel pipe, a bar steel, or a steel wire. In the present invention, a welded
20 structure or a steel structure which is constructed by using such a steel material can also be used. The thickness of the steel material is not particularly limited, and is usually 3 to 50 mm. A preferable lower limit is 6 mm, and more preferably 10 mm; and a preferable upper limit is 40 mm, and more preferably 30 mm.

[0062]

The strength (tensile strength) of a steel plate used for a ballast tank is usually from 400 MPa to 650 MPa, and a steel plate having such a strength may be used. A manufacturing method
5 of a steel plate having such a strength is generally by being as-rolled, a TMCP (Thermo-Mechanical Control Process), or a normalizing heat treatment (Normalizing) as prescribed in regulations of classification societies such as NK, ABS, LR, or the like. A quenched or quenched-and-tempered steel plate is
10 scarcely used. The steel material used in the present invention may therefore be limited to a steel plate manufactured by being as rolled, a TMCP, or normalizing.

[0063]

[Coating Film]

15 A coating film constituting the anti-corrosion steel material of the present invention is formed by curing an alkali-silicate inorganic zinc coating composition containing alkali silicate and zinc particles. In the following, components contained in the alkali-silicate inorganic zinc coating
20 composition will be described in detail.

[0064]

<Components Contained in Coating Composition>

<<Alkali Silicate>>

Alkali silicate used in the present invention is a compound

represented by the general formula $M1_2O \cdot nSiO_2$ [in the formula, M1 is an alkali metal, or an amine component or an ammonium component, n is a positive number, usually 1 to 100, and preferably 1 to 70].

[0065]

5 Examples of alkali silicate containing an alkali metal as M1 include alkali metal silicate composed of an alkali metal and a silicic acid, and examples of such a compound include silicate compounds such as lithium silicate ($Li_2O \cdot SiO_2$ or the like), sodium silicate ($Na_2O \cdot SiO_2$, $Na_2O \cdot 2SiO_2$, $Na_2O \cdot 4SiO_2$, or the like), and
10 potassium silicate ($K_2O \cdot SiO_2$ or the like).

[0066]

 Examples of alkali silicate containing an amine component or ammonium component as M1 include an ammonium silicate composed of a primary amine, a secondary amine, or a tertiary amine and
15 a silicic acid, and a quaternary ammonium silicate composed of a quaternary ammonium and a silicic acid. A part of an amine component and an ammonium component derived from ammonium silicates does not volatilize during formation of the coating film to remain in the coating film, and can contribute to a corrosion
20 prevention effect as an alkaline component.

[0067]

 Examples of a primary amine, a secondary amine, a tertiary amine component include amine components represented by formula (1): NR_3 . In the formula (1), R is each independently a hydrogen

atom, a hydrocarbon group having 1 to 4 carbon atoms, or a group formed by substituting one or more hydrogen atoms which the hydrocarbon group includes with a substituent such as a hydroxyl group. It is noted that not all Rs are hydrogen atoms at the same
5 time, and two Rs may be bonded to each other to form a cyclic group. R is preferably each independently a hydrogen atom, an alkyl group, or a hydroxyalkyl group.

[0068]

Examples of a quaternary ammonium component include an
10 ammonium cation represented by formula (2): NR_4^+ . In the formula (2), R is each independently a hydrocarbon group having 1 to 4 carbon atoms, or a group formed by substituting one or more hydrogen atoms which the hydrocarbon group includes with a substituent such as a hydroxyl group. It is noted that two Rs
15 may be bonded to each other to form a cyclic group. R is preferably each independently an alkyl group or a hydroxyalkyl group.

[0069]

In the formulae (1) and (2), the number of carbon atoms in the alkyl group is usually 1 to 4, and preferably 1 to 2. The
20 number of carbon atoms in the hydroxyalkyl group is usually 1 to 4, and preferably 1 to 2.

[0070]

Specific examples of the amine component and the ammonium component include a quaternary ammonium component such as

tetramethyl ammonium, tetraethyl ammonium, tetrapropyl ammonium, methyl triethanol ammonium, ethyl triethanol ammonium, methyl tripropanol ammonium, isopropyl triethanol ammonium, dimethyl diethanol ammonium, or tetraethanol ammonium; a primary, secondary, or tertiary amine component such as methyl amine, ethyl amine, ethanol amine, diethanol amine, or triethanol amine. Among these, the tertiary amine component and the quaternary ammonium component are preferable, and the quaternary ammonium component is more preferable.

10 [0071]

Among alkali silicates containing an amine component or an ammonium component, from the aspect of residual property in the coating film during formation of the coating film, an odor of the coating, or the like, the ammonium silicate using the tertiary amine component and the quaternary ammonium silicate is preferable, and the quaternary ammonium silicate is more preferable.

[0072]

Alkali silicate containing an amine component or an ammonium component is commercially available, for example, from Nissan Chemical Industries, Ltd. under the trade names of QAS-25 (SiO_2 solid content: 25% by mass) and QAS-40 (SiO_2 solid content: 40% by mass), or from Nippon Chemical Industrial Co., Ltd. under the trade names of ammonium silicate 17804 (SiO_2 solid content: 40% by mass) and ammonium silicate 88J3 (SiO_2 solid content: 20% by

mass).

[0073]

Alkali silicate is a compound which functions as a binder component, and is a source of an alkali metal and an amine component
5 or an ammonium component which are alkaline components for exhibiting a corrosion prevention effect by an interaction with Cr contained in the steel material.

[0074]

Alkali silicate may be used singly, or in combination of
10 two or more kinds thereof.

[0075]

<<Anhydrous Silicic Acid>>

An anhydrous silicic acid can be used for obtaining favorable self-curability in the inorganic zinc coating
15 composition. An anhydrous silicic acid can be used for adjusting an atomic molar ratio (Si/M) as described below.

[0076]

When an anhydrous silicic acid is used, the anhydrous silicic acid can be added to the coating composition as a hydrosol.
20 A hydrosol of anhydrous silicic acid (hereinafter also referred to as "aqueous silica sol") is a colloidal solution in which water is used as a dispersion medium and ultrafine particles of the anhydrous silicic acid are dispersed in water, and examples thereof generally include aqueous colloidal silica. When the

inorganic zinc coating composition contains an aqueous silica sol, self-curing of the coating film proceeds by a dehydration condensation reaction of the aqueous silica sol.

[0077]

5 <<Zinc Particles>>

Zinc particles are added to the alkali-silicate inorganic zinc coating composition in order to obtain a sacrificial corrosion prevention effect for the steel material. For such zinc particles, for example, zinc powder, zinc alloy powder, or a
10 mixture thereof can be used. Examples of zinc alloy include an alloy of aluminum or tin and zinc.

[0078]

The average particle size of zinc particles is preferably, for example, 2 to 20 μm . The average particle size of such zinc
15 particles can be measured by determining the specific surface area of the particle using a Blaine air permeability apparatus.

[0079]

<<Acid component and Hydrogencarbonate>>

The alkali-silicate inorganic zinc coating composition is
20 a self-curing composition. Specifically, when the coating composition absorbs a carbonic acid gas in the air and moisture, an alkali produced salt composed of carbonate such as sodium carbonate, potassium carbonate, lithium carbonate, or ammonium carbonate is deposited, and the composition is cured, and

therefore the curing rate is high. For this reason, in a drying and curing process of the coating composition, an acid treatment which has been needed for a conventional post curing alkali-silicate inorganic zinc coating composition, specifically,
5 a treatment in which a neutralization reaction is allowed to proceed by performing an acid treatment on the surface of dried coating film to cure a coating film, is not needed. In addition, there is a corrosion prevention effect by an interaction between an alkaline component contained in the coating composition and
10 Cr contained in the steel material.

[0080]

The alkali-silicate inorganic zinc coating composition may, as needed, further contain an acid component and hydrogencarbonate. This makes it possible to further improve self-curability of the
15 coating composition.

[0081]

The type of the acid component is not particularly defined as long as the acid component is an acid component not containing a halogen ion, and for example, a boric acid is preferably used.
20 The type of the hydrogencarbonate is not particularly defined, and at least one selected from, for example, sodium hydrogen carbonate, potassium hydrogen carbonate, calcium hydrogen carbonate, and ammonium hydrogen carbonate is preferably used. An alkali metal derived from these sodium hydrogen carbonate and

potassium carbonate and an ammonium component derived from ammonium hydrogen carbonate retained in the coating film without volatilizing can contribute to a corrosion prevention effect as an alkaline component.

5 [0082]

By further adding such an acid component and hydrogencarbonate to the composition, a neutralization reaction between the acid component and the hydrogencarbonate occurs to generate a carbonic acid gas in the drying and curing process of the coating composition. A reaction between this carbonic acid gas and an alkali metal and an amine component or an ammonium component in alkali silicate is accelerated, thereby improving curability. Although a favorable curability can be obtained since a neutralization reaction with alkali silicate occurs even with an acid component alone, a combination of the acid component and the hydrogencarbonate further improves the effect.

[0083]

A total content of the acid component and the hydrogencarbonate based on 100 parts by mass of a total of an aqueous solution or a hydrosol of alkali silicate and a hydrosol of an anhydrous silicic acid is preferably 0.1 to 5.0 parts by mass, and more preferably 0.5 to 3.0 parts by mass. When the content is not smaller than the lower limit, a more favorable curability can be obtained. When the content is not larger than

the upper limit, storage stability of a silicate compound of alkali silicate is favorable.

[0084]

<<Water as Dispersion Medium>>

5 The alkali-silicate inorganic zinc coating composition usually contains water as a dispersion medium. When the coating composition is prepared, for example, an aqueous solution or a hydrosol of alkali silicate, and a hydrosol of an anhydrous silicic acid can be mixed. Water as a dispersion medium may be derived
10 from an aqueous solution or a sol of these components, or may be separately added.

[0085]

 The water content of the alkali-silicate inorganic zinc coating composition is preferably 3 to 50% by mass, more preferably
15 10 to 30% by mass based on the total amount of the composition. The content within the range is preferable from the viewpoint of dispersibility of each component contained in the coating composition.

[0086]

20 <<Alkyl Silicate Binder and Organic Solvent>>

 The alkali-silicate inorganic zinc coating composition preferably substantially does not contain alkyl silicate binders or organic solvents. In other words, the coating composition is preferably a water-based coating composition.

[0087]

The expression "substantially does not contain alkyl silicate binders or organic solvents" means that the content of the alkyl silicate binder is 1% by mass or smaller based on the total amount of the composition, and is preferably 0.5% by mass or smaller, and more preferably 0% by mass; and the content of the organic solvent is 0.5% by mass or smaller based on the total amount of the composition, and is preferably 0.3% by mass or smaller, and more preferably 0% by mass.

10 [0088]

The term "alkyl silicate binder" is an alkyl silicate compound such as tetraalkoxy silicate, alkyl trialkoxy silicate, dialkyl dialkoxo silicate, and a partial condensate thereof.

[0089]

15 Mostly, a conventional inorganic zinc coating film is formed by drying and curing an organic solvent-based coating containing an alkyl silicate binder. Such an organic solvent-based coating needs a large amount of an organic solvent in order to prepare the coating, and the thickness of the coating film needs to be large since a large amount of zinc particles are needed to obtain a sacrificial corrosion prevention effect of a steel material.

20

[0090]

Setting the contents of an alkyl silicate binder and an organic solvent in the above-described ranges means that the

inorganic zinc coating composition is not an organic solvent-based coating but a water-based coating. The water-based coating does not need organic solvents, which is preferable from the viewpoint of VOC, and, since there is a corrosion prevention effect due to an interaction between an alkaline component contained in the coating film and Cr contained in the steel material, the film thickness can be made small compared with a conventional inorganic zinc coating film.

[0091]

10 <<Organic Resin>>

The alkali-silicate inorganic zinc coating composition preferably substantially does not contain organic resins. When the coating composition does not contain organic resins, a sacrificial corrosion prevention effect of zinc particles improves.

[0092]

The expression "substantially does not contain organic resins" means that the content of the organic resin is 1% by mass or smaller based on the total amount of the composition, and is preferably 0.5% by mass or smaller, and more preferably 0% by mass.

[0093]

<Atomic Molar Ratio (Si/M)>

In the present invention, the coating film formed of the alkali-silicate inorganic zinc coating composition contains a

silicon atom, and at least one atom selected from an alkali metal atom and a nitrogen atom. Here, an alkali metal atom and a nitrogen atom are also collectively referred to as "M".

[0094]

5 In the present invention, the ratio of the number of moles of silicon atoms Si in the coating film to the total number of moles of alkali metal atoms and nitrogen atoms in the coating film, or the atomic molar ratio (Si/M) is 2.0 to 125. The upper limit of the atomic molar ratio (Si/M) is preferably 60, and more
10 preferably 35; and the lower limit of the atomic molar ratio (Si/M) is preferably 2.2, and more preferably 2.3. A more preferable numerical range of the atomic molar ratio (Si/M) is 2.2 to 60, and a further preferable numerical range is 2.3 to 35. The nitrogen atom is preferably a nitrogen atom derived from the
15 above-described ammonium silicate, or quaternary ammonium silicate.

[0095]

 When the atomic molar ratio is in the above-described range, both corrosion resistance of the coating film and an interaction
20 between an alkaline component in the coating film and Cr in the steel material can be realized. When the ratio of Si in the composition is too high, the ratios of an alkali metal atom and a nitrogen atom in the composition are low, and therefore, a sufficient interaction with Cr in the steel material cannot be

obtained. When the ratio of Si in the composition is too low, corrosion resistance of the coating film cannot be improved.

[0096]

Here, when a plurality of kinds of alkali silicates are used,
5 the number of moles of M is the total number of moles of an alkali metal and a nitrogen atom which can be contained in the coating film. In other words, when one or more selected from, for example, lithium silicate, sodium silicate, potassium silicate, ammonium silicate, and quaternary ammonium silicate are used as alkali
10 silicate, the atomic molar ratio in the coating film is a value represented by (the number of moles of Si) / (the number of moles of Li + Na + K + N), and a component which is not used in alkali silicate may be dealt by setting the number of moles to 0. The mixing ratio (ratio of Li/Na/K/N) of alkali metal atoms, and a
15 nitrogen atom is not particularly limited.

[0097]

The atomic molar ratio in the coating film can be realized by adjusting the kind and amount of alkali silicate which is added when the alkali-silicate inorganic zinc coating composition is
20 manufactured, amount of an anhydrous silicic acid which is added as needed, amount of hydrogencarbonate which is added as needed, or the like. When ammonium silicate and/or quaternary ammonium silicate are/is used, a part of a nitrogen atom-containing component (for example: amine component, ammonium component)

derived from the silicate volatilizes during formation of the coating film, and therefore, the amount is adjusted in consideration thereof.

[0098]

5 The number of moles of Si or M contained in the self-cured coating film can be re-measured by utilizing a known measurement method such as an ICP emission spectrometer, a fluorescent X-ray spectroscopy, or a trace total nitrogen analyzer.

[0099]

10 <Mass Ratio of Binder Component and Zinc Particles>

 In the alkali-silicate inorganic zinc coating composition, the mass ratio represented by "the solid content mass of a binder component / the mass of zinc particles" is 0.01 to 0.35, and preferably 0.02 to 0.25. The solid content of a binder component
15 means, for example, alkali silicate and an anhydrous silicic acid which is used as needed.

[0100]

 The mass ratio in the above-described range can keep favorably a balance between corrosion resistance of the coating
20 film and a sacrificial corrosion prevention effect. Specifically, when the mass ratio is 0.01 or higher, corrosion resistance of the coating film due to alkali silicate or the like which is a binder component can be sufficiently obtained, and when the mass ratio is 0.35 or lower, a sacrificial corrosion prevention effect

due to zinc particles can be sufficiently obtained.

[0101]

<Relationship between Atomic Molar Ratio (Si/M) and Cr Content>

5 As described in the following [Examples], from Fig. 1 and
Fig. 2 illustrating the result of a CCT test (the following
corrosion test 3) using artificial sea water, in order to prevent
rusting in a CCT test for one year (365 days) at an acceleration
of 6 times, the steel material and the coating film preferably
10 satisfies an empirical expression (1): $[Cr] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\} \times 20 (\mu\text{m}) / (\text{the thickness } (\mu\text{m}) \text{ of the coating film formed on the surface of the steel material}).$

[0102]

 Here, according to rules for steel ships CSR-T, a local
15 corrosion reserve thickness at a portion positioned upward in a
ballast tank where the severest corrosion is observed is 4.0 mm.
Since the corrosion rate in the ballast tank is at most about 0.5
(mm/year), the corrosion reserve thickness is reached in eight
years. In consideration of eight years of the steel material
20 corrosion period, for example, in order to realize more excellent
corrosion resistance over 15 years, the rust prevention period
is preferably seven years.

[0103]

In a CCT test (the following corrosion test 3) for one year

illustrated in Fig. 1 and Fig. 2, six cycles in each of which a day-and-night environment in a ballast tank is assumed are performed in one day, and the acceleration is six times. It is well-known that a rust prevention period is proportional to the thickness of a coating film.

[0104]

By this, in the present invention, in order to realize more excellent corrosion resistance than conventional techniques over 15 years (in other words, corrosion resistance over a longer period than that of conventional techniques), the steel material and the coating film which is formed of the alkali-silicate inorganic zinc coating composition preferably satisfy the following conditional expression (1).

[0105]

Conditional expression (1): $[Cr] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\} \times 20 \text{ (}\mu\text{m)} / (\text{thickness (}\mu\text{m) of the coating film formed on the surface of the steel material}) \times a/b$

In the conditional expression (1), [Cr] is the Cr content (% by mass) in the steel material. The molar ratio (Si/M) is the ratio of the number of moles of silicon atoms Si in the coating film to the total number of moles of alkali metal atoms and nitrogen atoms in the coating film. Here, a and b are each determined based on a rust prevention period and acceleration in a CCT test, and in the case of realizing the corrosion resistance over 15 years,

it is set that $a = 7$ and $b = 6$.

[0106]

In order to realize more excellent corrosion resistance over 20 years, the rust prevention period is preferably set to 12 years, and therefore, the steel material and the coating film preferably satisfy the conditional expression (1) where $a = 12$, $b = 6$. In order to realize more excellent corrosion resistance over 25 years, the rust prevention period is preferably set to 17 years, and therefore, the steel material and the coating film preferably satisfy the conditional expression (1) where $a = 17$, $b = 6$. In order to prevent rusting for 25 years, the steel material and the coating film preferably satisfy the conditional expression (1) where $a = 25$, $b = 6$.

[0107]

When the steel material and the coating film satisfy the conditional expression (1) in addition to the coating film satisfying the conditions of the molar ratio (Si/M) and the mass ratio, an anti-corrosion steel material which is particularly preferable for realizing corrosion resistance over a long period of time is obtained.

[0108]

When the steel material and the coating film satisfy the conditional expression (1), a film thickness needed to realize corrosion resistance of the above-described period (for example,

15 years, 20 years, 25 years) depends on the amount of Cr of the steel material, and can be far smaller than a film thickness of 320 μm or larger in a coating standard obligated by the international convention described below. In this case, multiple
5 layer-application is not required, and the coating film can also be made into a single film. When corrosion resistance over the above-described period is needed, an epoxy resin coating may be further coated on the anti-corrosion steel material comprising the steel material and the coating film satisfying the conditional
10 expression (1).

[0109]

<Preparation of Alkali-silicate Inorganic Zinc Coating Composition>

The alkali-silicate inorganic zinc coating composition can
15 be manufactured by, for example, stirring or mixing the above-described components. During the stirring or the mixing, a known mixing or stirring apparatus and disperser such as an electric stirrer and a sand mill can be appropriately used.

[0110]

20 [Long-Term Corrosion Resistance of Anti-Corrosion Steel Material]

A liquid property (it can be measured, for example, by water in contact with the coating film before the formation of a corrosion product) of the coating film composed of the

alkali-silicate inorganic zinc coating composition is alkaline. By adding various alloy elements including Cr to the steel material which is to be a base material, a passive film is formed on an interface of the steel material under alkali conditions, and
5 therefore, corrosion resistance of the steel material over a long period of time can be improved.

[0111]

Since the coating film contains zinc particles, a corrosion product of zinc is formed on the coating film, and a sacrificial
10 corrosion prevention effect of zinc protects the steel material itself. Further, the formed corrosion product of zinc prevents an alkaline component (for example, alkali metal ion, amine, ammonium ion) in the coating film or the steel material elements from being eluted outside, and liquid properties of the coating
15 film are maintained. Under alkali conditions maintained as described above, a passive film is formed. Consequently, corrosion resistance of the steel material over a long period of time can be maintained.

[0112]

20 Although, in a corrosive environment, the structure and composition of a highly protective film formed under the coating cannot be directly observed, in the present invention, from various corrosion test results, a highly protective film is considered to be formed.

[0113]

The anti-corrosion steel material of the present invention has excellent long-term corrosion resistance as described above, specifically long-term anti-rusting properties, and therefore, a top coating film such as an organic resin coating film is not required on the alkali-silicate inorganic zinc coating film for the purpose of improving corrosion resistance . For this reason, the anti-corrosion steel material of the present invention is excellent also from the viewpoint of painting work process compared with a conventional alkyl silicate coating or epoxy coating.

[0114]

<Method of Forming Coating Film; Method of Preventing Corrosion of Steel Material>

In the present invention, the alkali-silicate inorganic zinc coating composition is coated on the surface of the steel material by a known method such as air spraying or airless spraying to form an undried coating film, and the coating film is cured by drying, thereby forming a coating film. The curing conditions are, for example, that the temperature is usually 5 to 30°C, preferably normal temperature, that the relative humidity is usually 5 to 85%, and preferably 10 to 60%, and that the curing time is usually 1 to 30 days, and preferably 2 to 15 days. By the drying, the undried coating film is self-cured. As described

above, the anti-corrosion steel material comprising the steel material and the coating film having a thickness of 10 μm or larger formed on the surface of the steel material can be obtained.

[0115]

5 In this case, in order to obtain an interaction between an alkaline component in the coating film and Cr in the steel material, the above-described coating composition is coated such that the thickness of the coating film is at least 10 μm . The thickness of the coating film is preferably set to 200 μm or smaller, more
10 preferably 120 μm or smaller, and further preferably 80 μm or smaller.

[0116]

When the thickness of the coating film is smaller than 10 μm , corrosion of zinc particles after a corrosion test is
15 accelerated, and a sacrificial corrosion prevention effect disappears at an early stage, whereby an effect of protection by the corrosion product cannot be sufficiently obtained. When the thickness of the coating film is 10 μm or larger, the surface of the coating film is protected by a corrosion product of mildly
20 alkaline zinc particles, and further, an alkaline component in the coating film is also maintained. As a result, a highly protective film is formed on the surface of the steel material by a synergistic effect among the corrosion product, the alkaline component, and Cr, thereby obtaining excellent corrosion

resistance over a long period of time. The thickness of the coating film is preferably 20 μm or larger, more preferably 30 μm or larger, and further preferably 50 μm or larger.

[0117]

5 In a coating standard obligated by the international convention regarding a sea water ballast tank of a ship, multiple layer-application of an epoxy resin coating is required, and the dry film thickness (film thickness) of a coating film has changed from previous 250 μm to 320 μm , considerably increasing the number
10 of working processes for coating. For this reason, a corrosion prevention technique (for example, making a coating film into a single film or a thin film) which can reduce the number of working proesses for coating is demanded. In the present invention, even
15 in cases where the thickness of the coating film is 80 μm or smaller, when the alkali-silicate inorganic zinc coating film is provided on the steel material, excellent corrosion resistance over a longer period of time can be obtained.

[0118]

[Ballast Tank]

20 A ballast tank of the present invention is constituted by using the anti-corrosion steel material of the present invention. Such a ballast tank does not need a further top coating film on the alkali-silicate inorganic zinc coating film, and has excellent long-term corrosion resistance.

Examples

[0119]

In the following, the present invention will be specifically described by way of Examples and Comparative Examples, but the present invention is not limited thereto. In the descriptions in the following Examples or the like, the term "part" implies "part by mass" unless otherwise specifically indicated.

[0120]

<Manufacturing of Steel Plate Which is Base Material>

10 A steel whose composition is listed on Table 1 was melted to form a steel plate having a plate thickness of 14 mm by a usual manufacturing process such as hot rolling or normalizing heat treatment. Regarding elements listed on Table 1, the balance is Fe and inevitable impurities. In Table 1, Steel Type Nos. A-1
15 to A-22 correspond to steels (steels of the present invention) used in the present invention, and Steel Type Nos. B-1 to B-2 correspond to conventional steels.

[0121]

[Table 1]

Table 1

Steel Type No.	C	Si	Mn	Cr	P	S	N	Al	Cu	Ni	Mo	W	Sn	Sb	Others
A-1	0.08	0.01	1.20	0.80	0.020	0.004	0.008	0.030	-	-	-	0.30	0.05	-	
A-2	0.05	0.01	0.90	0.80	0.020	0.002	0.006	0.020	0.30	0.30	0.50	0.50	-	-	Ti:0.01, REM:0.001
A-3	0.08	0.31	1.21	0.80	0.030	0.003	0.003	0.030	-	0.10	-	-	-	-	Ti:0.012
A-4	0.06	0.21	1.01	1.00	0.007	0.001	0.005	0.030	-	-	0.10	-	-	-	Ti:0.012, Mg:0.001
A-5	0.06	0.21	0.98	1.00	0.030	0.002	0.004	0.020	0.30	1.01	-	-	-	-	Ti:0.012, B:0.0005
A-6	0.05	0.30	0.60	2.00	0.006	0.001	0.005	0.020	-	-	-	-	-	-	
A-7	0.08	0.31	1.21	2.00	0.008	0.004	0.004	0.030	0.15	-	-	-	-	0.05	Zr:0.01
A-8	0.05	0.50	1.50	2.00	0.020	0.004	0.005	0.020	0.10	0.20	0.50	-	0.01	-	
A-9	0.10	0.05	0.70	2.00	0.007	0.003	0.004	0.010	-	-	-	-	-	-	Nb:0.01, V:0.01
A-10	0.03	0.25	0.70	2.00	0.009	0.002	0.004	0.003	-	-	-	-	-	-	Ti:0.02, Ca:0.002
A-11	0.05	3.00	1.50	3.00	0.010	0.004	0.006	0.020	0.50	0.05	-	0.01	0.08	-	
A-12	0.04	0.35	3.00	3.00	0.018	0.006	0.007	0.030	-	-	-	-	-	-	Ti:0.01, REM:0.001
A-13	0.004	0.35	0.50	6.00	0.017	0.001	0.004	1.100	-	-	-	-	-	-	
A-14	0.06	0.35	0.60	1.00	0.020	0.001	0.006	0.004	-	-	-	-	-	-	
A-15	0.06	0.19	0.95	0.20	0.008	0.002	0.003	0.029	-	-	-	-	-	-	
A-16	0.05	0.31	1.02	0.40	0.015	0.009	0.002	0.027	-	-	-	-	-	-	
A-17	0.04	0.17	0.98	0.75	0.012	0.008	0.003	0.035	-	-	-	-	-	-	0.014Ti
A-18	0.09	0.18	1.30	1.20	0.006	0.005	0.002	0.029	-	-	-	-	-	-	
A-19	0.07	0.17	0.88	1.50	0.007	0.005	0.004	0.028	-	-	-	-	-	-	0.014Ti, 0.006Nb
A-20	0.08	0.29	0.95	1.20	0.008	0.004	0.003	0.032	-	-	-	-	-	-	0.012Ti, 0.010Nb
A-21	0.05	0.25	0.95	1.50	0.010	0.005	0.003	0.033	-	-	-	-	-	-	
A-22	0.03	0.24	0.80	1.00	0.006	0.008	0.003	0.035	0.95	0.5	-	-	-	-	
B-1	0.13	0.01	1.20	0.003	0.020	0.003	0.006	0.020	-	-	-	-	-	-	
B-2	0.08	0.31	0.97	0.04	0.020	0.002	0.004	0.030	-	-	-	-	-	-	

* Unit: % by mass

[0122]

<Manufacturing of Alkali-Silicate Inorganic Zinc Coating Composition>

[Preparation Example 2]

5 75 parts of an aqueous lithium silicate solution "Lithium Silicate 1:4" (trade name; molar ratio ($\text{SiO}_2/\text{Li}_2\text{O}$) = 4.0 (catalog value); solid content concentration = 22.6% by mass; manufactured by THE HONJO CHEMICAL CORPORATION), and 22.5 parts of aqueous colloidal silica "SNOWTEX 20" (trade name; solid content
10 concentration = 20% by mass; manufactured by Nissan Chemical Industries, Ltd.) were charged into a container while stirring. The obtained mixture was used as a base component. To this base component, 325 parts of zinc dust "F-2000" (trade name; average particle size: 4 μm ; manufactured by THE HONJO CHEMICAL
15 CORPORATION) was added as a zinc powder. The obtained composition was referred to as coating C-1.

[0123]

[Preparation Example 1, 3 to 36]

Coatings were obtained in a similar manner to Preparation
20 Example 2 except that the amount of each component was changed as described in Tables 2-1 and 2-2. In Tables 2-1 and 2-2, coating Nos. C-1 to C-25 correspond to alkali-silicate inorganic zinc coating compositions used in the present invention, and coating Nos. D-1 to D-11 correspond to coating compositions for

comparison.

[0124]

The atomic molar ratios (Si/M) in Tables 2-1 and 2-2 are values measured for a coating film formed in the section <Formation of Coating Film> by using a CIROS CCD (manufactured by Rigaku Corporation) as an ICP emission spectrometer, and a TN-110 type (manufactured by Mitsubishi Chemical Analytech Co., Ltd.) as a trace total nitrogen analyzer.

[0125]

10 [Table 2-1]

Table 2-1

	Coating No.	Aqueous Alkali Metal Silicate Solution (Parts By Mass)				Aqueous Sol of Quaternary Ammonium Silicate (Parts by Mass)	Aqueous Colloidal Silica (Parts by Mass)	Acid Component and Hydrogencarbonate (Parts by Mass)		Zinc Particles (Parts by Mass)		Atomic Molar Ratio				Binder Content /Zinc Particles (Mass Ratio)
		Aqueous Lithium Silicate Solution	Aqueous Sodium Silicate Solution 1	Aqueous Sodium Silicate Solution 2	Aqueous Potassium Silicate Solution			5% by Mass Aqueous Boric Acid Solution	8% by Mass Aqueous Sodium Hydrogencarbonate Solution	Zinc Powder	Zinc Alloy Powder	Si/Li	Si/Na	Si/K	Si/N	Si/M
Preparation Example 1	D-1	97.5								325		1.8				1.8
Preparation Example 2	C-1	75					22.5			325		2.4				2.4
Preparation Example 3	C-2	3.52					94.0			325		50.1				50.1
Preparation Example 4	C-3	1.76					96.0			325		100.4				100.4
Preparation Example 5	D-2	1.18					96.8			325		150.1				150.1
Preparation Example 6	D-3			75						325			1.9			1.9
Preparation Example 7	C-4		43				33.8			325			2.4			2.4
Preparation Example 8	C-5		2				94.0			325			50.0			50.0
Preparation Example 9	C-6		1				95.5			325			100.0			100.0
Preparation Example 10	D-4		0.66				96.2			325			151.9			151.9
Preparation Example 11	D-5				96					320				1.8		1.8
Preparation Example 12	C-7				72		25.1			323				2.4		2.4
Preparation Example 13	C-8				2.9		95.5			328				58.5		58.5
Preparation Example 14	C-9				1.65		95.0			327				100.9		100.9
Preparation Example 15	D-6				1.11		96.0			325				150.7		150.7
Preparation Example 16	C-10					68	12.0			325					34.2	34.2
Preparation Example 17	C-11					46	39.3			325					50.5	50.5
Preparation Example 18	C-12					23	68.0			325					101.0	101.0
Preparation Example 19	D-7					15	77.0			325					153.2	153.2
Preparation Example 20	C-13	20	20			20	22.0			325		8.8	5.0		116.0	3.1
Preparation Example 21	C-14	1.2	1.2			1.2	90.0			325		142.4	81.2		1890	50.3
Preparation Example 22	C-15	0.6	0.6			0.6	95.0			325		293.0	167.2		3890	103.6
Preparation Example 23	D-8	0.4	0.4			0.4	95.0			325		436.2	248.8		5790	154.2

*1: The value in the 5% by mass aqueous boric acid solution column on the right is parts by mass of boric acid based on 100 parts by mass of an aqueous alkali metal silicate solution, an aqueous sol of quaternary ammonium silicate, and an aqueous colloidal silica.

*2: The value in the 8% by mass aqueous sodium hydrogencarbonate solution column on the right is parts by mass of sodium hydrogencarbonate based on 100 parts by mass of an aqueous alkali metal silicate solution, an aqueous sol of quaternary ammonium silicate, and an aqueous colloidal silica.

[0126]

[Table 2-2]

Table 2-2

		Aqueous Alkali Metal Silicate Solution (Parts By Mass)					Aqueous Sol of Quaternary Ammonium Silicate (Parts by Mass)	Aqueous Colloidal Silica (Parts by Mass)	Acid Component and Hydrogencarbonate (Parts by Mass)			Zinc Particles (Parts by Mass)		Atomic Molar Ratio					Binder Content /Zinc Particles (Mass Ratio)
		Aqueous Lithium Silicate Solution	Aqueous Sodium Silicate Solution 1	Aqueous Sodium Silicate Solution 2	Aqueous Potassium Silicate Solution				5% by Mass Aqueous Boric Acid Solution	8% by Mass Aqueous Sodium Hydrogencarbonate Solution	Zinc Powder	Zinc Alloy Powder	Si/Li	Si/Na	Si/K	Si/N	Si/M		
Preparation Example 24	Coating No.	D-9	65.8	6.6				23.0				3800		2.7	15.4			2.3	0.006
Preparation Example 25		C-16	65.8	6.6				23.0				1900		2.7	15.4			2.3	0.01
Preparation Example 26		C-17	65.8	6.6				23.0				320		2.7	15.4			2.3	0.07
Preparation Example 27		C-18	65.8	6.6				23.0				190		2.7	15.4			2.3	0.11
Preparation Example 28		C-19	65.8	6.6				23.0				96		2.7	15.4			2.3	0.22
Preparation Example 29		C-20	65.8	6.6				23.0				64		2.7	15.4			2.3	0.34
Preparation Example 30	Coating No.	D-10	65.8	6.6				23.0				48		2.7	15.4			2.3	0.45
Preparation Example 31		C-21	63	3.3			5.5		23.1			322		2.8	30.2	30.3		2.3	0.07
Preparation Example 32		C-22	65.8	6.6					23.0	10	0.5	1	0.08	320	2.7	14.8		2.3	0.07
Preparation Example 33		C-23	65.8	6.6					23.0					320	2.7	15.4		2.3	0.07
Preparation Example 34		D-11	93						5				325	1.9				1.9	0.07
Preparation Example 35		C-24			47				27				325			2.1		2.1	0.07
Preparation Example 36		C-25	12.5									325		14.1			34.4	10.0	0.060

*1: The value in the 5% by mass aqueous boric acid solution column on the right is parts by mass of boric acid based on 100 parts by mass of an aqueous alkali metal silicate solution, an aqueous sol of quaternary ammonium silicate, and an aqueous colloidal silica.

*2: The value in the 8% by mass aqueous sodium hydrogencarbonate solution column on the right is parts by mass of sodium hydrogencarbonate based on 100 parts by mass of an aqueous alkali metal silicate solution, an aqueous sol of quaternary ammonium silicate, and an aqueous colloidal silica.

[0127]

Details of each component in Tables 2-1 and 2-2 are as follow:

- Aqueous lithium silicate solution: "Lithium Silicate 1: 4"
 5 (trade name; molar ratio ($\text{SiO}_2/\text{Li}_2\text{O}$) = 4.0; solid content concentration = 22.6% by mass; manufactured by THE HONJO CHEMICAL CORPORATION)
- Aqueous sodium silicate solution 1: "J sodium silicate No. 3"
 (trade name; molar ratio ($\text{SiO}_2/\text{Na}_2\text{O}$) = 3.2; solid content
 10 concentration = 40% by mass; manufactured by Nippon Chemical Industrial Co., Ltd.)
- Aqueous sodium silicate solution 2: "J sodium silicate No. 4"
 (trade name; molar ratio ($\text{SiO}_2/\text{Na}_2\text{O}$) = 3.4; solid content
 concentration = 35% by mass; manufactured by Nippon Chemical
 15 Industrial Co., Ltd.)
- Aqueous potassium silicate solution: "2K potassium silicate"
 (trade name; molar ratio ($\text{SiO}_2/\text{K}_2\text{O}$) = 3.6; solid content
 concentration = 30% by mass; manufactured by Nippon Chemical
 Industrial Co., Ltd.)
- 20 • Quaternary ammonium silicate: "QAS-25" (trade name; quaternary ammonium component is used; solid content concentration = 25% by mass; manufactured by Nissan Chemical Industries, Ltd.)

The molar ratio ($\text{SiO}_2/\text{M}_2\text{O}$) is a catalog value.

- Aqueous colloidal silica: trade name "SNOWTEX 20" (trade name;

solid content concentration = 20% by mass; manufactured by Nissan Chemical Industries, Ltd.)

- Zinc powder: zinc dust "F-2000" (trade name; average particle size: 4 μm ; manufactured by THE HONJO CHEMICAL CORPORATION)
- 5 • Zinc alloy powder: "Zinc flake ZnAl7" (trade name; average particle size: 18 μm ; alloy powder of 93% by mass of zinc and 7% by mass of aluminum; manufactured by ECKART GmbH)

<Formation of Coating Film>

From the steel plate illustrated in Table 1, a test piece
10 having width: 70 mm, length: 150 mm, and thickness: 3 mm was taken, and the taken test piece was subjected to degreasing, and a blast treatment under conditions equivalent to a rust removal level Sa 2 1/2 or higher in accordance with ISO 8501-1. On the surface of the test piece, an alkali-silicate inorganic zinc coating
15 composition illustrated in Tables 2-1 and 2-2 was coated, and then, the test piece was left to stand in a thermostatic chamber at a temperature of 23°C, and a relative humidity of 50% for 1 week to be self-cured, thereby forming a coating film. A dried and cured coating film was taken, and the atomic molar ratio (Si/M)
20 in the coating film was determined by measuring the amount of Si and the amount of M by using a CIROS CCD (manufactured by Rigaku Corporation) as an ICP emission spectrometer, and a TN-110 type (manufactured by Mitsubishi Chemical Analytech Co., Ltd.) as a trace total nitrogen analyzer. Combinations of steel plates and

alkali-silicate inorganic zinc coating compositions, and the thicknesses of coating films are as illustrated in the following Table 3 (Table 3-1, Table 3-2), and Tables 4 to 8.

[0128]

5 <Evaluation of Anti-Corrosion Steel Material>

A test piece on which a coating film composed of an alkali-silicate inorganic zinc coating composition was formed was subjected to a pre-test treatment such as a covering on a surface other than the test surface, and the following test was performed.

10 [0129]

<Corrosion Test 1>

A performed corrosion test 1 was a cyclic corrosion test. A test was performed 1080 cycles each of which includes spraying by using artificial sea water at 35°C for 1h; drying at 60°C, at
15 an RH (relative humidity) of 15 to 25%, for 2h; and wetting at 50°C, at an RH of 98% or higher, for 1h, in other words, a corrosion test (cyclic corrosion test; CCT test) in which an artificial sea water spraying step, a drying step, and a wetting step were sequentially repeated was performed.

20 [0130]

After completing the test, anti-rusting properties were evaluated by visual inspection. In the corrosion test 1, a rating-number method in accordance with JIS Z2371 (salt spray test method) was used: in the evaluation criteria α , up to 9.8-1: AA,

more than 9.8-1 and up to 9.3-2: BB, and 9.3-3 or more: CC, in the evaluation criteria β , up to 9.8-1: A, more than 9.8-1 and up to 5-2: B, and 5-3 or more: C.

[0131]

5 The obtained results were listed on the following Tables 3 to 8 in combination. Here, an influence which the Cr content in the steel material has on the result of the corrosion test was listed on Table 4, and an influence which the thickness of the coating film has on the result of the corrosion test was listed
10 on Table 5.

[0132]

<Corrosion Test 2>

In a corrosion test 2, a coating film was formed on a test piece such that the thickness of the coating film was 15 μm in
15 a similar manner to the <formation of coating film>, and an 840-cycle cyclic corrosion test was performed to evaluate an influence which the atomic molar ratio (Si/M) in the coating film had on the result of the corrosion test. The evaluation of the corrosion test 2 was performed in similar criteria to those of
20 the corrosion test 1. The obtained results were listed on the following Table 6.

[0133]

<Corrosion Test 3>

In a corrosion test 3, a cyclic corrosion test similar to

that of corrosion test 1 was performed up to 2190 cycles, and anti-rusting properties were evaluated by visual inspection. In the corrosion test 3, from the viewpoint of determining whether rusting was suppressed or not, a rating-number method in accordance with JIS Z2371 (salt spray test method) was used: up to 9.8-1: A, more than 9.8-1 and up to 5-2: B, 5-3 and more: C. The obtained results were listed on the following Tables 3 to 8.

[0134]

[Table 3-1]

Table 3-1

	Steel Type No.	Coating No.	Film Thickness (μm)	Cr Content (% by Mass)	Atomic Molar Ratio (Si/M)	Result of Corrosion Test 1 (Evaluation Criteria α)	Result of Corrosion Test 1 (Evaluation Criteria β)	Value of Specific Expression	Judgment of Empirical Expression (1)	Result of Corrosion Test 3	Judgment of Conditional Expression (1)
Comparative Example 1	B-1	C-1	15	0.003	2.4	CC	C	0.96	×	C	×
Comparative Example 2	B-2	C-14	200	0.04	50.3	CC	B	0.15	×	C	×
Comparative Example 3	B-1	C-3	75	0.003	100.4	CC	C	0.44	×	C	×
Comparative Example 4	B-2	D-5	75	0.04	1.8	CC	C	0.17	×	C	×
Comparative Example 5	B-1	C-1	8	0.003	2.4	CC	C	1.80	×	C	×
Comparative Example 6	B-1	C-20	15	0.003	2.3	CC	C	0.94	×	C	×
Comparative Example 7	A-6	D-1	15	2.00	1.8	CC	C	0.86	○	C	○
Comparative Example 8	A-4	D-2	25	1.00	150.1	CC	C	1.40	×	C	×
Comparative Example 9	A-1	D-3	200	0.80	1.9	CC	C	0.07	○	C	○
Comparative Example 10	A-6	D-4	75	2.00	151.9	CC	C	0.47	○	C	○
Comparative Example 11	A-13	D-5	15	6.00	1.8	CC	C	0.86	○	C	○
Comparative Example 12	A-2	D-6	75	0.80	150.7	CC	C	0.47	○	C	○
Comparative Example 13	A-8	D-7	55	2.00	153.2	CC	C	0.64	○	C	○
Comparative Example 14	A-2	D-9	25	0.80	2.3	CC	C	0.57	○	C	○
Comparative Example 15	A-13	D-10	35	6.00	2.3	CC	C	0.40	○	C	○
Comparative Example 16	A-12	D-11	10	3.00	1.9	CC	C	1.32	○	C	○
Comparative Example 17	A-3	D-8	15	0.80	154.2	CC	C	2.35	×	C	×
Comparative Example 18	A-7	C-20	8	2.00	2.3	CC	C	1.77	○	C	×
Example 1	A-1	C-3	150	0.80	100.4	AA	A	0.22	○	A	○
Example 2	A-2	C-4	200	0.80	2.4	AA	A	0.07	○	A	○
Example 3	A-1	C-17	25	0.80	2.3	BB	B	0.57	○	B	○
Example 4	A-2	C-17	75	0.80	2.3	AA	A	0.19	○	A	○
Example 5	A-3	C-17	75	0.80	2.3	AA	A	0.19	○	A	○
Example 6	A-4	C-17	75	1.00	2.3	AA	A	0.19	○	A	○
Example 7	A-5	C-17	150	1.00	2.3	AA	A	0.09	○	A	○
Example 8	A-6	C-17	75	2.00	2.3	AA	A	0.19	○	A	○
Example 9	A-7	C-20	75	2.00	2.3	AA	A	0.19	○	A	○
Example 10	A-7	C-20	15	2.00	2.3	BB	B	0.94	○	B	○

[0135]

[Table 3-2]

Table 3-2

	Steel Type No.	Coating No.	Film Thickness (μm)	Cr Content (% by Mass)	Atomic Molar Ratio (Si/M)	Result of Corrosion Test 1 (Evaluation Criteria α)	Result of Corrosion Test 1 (Evaluation Criteria β)	Value of Specific Expression	Judgment of Empirical Expression (1)	Result of Corrosion Test 3	Judgment of Conditional Expression (1)
Example 11	A-8	C-16	10	2.00	2.3	BB	B	1.42	○	B	○
Example 12	A-9	C-18	25	2.00	2.3	AA	A	0.57	○	A	○
Example 13	A-10	C-1	35	2.00	2.4	AA	A	0.41	○	A	○
Example 14	A-11	C-7	55	3.00	2.4	AA	A	0.26	○	A	○
Example 15	A-11	C-17	75	3.00	2.3	AA	A	0.19	○	A	○
Example 16	A-12	C-4	75	3.00	2.4	AA	A	0.19	○	A	○
Example 17	A-12	C-8	75	3.00	58.5	AA	A	0.40	○	A	○
Example 18	A-13	C-17	75	6.00	2.3	AA	A	0.19	○	A	○
Example 19	A-13	C-2	75	6.00	50.1	AA	A	0.39	○	A	○
Example 20	A-13	C-5	75	6.00	50.0	AA	A	0.39	○	A	○
Example 21	A-13	C-6	75	6.00	100.0	AA	A	0.44	○	A	○
Example 22	A-14	C-17	75	1.00	2.3	AA	A	0.19	○	A	○
Example 23	A-14	C-20	75	1.00	2.3	AA	A	0.19	○	A	○
Example 24	A-11	C-10	75	3.00	34.2	AA	A	0.37	○	A	○
Example 25	A-12	C-11	75	3.00	50.5	AA	A	0.39	○	A	○
Example 26	A-13	C-12	75	6.00	101.0	AA	A	0.44	○	A	○
Example 27	A-11	C-13	75	3.00	3.1	AA	A	0.21	○	A	○
Example 28	A-12	C-14	75	3.00	50.3	AA	A	0.39	○	A	○
Example 29	A-13	C-15	75	6.00	103.6	AA	A	0.44	○	A	○
Example 30	A-6	C-23	75	2.00	2.3	AA	A	0.19	○	A	○
Example 31	A-5	C-21	75	1.00	2.3	AA	A	0.19	○	A	○
Example 32	A-10	C-22	75	2.00	2.3	AA	A	0.19	○	A	○
Example 33	A-13	C-9	75	6.00	100.9	AA	A	0.44	○	A	○
Example 34	A-6	C-19	75	2.00	2.3	AA	A	0.19	○	A	○
Example 35	A-11	C-24	75	3.00	2.1	AA	A	0.18	○	A	○
Example 36	A-20	C-13	75	1.20	3.1	AA	A	0.21	○	A	○
Example 37	A-21	C-13	45	1.50	3.1	AA	A	0.35	○	A	○
Example 38	A-22	C-13	60	1.00	3.1	AA	A	0.26	○	A	○

Corrosion Test 1(α): Rusting: CC, Small Rusting: BB, No Rusting: AA, CCT Test Using Artificial Sea Water for 180 days

Corrosion Test 1(β), 3: Large Rusting: C, Small Rusting: B, No Rusting: A, CCT Test Using Artificial Sea Water for 180 days (Corrosion Test 1), 365 Days (Corrosion Test 3)

Specific Expression: $(0.25 \times \ln(\text{Molar Ratio}) + 0.5)/(\text{Film Thickness } (\mu\text{m})/20(\mu\text{m}))$ Empirical Expression (1): $[\text{Cr}] \geq (0.25 \times \ln(\text{Molar Ratio}) + 0.5)/(\text{Film Thickness } (\mu\text{m})/20(\mu\text{m}))$ Conditional Expression (1): $[\text{Cr}] \geq (0.25 \times \ln(\text{Molar Ratio}) + 0.5)/(\text{Film Thickness } (\mu\text{m})/20(\mu\text{m})) \times 7/6$

[0136]

[Table 4]

Table 4: Cr content

	Steel Type No.	Cr Content (% by Mass)	Coating No.	Atomic Molar Ratio (Si/M)	Film Thickness (μm)	Result of Corrosion Test 1 (Evaluation Criteria α)	Result of Corrosion Test 1 (Evaluation Criteria β)	Value of Specific Expression	Judgment of Empirical Expression (1)	Result of Corrosion Test 3	Judgment of Conditional Expression (1)
Example A1	A-2	0.80	C-15	103.6	75	AA	A	0.44	○	B	○
Example A2	A-3	0.80	C-15	103.6	75	AA	A	0.44	○	B	○
Example A3	A-4	1.00	C-15	103.6	75	AA	A	0.44	○	B	○
Example A4	A-6	2.00	C-15	103.6	75	AA	A	0.44	○	A	○
Example A5	A-11	3.00	C-15	103.6	75	AA	A	0.44	○	A	○
Example A6	A-13	6.00	C-15	103.6	75	AA	A	0.44	○	A	○
Example A7	A-14	1.00	C-15	103.6	75	AA	A	0.44	○	B	○
Comparative Example A1	B-1	0.003	C-15	103.6	75	CC	C	0.44	×	C	×
Comparative Example A2	B-2	0.04	C-15	103.6	75	CC	C	0.44	×	C	×

Corrosion Test 1(α): Rusting: CC, Small Rusting: BB, No Rusting: AA, CCT Test Using Artificial Sea Water for 180 days

Corrosion Test 1(β), 3: Large Rusting: C, Small Rusting: B, No Rusting: A, CCT Test Using Artificial Sea Water for 180 days (Corrosion Test 1), 365 Days (Corrosion Test 3)

Specific Expression: $(0.25 \times \ln(\text{Molar Ratio}) + 0.5)/(\text{Film Thickness } (\mu\text{m})/20(\mu\text{m}))$

Empirical Expression (1): $[\text{Cr}] \geq (0.25 \times \ln(\text{Molar Ratio}) + 0.5)/(\text{Film Thickness } (\mu\text{m})/20(\mu\text{m}))$

Conditional Expression (1): $[\text{Cr}] \geq (0.25 \times \ln(\text{Molar Ratio}) + 0.5)/(\text{Film Thickness } (\mu\text{m})/20(\mu\text{m})) \times 7/6$

[0137]

[Table 5]

Table 5: Thickness of Coating Film

	Steel Type No.	Cr Content (% by Mass)	Coating No.	Atomic Molar Ratio (Si/M)	Film Thickness (μm)	Result of Corrosion Test 1 (Evaluation Criteria α)	Result of Corrosion Test 1 (Evaluation Criteria β)	Value of Specific Expression	Judgment of Empirical Expression (1)	Result of Corrosion Test 3	Judgment of Conditional Expression (1)
Comparative Example B1	A-7	2.00	C-24	2.1	8	CC	C	1.71	○	C	○
Comparative Example B2	B-1	0.003	C-24	2.1	8	CC	C	1.71	×	C	×
Example B1	A-7	2.00	C-24	2.1	15	AA	A	0.91	○	B	○
Comparative Example B3	B-1	0.003	C-24	2.1	15	CC	C	0.91	×	C	×
Example B2	A-7	2.00	C-24	2.1	75	AA	A	0.18	○	A	○

Corrosion Test 1(α): Rusting: CC, Small Rusting: BB, No Rusting: AA, CCT Test Using Artificial Sea Water for 180 days

Corrosion Test 1(β), 3: Large Rusting: C, Small Rusting: B, No Rusting: A, CCT Test Using Artificial Sea Water for 180 days (Corrosion Test 1), 365 Days (Corrosion Test 3)

Specific Expression: $(0.25 \times \ln(\text{Molar Ratio}) + 0.5) / (\text{Film Thickness } (\mu\text{m}) / 20(\mu\text{m}))$

Empirical Expression (1): $[\text{Cr}] \geq (0.25 \times \ln(\text{Molar Ratio}) + 0.5) / (\text{Film Thickness } (\mu\text{m}) / 20(\mu\text{m}))$

Conditional Expression (1): $[\text{Cr}] \geq (0.25 \times \ln(\text{Molar Ratio}) + 0.5) / (\text{Film Thickness } (\mu\text{m}) / 20(\mu\text{m})) \times 7/6$

[0138]

[Table 6]

Table 6: Atomic Molar Ratio (Si/M)

	Steel Type No.	Cr Content (% by Mass)	Coating No.	Atomic Molar Ratio (Si/M)	Result of Corrosion Test 2	Result of Corrosion Test 1 (Evaluation Criteria β)	Value of Specific Expression	Judgment of Empirical Expression (1)	Result of Corrosion Test 3	Judgment of Conditional Expression (1)
Comparative Example C1	A-1	0.80	D-3	1.9	CC	C	0.88	x	C	x
Example C1	A-2	0.80	C-4	2.4	AA	A	1.0	x	C	x
Example C2	A-1	0.80	C-3	100.4	AA	A	2.2	x	C	x
Comparative Example C2	A-2	0.80	D-6	150.7	CC	C	2.3	x	C	x
Comparative Example C3	A-3	0.80	D-8	154.2	CC	C	2.3	x	C	x
Comparative Example C4	A-6	2.00	D-1	1.8	CC	C	0.9	o	C	o
Example C3	A-10	2.00	C-1	2.4	AA	A	1.0	o	B	o
Comparative Example C5	A-6	2.00	D-4	151.9	CC	C	2.3	x	C	x
Comparative Example C6	A-13	6.00	D-5	1.8	CC	C	0.9	o	C	o
Example C4	A-13	6.00	C-2	50.1	AA	A	2.0	o	A	o
Example C5	A-13	6.00	C-5	50.0	AA	A	2.0	o	A	o
Example C6	A-13	6.00	C-6	100.0	AA	A	2.2	o	B	o
Example C7	A-13	6.00	C-9	100.9	AA	A	2.2	o	B	o
Example C8	A-13	6.00	C-12	101.0	AA	A	2.2	o	B	o
Example C9	A-13	6.00	C-15	103.6	AA	A	2.2	o	B	o
Comparative Example C7	B-1	0.003	C-1	2.4	CC	C	1.0	x	C	x

Corrosion Test 2: Rusting: CC, Small Rusting: BB, No Rusting: AA, CCT Test Using Artificial Sea Water for 140 days

Corrosion Test 1 (β), 3: Large Rusting: C, Small Rusting: B, No Rusting: A, CCT Test Using Artificial Sea Water for 180 days (Corrosion Test 1), 365 Days (Corrosion Test 3)

Specific Expression: $(0.25 \times \ln(\text{Molar Ratio}) + 0.5) / (\text{Film Thickness } (\mu\text{m}) / 20(\mu\text{m}))$ Empirical Expression (1): $[\text{Cr}] \geq (0.25 \times \ln(\text{Molar Ratio}) + 0.5) / (\text{Film Thickness } (\mu\text{m}) / 20(\mu\text{m}))$ Conditional Expression (1): $[\text{Cr}] \geq (0.25 \times \ln(\text{Molar Ratio}) + 0.5) / (\text{Film Thickness } (\mu\text{m}) / 20(\mu\text{m})) \times 7/6$

[0139]

[Table 7]

Table 7

	Steel Type No.	Coating No.	Film Thickness (μm)	Cr Content (% by Mass)	Atomic Molar Ratio (Si/M)	Result of Corrosion Test 1 (Evaluation Criteria α)	Result of Corrosion Test 1 (Evaluation Criteria β)	Value of Specific Expression	Judgment of Empirical Expression (1)	Result of Corrosion Test 3
Example D1	A-16	C-1	20	0.40	2.4	AA	A	0.72	x	C
Example D2	A-17	C-10	20	0.75	34.2	AA	A	1.38	x	C
Example D3	A-18	C-10	20	1.20	34.2	AA	A	1.38	x	C
Example D4	A-16	C-25	20	0.40	10.0	BB	B	1.08	x	C
Example D5	A-17	C-25	20	0.75	10.0	AA	A	1.08	x	C
Example D6	A-18	C-2	20	1.20	50.1	AA	A	1.48	x	C
Example D7	A-17	C-3	20	0.75	100.4	BB	B	1.65	x	C
Example D8	A-18	C-3	20	1.20	100.4	AA	A	1.65	x	C
Example D9	A-19	C-3	20	1.50	100.4	AA	A	1.65	x	C
Example E1	A-17	C-1	20	0.75	2.4	AA	A	0.72	o	B
Example E2	A-18	C-1	20	1.20	2.4	AA	A	0.72	o	B
Example E3	A-18	C-25	20	1.20	10.0	AA	A	1.08	o	B
Example E4	A-19	C-25	20	1.50	10.0	AA	A	1.08	o	B
Example E5	A-19	C-2	20	1.50	50.1	AA	A	1.48	o	B
Example E6	A-19	C-10	20	1.50	34.2	AA	A	1.38	o	B
Example E7	A-10	C-10	20	2.00	34.2	AA	A	1.38	o	B
Example E8	A-10	C-2	20	2.00	50.1	AA	A	1.48	o	B
Example E9	A-10	C-3	20	2.00	100.4	AA	A	1.65	o	B

Corrosion Test 1(α): Rusting: CC, Small Rusting: BB, No Rusting: AA, CCT Test Using Artificial Sea Water for 180 days

Corrosion Test 1(β), 3: Large Rusting: C, Small Rusting: B, No Rusting: A, CCT Test Using Artificial Sea Water for 180 days (Corrosion Test 1), 365 Days (Corrosion Test 3)

Specific Expression: $(0.25 \times \ln(\text{Molar Ratio}) + 0.5) / (\text{Film Thickness } (\mu\text{m}) / 20(\mu\text{m}))$

Empirical Expression (1): $[\text{Cr}] \geq (0.25 \times \ln(\text{Molar Ratio}) + 0.5) / (\text{Film Thickness } (\mu\text{m}) / 20(\mu\text{m}))$

[0140]

[Table 8]

Table 8

	Steel Type No.	Coating No.	Film Thickness (μm)	Coating Thickness (μm)	Atomic Molar Ratio (S/M)	Result of Corrosion Test 1 (Evaluation Criteria α)	Result of Corrosion Test 1 (Evaluation Criteria β)	Value of Specific Expression	Judgment of Empirical Expression (1)	Result of Corrosion Test 3
Example D10	A-15	C-13	26	0.20	3.1	BB	B	0.60	x	C
Example D11	A-15	C-13	70	0.20	3.1	AA	A	0.22	x	C
Example D12	A-16	C-13	17	0.40	3.1	BB	B	0.92	x	C
Example D13	A-16	C-13	26	0.40	3.1	AA	A	0.60	x	C
Example D14	A-17	C-13	11	0.75	3.1	AA	A	1.42	x	C
Example D15	A-17	C-13	17	0.75	3.1	AA	A	0.92	x	C
Example D16	A-18	C-13	11	1.20	3.1	AA	A	1.42	x	C
Example E10	A-15	C-13	100	0.20	3.1	AA	A	0.16	o	A
Example E11	A-16	C-13	45	0.40	3.1	AA	A	0.35	o	A
Example E12	A-16	C-13	70	0.40	3.1	AA	A	0.22	o	A
Example E13	A-17	C-13	26	0.75	3.1	AA	A	0.60	o	A
Example E14	A-17	C-13	45	0.75	3.1	AA	A	0.35	o	A
Example E15	A-18	C-13	17	1.20	3.1	AA	A	0.92	o	A
Example E16	A-10	C-13	11	2.00	3.1	AA	A	1.42	o	A

Corrosion Test 1(α): Rusting: CC, Small Rusting: BB, No Rusting: AA, CCT Test Using Artificial Sea Water for 180 days

Corrosion Test 1(β), 3: Large Rusting: C, Small Rusting: B, No Rusting: A, CCT Test Using Artificial Sea Water for 180 days (Corrosion Test 1), 365 Days (Corrosion Test 3)

Specific Expression: $(0.25 \times \ln(\text{Molar Ratio}) + 0.5) / (\text{Film Thickness } (\mu\text{m}) / 20(\mu\text{m}))$

Empirical Expression (1): $[\text{Cr}] \geq (0.25 \times \ln(\text{Molar Ratio}) + 0.5) / (\text{Film Thickness } (\mu\text{m}) / 20(\mu\text{m}))$

[0141]

Table 4 shows results obtained when an alkali-silicate inorganic zinc coating film was provided on the surfaces of steels of the present invention and conventional steels, and the corrosion tests 1 and 3 were performed. According to Table 4, when the inorganic zinc coating film is provided on a steel of the present invention, anti-rusting properties were more improved than expected from the result of a conventional steel. A rust generated on a steel on which the inorganic zinc coating film was provided was analyzed by wide angle X-ray diffraction to observe a corrosion product containing Fe or Zn. Accordingly, one of the reasons for improvement of anti-rusting properties of a steel of the present invention on which an inorganic zinc coating film was provided is thought to be due to a synergistic effect between Cr contained in the steel material in a specific amount and the corrosion product.

[0142]

Table 5 shows results obtained when inorganic zinc coating films having various film thicknesses were provided on the surfaces of steels of the present invention and conventional steels, and the corrosion tests 1 and 3 were performed. According to Table 5, under conditions in which the film thickness was 8 μm , a result that anti-rusting properties were poor was obtained also in a steel of the present invention in a similar manner to

a conventional steel. On the other hand, under conditions in which the film thickness was 10 μm or larger, while a result that anti-rusting properties were still poor was obtained in a conventional steel, a result that anti-rusting properties were
5 excellent was obtained in a steel of the present invention.

[0143]

Table 6 shows results obtained when an alkali-silicate inorganic zinc coating film in the present invention or an inorganic zinc coating film to compare is provided on a steel of
10 the present invention or a conventional steel, and the corrosion tests 2 and 3 were performed. When a steel of the present invention was used, and the atomic molar ratio (Si/M) in the coating film was in a range of 2.0 to 125, a result that anti-rusting properties were excellent was obtained. On the other hand, in cases where
15 the molar ratio was outside the range, a result that anti-rusting properties were poor was obtained even when a steel of the present invention was used. Even in cases where the molar ratio was inside the range, a result that anti-rusting properties were poor was obtained when a conventional steel was used. Accordingly, it is
20 thought that excellent corrosion resistance over a long period of time was obtained due to a synergistic effect among a corrosion product, an alkaline component, and Cr.

[0144]

Table 7 shows results obtained when

an alkali-silicate inorganic zinc coating film of the present invention is provided on a steel of the present invention, and the corrosion tests 1 and 3 were performed. In Examples D1 to D9, since the atomic molar ratio (Si/M) in the coating film was
5 in a range of 2.0 to 125, a result that anti-rusting properties were excellent was obtained in the corrosion test 1 for 180 days. In Examples E1 to E9, a result of particularly excellent anti-rusting properties, in which an evaluation according to the rating-number method was B (more than 9.8-1 and up to 5-2), was
10 obtained even in the corrosion test 3 for 365 days.

[0145]

Regarding Examples D1 to D9 and Examples E1 to E9, Fig. 1 illustrates a graph obtained by plotting the Cr content in the steel material with respect to the atomic molar ratio (Si/M)
15 (logarithmic scale) in the coating film.

[0146]

From numerical analysis results for points in Fig. 1, a straight line: $\{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\}$ can be drawn which divides Examples D1 to D9 in which an evaluation according
20 to rating-number method was C in the corrosion test 3 and Examples E1 to E9 in which an evaluation according to rating-number method was B in the corrosion test 3. From this result, in Examples E1 to E9 satisfying an expression: $[\text{Cr}] \geq \{0.25 \times \ln(\text{molar ratio}$

(Si/M)) + 0.5}, it is found that a coating film having a film thickness of 20 μm had excellent anti-rusting properties even in the corrosion test 3 for a longer period of 365 days. In other words, in the case of a combination of a steel material and a coating film satisfying the above-described expression, it is found that an anti-corrosion coating film having excellent anti-rusting properties over a year in the corrosion test 3 was obtained.

[0147]

Table 8 shows results obtained when an alkali-silicate inorganic zinc coating film of the present invention was provided on a steel of the present invention, and the corrosion tests 1 and 3 were performed. Since, in Examples D10 to D16, the atomic molar ratio (Si/M) of the coating film is in a range of 2.0 to 125, a result that anti-rusting properties were excellent was obtained in the corrosion test 1 for 180 days. Further, in Examples E10 to E16 satisfying an expression: $[\text{Cr}] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\} \times 20 (\mu\text{m}) / (\text{the film thickness } (\mu\text{m}) \text{ of the coating film formed on the surface of the steel material})$, a result that anti-rusting properties were excellent was obtained even in the corrosion test 3 for a longer period of 365 days. The results are illustrated in Fig. 2 (in logarithm).

[0148]

From numerical analysis results for points in Fig. 2, it is found that the Cr content needed in a steel material is inversely proportional to the film thickness of the coating film. For this reason, it is found that the expression: $\{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\}$ obtained in Table 7 and Fig. 1 needs to be multiplied by $20 \text{ } (\mu\text{m}) / (\text{the film thickness } (\mu\text{m}) \text{ of the coating film})$.

[0149]

Consequently, when a coating film and a steel material satisfy the empirical expression (1): $[\text{Cr}] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\} \times 20 \text{ } (\mu\text{m}) / (\text{the thickness } (\mu\text{m}) \text{ of the coating film formed on the surface of the steel material})$, an anti-corrosion steel material having excellent anti-rusting properties can be obtained even in the corrosion test 3 for a longer period of 365 days.

[0150]

As described in Tables 3 to 6, even in cases where the empirical expression (1) is satisfied, when the thickness of the coating film is smaller than $10 \text{ } \mu\text{m}$, when the atomic molar ratio (Si/M) is outside the range of 2.0 to 125, or when the binder solid content / zinc particles (mass ratio) is outside the range of 0.01 to 0.35, an anti-corrosion steel material having excellent anti-rusting properties cannot be obtained in the corrosion tests 1 and 3. For this reason, when the thickness of the coating film, the atomic molar ratio (Si/M), and the binder solid content / zinc

particles (mass ratio) are in the above-described range, and satisfy the empirical expression (1), an anti-corrosion steel material having particularly excellent anti-rusting properties can be obtained in the corrosion test 3.

CLAIMS

1. An anti-corrosion steel material comprising:

a steel material, and

a coating film having a thickness of 10 μm or larger which

5 is formed on the surface of the steel material; wherein

the steel material contains, in terms of % by mass,

C: 0.001% to 0.20%,

Si: 0.01% to 3.0%,

Mn: 0.1% to 3.0%, and

10 Cr: 0.1% to 9.99%;

the coating film is formed by curing an alkali-silicate inorganic zinc coating composition, the coating film contains a silicon atom, and at least one atom selected from an alkali metal atom and a nitrogen atom, and the molar ratio represented by {the
15 number of moles of silicon atoms Si in the coating film}/{the total number of moles of alkali metal atoms and nitrogen atoms in the coating film} is 2.0 to 125; and

the inorganic zinc coating composition contains alkali silicate and zinc particles, and the mass ratio represented by
20 "the solid content mass of a binder component / the mass of zinc particles" is 0.01 to 0.35.

2. The anti-corrosion steel material according to claim 1, wherein the Cr content in the steel material and the molar ratio

in the coating film satisfy the following conditional expression
(1).

Conditional expression (1): $[Cr] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)} + 0.5) \times 20 (\mu\text{m}) / (\text{the film thickness } (\mu\text{m}) \text{ of the coating film which is formed on the surface of the steel material}) \times a/b$
5 [in the conditional expression (1), the [Cr] is the Cr content (% by mass) in the steel material; the molar ratio (Si/M) is represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms
10 and nitrogen atoms in the coating film}; a is 7, and b is 6.]

3. The anti-corrosion steel material according to claim 1, wherein the Cr content in the steel material and the molar ratio in the coating film satisfy the following conditional expression
15 (1).

Conditional expression (1): $[Cr] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)} + 0.5) \times 20 (\mu\text{m}) / (\text{the film thickness } (\mu\text{m}) \text{ of the coating film which is formed on the surface of the steel material}) \times a/b$
[in the conditional expression (1), the [Cr] is the Cr content
20 (% by mass) in the steel material; the molar ratio (Si/M) is represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms and nitrogen atoms in the coating film}; a is 17, b is 6.]

4. The anti-corrosion steel material according to any one of claims 1 to 3, wherein the coating film contains a silicon atom and an alkali metal atom.

5 5. The anti-corrosion steel material according to any one of claims 1 to 4, wherein the coating film contains a silicon atom and a nitrogen atom.

6. The anti-corrosion steel material according to any one
10 of claims 1 to 5, wherein the alkali silicate is a compound represented by $M1_2O \cdot nSiO_2$ [in the formula, M1 is an alkali metal, or an amine component or an ammonium component, and n is a positive number.]

15 7. The anti-corrosion steel material according to any one of claims 1 to 6, wherein the alkali silicate contains at least one selected from lithium silicate, sodium silicate, and potassium silicate.

20 8. The anti-corrosion steel material according to any one of claims 1 to 7, wherein the alkali silicate contains at least one selected from an ammonium silicate composed of a primary amine, a secondary amine, or a tertiary amine and a silicic acid, and a quaternary ammonium silicate composed of a quaternary ammonium

and a silicic acid.

9. The anti-corrosion steel material according to any one of claims 1 to 8, wherein the alkali silicate contains a quaternary ammonium
5 silicate composed of a quaternary ammonium and a silicic acid.

10. The anti-corrosion steel material according to any one of claims 1 to 9, wherein in the inorganic zinc coating composition, the content of an alkyl silicate binder is 1% by mass or smaller and the
10 content of an organic solvent is 0.5 % by mass or smaller based on the total amount of the composition.

11. The anti-corrosion steel material according to any one of claims 1 to 10, wherein the thickness of the coating film is 200 μm
15 or smaller.

12. The anti-corrosion steel material according to any one of claims 1 to 11, which is composed of the steel material and the coating film, which does not comprise a top coating film on the coating film,
20 and which is for a ballast tank.

13. The anti-corrosion steel material according to any one of claims 1 to 12, wherein

the steel material contains, in terms of % by mass,

Cr: 0.3% to 3.0%.

14. The anti-corrosion steel material according to any one of claims 1 to 13, wherein

5 in the steel material, the contents of elements other than C, Si, Mn and Cr, in terms of % by mass, are,

Al: 2.0% or smaller,

Cu: 1.0% or smaller,

Ni: 2.0% or smaller,

10 Mo: 0.5% or smaller,

W: 0.5% or smaller,

Sn: 0.5% or smaller,

Sb: 0.5% or smaller,

V: 0.2% or smaller,

15 Nb: 0.08% or smaller,

Ti: 0.1% or smaller,

Mg: 0.01% or smaller,

Zr: 0.05% or smaller,

B: 0.0050% or smaller,

20 Ca: 0.02% or smaller,

REM: 0.02% or smaller,

P: 0.03% or smaller,

S: 0.01% or smaller,

N: 0.02% or smaller, and

the balance: iron and inevitable impurities.

15. A ballast tank constituted by using the anti-corrosion steel material according to any one of claims 1 to 14.

5

16. A manufacturing method of an anti-corrosion steel material comprising

a step of forming a coating film containing a silicon atom, and at least one atom selected from an alkali metal atom and a nitrogen atom, and having a molar ratio represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms and nitrogen atoms in the coating film} of 2.0 to 125,

10

by applying an alkali-silicate inorganic zinc coating composition containing alkali silicate and zinc particles and having a mass ratio represented by "the solid content mass of a binder component / the mass of zinc particles" of 0.01 to 0.35 on the surface of a steel material containing,

15

in terms of % by mass,

20 C: 0.001% to 0.20%,
Si: 0.01% to 3.0%,
Mn: 0.1% to 3.0%, and
Cr: 0.1% to 9.99%

such that the thickness of the cured coating film is 10 μm or

larger.

17. The manufacturing method of an anti-corrosion steel material according to claim 16, wherein the Cr content in the steel material and the molar ratio in the coating film satisfy the following conditional expression (1).

Conditional expression (1): $[Cr] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\} \times 20 \text{ (}\mu\text{m)} / (\text{the film thickness (}\mu\text{m) of the coating film which is formed on the surface of the steel material}) \times a/b$
[in the conditional expression (1), the [Cr] is the Cr content (% by mass) in the steel material; the molar ratio (Si/M) is represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms and nitrogen atoms in the coating film}; a is 7, and b is 6.]

18. The manufacturing method of an anti-corrosion steel material according to claim 16 or 17, wherein a coating film is formed on the surface of the steel material by self-curing the inorganic zinc coating composition.

19. A method of preventing corrosion of a steel material comprising

a step of forming a coating film containing a silicon atom, and at least one atom selected from an alkali metal atom and a

nitrogen atom, and having a molar ratio represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms and nitrogen atoms in the coating film} of 2.0 to 125,

5 by applying an alkali-silicate inorganic zinc coating composition containing alkali silicate and zinc particles and having a mass ratio represented by "the solid content mass of a binder component / the mass of zinc particles" of 0.01 to 0.35 on the surface of a steel material containing,

10 in terms of % by mass,

C: 0.001% to 0.20%,

Si: 0.01% to 3.0%,

Mn: 0.1% to 3.0%, and

Cr: 0.1% to 9.99%

15 such that the thickness of the cured coating film is 10 μm or larger.

20. The method of preventing corrosion of a steel material according to claim 19, wherein the Cr content in the steel material and the molar ratio in the coating film satisfy the following conditional expression (1).

Conditional expression (1): $[\text{Cr}] \geq \{0.25 \times \ln(\text{molar ratio (Si/M)}) + 0.5\} \times 20 (\mu\text{m}) / (\text{the film thickness } (\mu\text{m}) \text{ of the coating film which is formed on the surface of the steel material}) \times a/b$

[in the conditional expression (1), the [Cr] is the Cr content (% by mass) in the steel material; the molar ratio (Si/M) is represented by {the number of moles of silicon atoms Si in the coating film} / {the total number of moles of alkali metal atoms and nitrogen atoms in the coating film}; a is 7, and b is 6.]

21. The method of preventing corrosion of steel material according to claim 19 or 20, wherein a coating film is formed on the surface of the steel material by self-curing the inorganic zinc coating composition.

ANTI-CORROSION STEEL MATERIAL, MANUFACTURING METHOD THEREOF,
METHOD OF PREVENTING CORROSION OF STEEL MATERIAL, AND BALLAST TANK

ABSTRACT

[Problem] To provide an anti-corrosion steel material in which excellent corrosion resistance can be maintained over a long period of time.

[Solution] An anti-corrosion steel material including a steel material, and a coating film having a thickness of 10 μm or larger which is formed on the surface of the steel material; characterized in that the steel material contains, in terms of % by mass, C: 0.001% to 0.20%, Si: 0.01% to 3.0%, Mn: 0.1% to 3.0%, and Cr: 0.1% to 9.99%; the coating film is formed by curing an alkali-silicate inorganic zinc coating composition, the coating film contains a silicon atom, and at least one atom selected from an alkali metal atom and a nitrogen atom, and the molar ratio represented by {the number of moles of silicon atoms Si in the coating film}/{the total number of moles of alkali metal atoms and nitrogen atoms in the coating film} is 2.0 to 125; and the inorganic zinc coating composition contains alkali silicate and zinc particles, and the mass ratio represented by "the solid content mass of a binder component / the mass of zinc particles" is 0.01 to 0.35.

[Fig. 1]