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(54) **CORROSION-RESISTANT STEEL MATERIAL FOR SHIP AND VESSEL**

(57) Anti-corrosion steel for ship is provided at low cost, which exhibits excellent corrosion resistance without depending on a surface condition of steel even under severe corrosion environment such as a ballast tank of a ship. Anti-corrosion steel for ship contains, in mass percent, C of 0.03 to 0.25%, Si of 0.05 to 0.50%, Mn of 0.1 to 2.0%, P of 0.025% or less, S of 0.01% or less, Al of 0.005 to 0.10%, W of 0.01 to 1.0%, Cr of 0.01% or

more and less than 0.20%, and furthermore contains as needed one or two selected from Sb of 0.001 to 0.3% and Sn of 0.001 to 0.3% and/or one or at least two selected from Ni of 0.005 to 0.25%, Mo of 0.01 to 0.5%, and Co of 0.01 to 1.0%, and contains the remainder including Fe and inevitable impurities.

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Description

Technical Field

5 **[0001]** The present invention relates to anti-corrosion steel used for ships such as a coal ship, an ore carrier, an ore coal carrier, a crude oil tanker, an LPG carrier, an LNG carrier, a chemical tanker, a container ship, a bulk carrier, a log carrier, a chip carrier, a refrigerated cargo ship, a pure car carrier, a heavy load carrier, a roll-on/roll-off ship, a limestone carrier, and a cement carrier, and particularly relates to anti-corrosion steel for ship used for a ballast tank and the like under a severe corrosion environment with seawater. The anti-corrosion steel for ship described in the invention includes
10 a thick steel plate, sheet steel, shape sheet, and bar steel.

Background Art

15 **[0002]** Since a ballast tank of a ship serves to enable stable navigation of a ship by being poured with seawater while no cargo is loaded, the tank is placed in an extremely severe corrosion environment. Therefore, an anti-corrosion paint film using epoxy paint is formed, in addition, cathodic protection is applied for preventing corrosion of steel used for the ballast tank.

20 **[0003]** However, even if such anti-corrosion measures are taken, corrosion environment of the ballast tank is still in a severe condition. That is, when the ballast tank is poured with seawater, in the case that cathodic protection works, corrosion can be inhibited from being developed in a region that is perfectly dipped in the seawater. However, a region near a top of the ballast tank, a back of an upper deck is particularly not dipped in seawater, and situated while being sprayed with seawater. Therefore, cathodic protection does not work in such a region. Furthermore, since the region is increased in temperature of a steel plate by sunlight, the region is in a more severe corrosion environment, and consequently drastically corroded. Moreover, when the ballast tank is not poured with seawater, cathodic protection does not
25 work at all, and consequently the tank is drastically corroded due to an effect of remaining adhesion salinity.

30 **[0004]** Life of an anti-corrosion paint film of a ballast tank is said to be typically about 10 years under such a drastic corrosion resistance, that is, half the life (20 years) of a ship. It is actual situation that corrosion resistance is kept by performing repair painting in the remaining ten years. However, since the ballast tank is in the severe corrosion environment as above, even if the repair painting is carried out, an effect of the painting is hard to be kept for a long time. Moreover, since the repair painting is performed as operation in a narrow space, operation environment is not preferable.. Thus, it is desirable to develop a steel material having an excellent corrosion resistance, which can lengthen a period before the repair painting to the utmost, and can reduce an operation load of the repair painting to the utmost.

35 **[0005]** Thus, several technologies have been proposed to improve corrosion resistance of steel itself used for a region placed in a severe corrosion environment such as the ballast tank. For example, patent document 1 discloses anti-corrosion low alloy steel including steel containing C of 0.20 mass% or less, the steel being added with Cu of 0.05 to 0.50 mass% and W of 0.01 to less than 0.05 mass% as elements that improves corrosion resistance, and furthermore added with one or at least two of Ge, Sn, Pb, As, Sb, Bi, Te and Be in a range of 0.01 to 0.2 mass% as the elements. Patent document 2 discloses anti-corrosion low alloy steel including steel containing C of 0.20 mass% or less, the steel being added with Cu of 0.05 to 0.50 mass% and W of 0.05 to 0.5 mass% as elements that improves corrosion resistance,
40 and furthermore added with one or at least two of Ge, Sn, Pb, As, Sb, Bi, Te and Be in a range of 0.01 to 0.2 mass% as the elements. Patent document 3 discloses anti-corrosion low alloy steel including steel containing C of 0.15 mass% or less, which is added with Cu of 0.05 to less than 0.15 mass% and W of 0.05 to 0.5 mass%.

45 **[0006]** Patent document 4 discloses a ballast tank in which anti-corrosion low alloy steel, which includes steel containing C of 0.15 mass% or less, the steel being added with P of 0.03 to 0.10 mass%, Cu of 0.1 to 1.0 mass%, and Ni of 0.1 to 1.0 mass% as elements that improve corrosion resistance, is coated with anti-corrosion paint such as tar epoxy paint, pure epoxy paint, epoxy paint without solvent, and urethane paint, and then covered with resin. This technology is intended to lengthen the life of anti-corrosion painting by improving corrosion resistance of steel itself, and thereby achieve a ship being free from maintenance over 20 to 30 years corresponding to the useful life of a ship.

50 **[0007]** Patent document 5 makes a proposal that steel containing C of 0.15 mass% or less is added with Cr of 0.2 to 5 mass% as an element that improves corrosion resistance in order to achieve a ship being free from maintenance. Furthermore, patent document 6 proposes an anti-corrosion method of a ballast tank characterized in that steel containing C of 0.15 mass% or less, which is added with Cr of 0.2 to 5 mass% as an element that improves corrosion resistance, is used as a component material, and oxygen gas concentration within a ballast tank has a value in a ratio of 0.5 or less with respect to a value of oxygen gas concentration in air.

55 **[0008]** Patent document 7 makes a proposal that steel containing C of 0.1 mass% or less is added with Cr of 0.5 to 3.5 mass% to improve corrosion resistance, so that a ship being free from maintenance is achieved. Furthermore, patent document 8 discloses steel for ship in which steel containing C of 0.001 to 0.025 mass% is added with Ni of 0.1 to 4.0 mass% to improve paint-film damage resistance, so that maintenance cost for repair painting and the like is reduced.

[0009] Patent document 9 discloses steel for ship in which steel containing C of 0.01 to 0.25 mass% is added with Cu of 0.01 to 2.00 mass% and Mg of 0.0002 to 0.0150 mass% so as to have corrosion resistance in use environment such as a shell of a ship, a ballast tank, a cargo oil tank, and an iron-ore cargo hold. Furthermore, patent document 10 discloses steel in which steel containing C of 0.001 to 0.2 mass% is compositely added with Mo, W and Cu, and limited in the added amount of P and S as impurities, thereby general corrosion or local corrosion that may occur in a crude oil tank is inhibited.

[0010] However, each of the patent documents 1 to 3 does not make adequate investigation on corrosion resistance under presence of a paint film of Zinc-primer or epoxy paint being typically coated on steel configuring a ballast tank or the like. Therefore, further investigation is necessary for improving corrosion resistance under presence of the paint film.

[0011] The steel described in the patent document 4 is added with a comparatively large amount of P, 0.03 to 0.10 mass%, to improve corrosion resistance of base metal, which is problematic in a point of weldability and toughness of a weld. The steel described in each of the patent documents 5 and 6 is added with a comparatively large amount of Cr, 0.2 to 5 mass%. The steel described in the patent document 7 is added with a comparatively large amount of Cr, 0.5 to 3.5 mass%. Either of them is problematic in the point of weldability and toughness of a weld, in addition, problematic in that manufacturing cost is increased. The steel described in the patent document 8 is comparatively low in C content, and comparatively high in Ni content, which is problematic in that manufacturing cost is increased.

[0012] The steel described in the patent document 9 is problematic in that Mg is essentially added, which causes unstableness in yield of steel manufacture, leading to unstableness in mechanical properties of the steel. Furthermore, the steel described in the patent document 10 is anti-corrosion steel used in the crude oil tank, namely, used under an environment having H₂S, and therefore the steel is unclear in corrosion resistance in the ballast tank having no H₂S. Furthermore, since corrosion resistance has not been investigated in a condition that zinc-primer being typically used for steel for a ballast tank is coated, further investigation on corrosion resistance is necessary to be used for a ballast tank.

Patent document 1: JP-A-48-050921

Patent document 2: JP-A-48-050922

Patent document 3: JP-A-48-050924

Patent document 4: JP-A-07-034197

Patent document 5: JP-A-07-034196

Patent document 6: JP-A-07-034270

Patent document 7: JP-A-07-310141

Patent document 8: JP-A-2002-266052

Patent document 9: JP-A-2000-017381

Patent document 10: JP-A-2004-204344

Disclosure of the Invention

[0013] Generally, a ship is built by welding steel materials such as a thick steel plate, sheet steel, shape steel, and bar steel, and surfaces of the steel materials are applied with anti-corrosion painting before use. The anti-corrosion painting is typically applied in a manner that zinc-primer is coated for primary rust prevention, and epoxy paint is coated as secondary painting (main painting) after subassembly or main assembly is performed. Therefore, the major part of steel surface of a ship has a double-layer structure thereon, which includes a zinc primer paint film and an epoxy paint film. However, since the zinc-primer is burned out by welding heat on a weld, zinc primer is repainted on the weld as touch up paint for rust prevention in a period after welding and before main painting. However, when the period before the main painting is short, repainting of zinc primer is not performed in some case. After a ship is built, the ship enters service, and in a ship that has been used for many years, there is a portion where the paint film is degraded and thus does not adequately act as a paint film, or there is a portion where the paint film is separated, so that a steel plate is bared.

[0014] As a result, three conditions exist on a surface of steel of a ship in service, including a portion of the double-layer structure in which a zinc primer paint film and an epoxy paint film are formed, a portion where only an epoxy paint film is formed, and a portion where the steel is bared. In any condition, steel having excellent corrosion resistance is required to improve corrosion resistance of the ship.

[0015] Thus, an object of the invention is to provide anti-corrosion steel for ship at low cost, which exhibits excellent corrosion resistance without depending on a surface condition of steel even under a severe corrosion environment such as a ballast tank of a ship, whereby a period before repair painting can be lengthened, consequently operation load of the repair painting can be reduced.

[0016] The inventors made earnest study for developing the steel that exhibits excellent corrosion resistance without depending on the surface condition of the steel even under the severe corrosion environment caused by seawater. As a result, the inventors found that W and Cr are contained as essential elements, in addition, elements that improve corrosion resistance such as Sb and Sn are contained in an appropriate range, thereby the steel that exhibits excellent

corrosion resistance can be obtained in any of the conditions of the double-layer structure of a zinc primer paint film and an epoxy paint film, only an epoxy paint film, and bare steel, and consequently they completed the invention.

[0017] That is, the invention includes anti-corrosion steel for ship containing C of 0.03 to 0.25 mass%, Si of 0.05 to 0.50 mass%, Mn of 0.1 to 2.0 mass%, P of 0.025 mass% or less, S of 0.01 mass% or less, Al of 0.005 to 0.10 mass%, W of 0.01 to 1.0 mass%, Cr of 0.01 mass% or more and less than 0.20 mass%, N of 0.001 to 0.008 mass%, and the remainder including Fe and inevitable impurities.

[0018] The steel of the invention is characterized by containing a component in at least one group between the following groups A and B, in addition to the above composition.

[0019] Group A; one or two selected from Sb of 0.001 to 0.3 mass% and Sn of 0.001 to 0.3 mass%.

[0020] Group B; one or at least two selected from Ni of 0.005 to 0.25 mass%, Mo of 0.01 to 0.5 mass%, and Co of 0.01 to 1.0 mass%.

[0021] Moreover, the steel of the invention is characterized by containing a component in at least one group among the following groups C to E, in addition to the above composition.

[0022] Group C; one or at least two selected from Nb of 0.001 to 0.1 mass%, Ti of 0.001 to 0.1 mass%, Zr of 0.001 to 0.1 mass%, and V of 0.002 to 0.2 mass%.

[0023] Group D; B of 0.0002 to 0.003 mass%.

[0024] Group E; one or at least two selected from Ca of 0.0002 to 0.01 mass%, REM of 0.0002 to 0.015 mass%, and Y of 0.0001 to 0.1 mass%.

[0025] Moreover, steel of the invention is characterized in that an epoxy paint film or a zinc primer paint film is formed on a surface of the steel, or both the zinc primer paint film and the epoxy paint film are formed thereon.

[0026] According to the invention, steel can be provided, the steel having excellent corrosion resistance even under a severe corrosion environment caused by seawater, which significantly contributes to lengthening of a period before repair painting, and reduction in operation load of repair painting.

Best Mode for Carrying Out the Invention

[0027] The inventors conducted the following experiment to develop steel having excellent corrosion resistance in any of the three portions that may exist on a surface of steel of a ship in service, that is, a portion of the double-layer structure of a zinc primer paint film and an epoxy paint film, a portion of only an epoxy paint film, and a bare steel portion.

[0028] Steel being added with various alloy elements were ingoted, then the ingots were hot-rolled into hot-rolled plates 5 mm in thickness, and then test pieces 5 mm thick, 100 mm wide, and 200 mm long, and test pieces 5 mm thick, 50 mm wide, and 150 mm long were taken from the hot-rolled plates. Then, a surface of each of the test pieces was subjected to shot blasting to remove scales or oil from the surface, and then the test pieces were subjected to the following three types of surface treatment, so that exposure test pieces were prepared.

[0029] Condition A: A double-layer film of a zinc primer film (about 15 μm) and a tar epoxy resin paint film (about 100 μm) is formed on a surface of a test piece.

[0030] Condition B: A single-layer film of a tar epoxy resin paint film (about 100 μm) is formed on a surface of a test piece.

[0031] Condition C: A surface of a test piece is subjected to shot blasting and remains bare (with no anti-corrosion film).

[0032] Then, the test pieces were subjected to a salt-spray alternate-drying-and-wetting corrosion test, which simulates a corrosion environment corresponding to a back of an upper deck of a ballast tank of an actual ship, based on a condition that an exposure test was performed by 132 cycles, each cycle including spraying of 5% NaCl solution at 35°C for 2 hr, leaving to stand at 60°C and RH25% for 4 hr, and leaving to stand at 50°C and RH95% for 2 hr, thereby the test pieces were evaluated in corrosion resistance. For the test pieces of the conditions A and B, each test piece having a paint film, corrosion resistance was evaluated in a way that a scratch in 80 mm in length, which reached a surface of base steel, was formed in a straight line by a box cutter through the paint film before the test, and area of a swollen paint film generated around the scratch was measured for evaluation after the test. For the test pieces having no paint film of the condition C, corrosion resistance was evaluated in a way that the test pieces were derusted after the test, and the average amount of decrease in thickness was calculated for evaluation from the amount of change in weight (amount of decrease) between the derusted test piece and a test piece before the test.

[0033] By summarizing results of the corrosion test, effects of respective alloy elements on corrosion resistance are collected in Table 1.

Table 1

Alloy element	Condition of test piece used in corrosion resistance test		
	Condition A (zinc primer paint film and tar epoxy resin paint film)	Condition B (tar epoxy resin paint film)	Condition C (bare steel)
W	2	4	4
Cr	5	0	0
Sb	1	1	1
Sn	0	1	1
Ni, Mo, Co	0 to 1	0 (Ni, Co), 0 to 1 (Mo)	0 to 1
W+Cr	6	4	4
W+Cr+Sb+Sn	6	6	6

(Effect on corrosion resistance)

[0034]

- 0; no effect
- 1 to 2; some effect
- 4; large effect
- 5 to 6; significantly large effect

To briefly describe the results,

[0035]

- 1) In the case of the condition A (double-layer paint film of the zinc primer paint film and the tar epoxy resin paint film), the most effective element for improving corrosion resistance is Cr, followed by W, and followed by Sb.
- 2) In the case of the condition B (only the tar epoxy resin paint film), the most effective element for improving corrosion resistance is W, followed by Sb, and followed by Sn.
- 3) In the case of the condition C (bare steel), the most effective element for improving corrosion resistance is W, followed by Sb, and followed by Sn.
- 4) When W and Cr are compositely contained, corrosion resistance at the condition A is improved compared with a case that each is singly contained, and furthermore, when Sb and Sn are contained in addition to them, a significant effect is exhibited in any of the conditions A, B and C.
- 5) Mo slightly improves corrosion resistance in any of the conditions A, B and C, and Ni and Co slightly improve corrosion resistance in the conditions A and C.

[0036] Based on the test results, the invention was designed to use a componential system in which W and Cr were compositely contained as essential elements for improving corrosion resistance. Furthermore, the invention was designed in a way that when more excellent corrosion resistance was required, a component design was used, in which one or two selected from Sb and Sn were contained in addition to W and Cr. Moreover, the invention was designed in a way that when further more excellent corrosion resistance was required, one or two or more selected from Ni, Mo and Co were additionally contained.

[0037] Next, a composition that the anti-corrosion steel for ship of the invention must have is specifically described.
C: 0.03 to 0.25 mass%

[0038] C is an effective element for increasing strength of steel, and needs to be contained by 0.03 mass% or more to obtain a desired strength in the invention. On the other hand, when C is contained by more than 0.25 mass%, toughness of HAZ (weld heat-affected zone) is reduced. Accordingly, C is contained in a range of 0.03 to 0.25 mass%. From a viewpoint of naturally obtaining certain strength together with certain toughness by rolling, C is preferably contained in a range of 0.05 to 0.20 mass%.

Si: 0.05 to 0.50 mass%

[0039] Si is an element to be added as a deoxidizer, or added for increasing strength of steel, and contained by 0.05 mass% or more in the invention. However, when Si is added by more than 0.50 mass%, toughness of steel is degraded,

therefore an upper limit of Si is specified to be 0.50 mass%.

Mn: 0.1 to 2.0 mass%

[0040] Mn is an element having an effect of preventing hot shortness, and increasing strength of steel, and added by 0.1 mass% or more. However, when Mn is added by more than 2.0 mass%, toughness of steel and weldability are reduced, therefore Mn is contained to be 2.0 mass% or less. Preferably, Mn is contained in a range of 0.5 to 1.6 mass%.
P: 0.025 mass% or less

[0041] P is a harmful element that may degrade toughness of steel as mother material, and furthermore degrade weldability and toughness of a weld, and therefore P is preferably reduced to the utmost. In particular, when the content of P exceeds 0.025 mass%, toughness of mother material and toughness of a weld are more significantly reduced. Accordingly, P is contained to be 0.025 mass% or less. Preferably, P is contained to be 0.014 mass% or less.

S: 0.01 mass% or less

[0042] Since S is a harmful element that may degrade toughness of steel and weldability, S is preferably reduced to the utmost, and contained to be 0.01 mass% or less in the invention.

Al: 0.005 to 0.10 mass%

[0043] Al is an element to be added as a deoxidizer, and added by 0.005 mass% or more. However, when Al is contained by more than 0.10 mass%, Al^{3+} eluted due to corrosion of base steel reduces pH of a surface of the base steel, leading to degradation in corrosion resistance, therefore an upper limit of Al is specified to be 0.10 mass%.

W: 0.01 to 1.0 mass%

[0044] W improves corrosion resistance under presence of both the zinc primer paint film and the epoxy paint film, and significantly improves corrosion resistance under presence of only the epoxy paint film. Moreover, W significantly improves corrosion resistance of steel even if the steel is bare. Therefore, W is one of the most important elements for improving corrosion resistance in the steel of the invention. The effect is exhibited in W content of 0.01 mass% or more. However, when W content is more than 1.0 mass%, the effect is saturated. Accordingly, the content of W is in a range of 0.01 to 1.0 mass%.

[0045] The reason why W has the effect of improving corrosion resistance is because as a steel plate is corroded, WO_4^{2-} is produced in produced rust, and presence of the WO_4^{2-} prevents chloride ions from entering a steel plate surface, and furthermore sparingly-soluble $FeWO_4$ is produced in a region having decreased pH such as an anode area of the steel plate surface, and presence of the $FeWO_4$ also prevents chloride ions from entering the steel plate surface. The chloride ions are thus prevented from entering the steel plate surface, thereby corrosion of the steel plate is effectively inhibited. Moreover, inhibitor operation of WO_4^{2-} also inhibits corrosion of steel.

Cr: 0.01 mass% or more and less than 0.20 mass%

[0046] Since Cr exhibits excellent corrosion resistance under presence of both the zinc primer paint film and the epoxy paint film, Cr is one of the important elements in the steel of the invention. It is presumed that under presence of zinc primer, Zn in the zinc primer is eluted, so that Zn-based corrosion products such as ZnO and $ZnCl_2 \cdot 4Zn(OH)_2$ are produced, and Cr acts on the Zn-based corrosion products so as to further improve corrosion prevention of base steel given by the Zn-based corrosion products. Such a corrosion resistance improvement effect of Cr under presence of the zinc primer is exhibited at the content of Cr of 0.01 mass% or more. However, when Cr is contained by 0.20 mass% or more, toughness of a weld is degraded. Accordingly, the content of Cr is in a range of 0.01 mass% or more and less than 0.20 mass%.

N: 0.001 to 0.008 mass%

[0047] N is a harmful component for toughness, and desirably reduced to the utmost in order to achieve improvement in toughness. However, N is industrially hard to be decreased to less than 0.001 mass%. Conversely, when N is contained by 0.008 mass% or more, toughness is significantly degraded. Accordingly, the content of N is in a range of 0.001 to 0.008 mass% in the invention.

[0048] The steel of the invention may contain the following components in addition to the above components for the purpose of further improving corrosion resistance.

One or two of 0.001 to 0.3 mass% Sb and 0.001 to 0.3 mass% Sn

[0049] Sb has an effect of improving corrosion resistance under presence of both the zinc primer paint film and the epoxy paint film, under presence of only the epoxy paint film, and in a condition of bare steel. Sn has an effect of improving corrosion resistance under presence of only the epoxy paint film, and in the condition of bare steel. The reason for the effects of Sb and Sn is considered to be that corrosion is inhibited in a region having decreased pH such as an anode area of the steel plate surface. While the effects are exhibited when either of Sn and Sb is contained by 0.001 mass% or more, in the case that the content is more than 0.3 mass%, toughness of each of mother material and HAZ is degraded, therefore each of Sn and Sb is preferably contained in a range of 0.001 to 0.3 mass%.

One or at least two of 0.005 to 0.25 mass% Ni, 0.01 to 0.5 mass% Mo, and 0.01 to 1.0 mass% Co

[0050] Ni, Mo and Co slightly improve corrosion resistance under presence of both the zinc primer paint film and the epoxy paint film, and in the condition of bare steel. Furthermore, Mo slightly improves corrosion resistance even under presence of only the epoxy paint film. Therefore, when corrosion resistance is desired to be further improved, the elements

may be supplementarily contained. The reason for the effects of Ni, Mo and Co is considered to be that they act to refine rust particles, in addition, Mo produces MoO_4^{2-} in rust and thus prevents chloride ions from entering a steel plate surface. The effects are exhibited in the Ni content of 0.005 mass% or more, Mo content of 0.01 mass% or more, and Co content of 0.01 mass% or more respectively.

[0051] However, even if Ni of more than 0.25 mass%, Mo of more than 0.5 mass%, and Co of more than 1.0 mass% are added respectively, the respective effects are saturated, which is economically disadvantageous. Accordingly, Ni, Mo and Co are preferably contained in the above range respectively.

[0052] Furthermore, the steel of the invention may contain the following components in addition to the above components for increasing strength of steel and/or improving toughness.

One or at least two of 0.001 to 0.1 mass% Nb, 0.001 to 0.1 mass% Ti, 0.001 to 0.1 mass% Zr, and 0.002 to 0.2 mass% V

[0053] Any of Nb, Ti, Zr and V is an element that improves strength of steel, and can be selectively contained depending on required strength. To obtain such an effect, preferably, each of Nb, Ti and Zr is contained by 0.001 mass% or more, and V is contained by 0.002 mass% or more. However, when Nb, Ti or Zr is added by more than 0.1 mass%, and when V is added by more than 0.2 mass%, toughness is reduced, therefore each of Nb, Ti, Zr and V is preferably added with each of the above values being specified as an upper limit value.

B: 0.0002 to 0.003 mass%

[0054] B is an element that improves strength of steel, and can be contained as needed. To obtain the effect, B is preferably contained by 0.0002 mass% or more. However, when B is added by more than 0.003 mass%, toughness is degraded. Accordingly, B is preferably contained in a range of 0.0002 to 0.003 mass%.

One or at least two of 0.0002 to 0.01 mass% Ca, 0.0002 to 0.015 mass% REM, and 0.0001 to 0.1 mass% Y

[0055] Any of Ca, REM and Y is an element having an effect of improving toughness of a weld heat-affected zone, and can be selectively contained as needed. While such an effect is obtained in the content of Ca of 0.0002 mass% or more, REM of 0.0002 mass% or more, and Y of 0.0001 mass% or more respectively, when Ca of more than 0.01 mass%, REM of more than 0.015 mass%, and Y of more than 0.1 mass% are added respectively, toughness is rather reduced, therefore Ca, REM and Y are preferably contained with the above values being specified as upper limit values respectively.

[0056] The steel of the invention preferably contains Fe and inevitable impurities as components other than the above. However, it will be appreciated that the invention is not intended to reject to contain a component other than the above if an effect of the component is within a level at which it does not kill the effect of the invention.

[0057] Next, a preferable method of manufacturing the anti-corrosion steel according to the invention is described.

[0058] Preferably, molten steel having the composition is produced by a typically known method such as a converter or an electric furnace, then formed into a steel material such as a slab or billet by a typically known method such as a continuous casting method or an ingot making method. It is appreciated that the molten steel may be additionally subjected to treatment such as ladle metallurgy or vacuum degassing.

[0059] Next, the steel material is preferably heated to a temperature of 1050 to 1250°C, then hot-rolled into desired size and shape. Alternatively, when temperature of the steel material is high in a level at which the steel material can be hot-rolled, the steel material is preferably directly hot-rolled into steel having the desired size and shape without being heated, or with being merely soaked.

[0060] In hot rolling, to secure strength, hot-finish-rolling finishing temperature and a cooling rate after hot finish rolling are preferably appropriately adjusted, wherein the hot-finish-rolling finishing temperature is preferably 700°C or more, and cooling after hot finish rolling is finished is preferably performed by air cooling or accelerated cooling at a cooling rate of 100 °C/s or less. Reheating may be performed after cooling.

Example

[0061] Steel having a composition shown in Table 2 was produced by a vacuum melting furnace or a converter, then slabs were loaded into a heating furnace and heated to 1150°C, and then hot-rolled into thick steel plates 25 mm in thickness, and then the steel plates obtained in such a way were examined in tensile and impact properties of mother material. Moreover, a heat cycle corresponding to submerge welding with input heat quantity of 150 kJ/cm was applied to the steel plates to simulate HAZ portions, and the simulated HAZ portions were provided for evaluation of an impact property (simulated-HAZ impact property).

[0062] Next, test pieces 5 mm thick, 100 mm wide, and 200 mm long, and test pieces 5 mm thick, 50 mm wide, and 150 mm long were taken from the respective thick steel plates, then a surface of each of the test pieces was subjected to shot blasting, and then the test pieces were subjected to surface treatment at the following conditions A to C, so that exposure test pieces were prepared.

[0063] Condition A: A double-layer film of a zinc primer film (about 15 μm) and a tar epoxy resin paint film (about 200 μm) was formed on a surface of a test piece. Condition B: A single-layer film of a tar epoxy resin paint film (about 200 μm) was formed on a surface of a test piece. Condition C: A surface of a test piece was subjected to shot blasting and

remained bare (with no anti-corrosion film).

[0064] The test pieces of the conditions A and B, each test piece having a paint film, were provided with a scratch in 80 mm in length in a straight line, which reached a surface of base steel, by a box cutter through the paint film.

[0065] Then, the test pieces were attached to a back of an upper deck of a ballast tank of an actual ship so as to be provided for an exposure test. A period of the exposure test was three years, and corrosion environment of the ballast tank was set as follows: about 20 days as a period in which seawater was filled in the ballast tank, and about 20 days as a period in which seawater was not filled therein were combined as one cycle, and the cycle was repeated. For the test pieces of the conditions A and B, each test piece having the paint film, corrosion resistance in the exposure test was evaluated in a way that area of a swollen paint film generated around the scratch was measured for evaluation. For the test pieces of the condition C having no paint film, corrosion resistance was evaluated in a way that the test pieces were derusted after the test, and the average amount of decrease in thickness was calculated from the amount of change in weight (amount of decrease) between the derusted test piece and a test piece before the test, and then assuming that No. 21 steel without containing any particular element that improves corrosion resistance was base steel (100), a ratio of a value of each test piece to a value of the base steel was calculated for evaluation.

[0066] Table 3 shows results of tensile and impact tests, and Table 4 shows results of exposure for two years and exposure for three years. From the result of the exposure for three years in Table 4, it is known that steel of each of Nos. 1 to 20 as inventive examples, which satisfy the composition of the invention, is 50% or less in swollen-paint-film area and thickness-decrease-amount with respect to the base steel (No. 21) in any of the test pieces at the conditions A to C, and therefore has excellent corrosion resistance. In the steel of No. 20, while the ratio to the base steel is 73% at the condition of both the zinc primer paint film and the tar epoxy paint film in a result of the exposure for two years, the ratio is 42% in a result of the exposure for three years, showing the anti-corrosion effect of W and Cr being exhibited.

[0067] On the contrary, in steel of each of Nos. 22 to 24 that do not satisfy the composition of the invention, even if corrosion resistance is improved compared with the base steel (No. 21), the ratio to the base steel is more than 50% in some condition. In No. 26, since Al content exceeds the upper limit value, corrosion resistance is degraded in all the conditions. In steel of each of Nos. 25 and 27, while a ratio of corrosion resistance to the base steel is 50% or less, an impact property of a weld is significantly degraded.

Industrial Applicability

[0068] The anti-corrosion steel for ship of the invention has excellent corrosion resistance under corrosion environment due to seawater, therefore the steel can be used for a ballast tank of a ship, in addition, can be applied to other uses where the steel is used in similar corrosion environment.

Table 2

Steel No.	Component (mass%)														
	C	Si	Mn	P	S	Al	W	Cr	N	Sb, Sn	Ni, Mo, Co	Nb, Ti, Zr, V	B	Ca, REM, Y	Remarks
1	0.15	0.32	0.95	0.009	0.002	0.030	0.05	0.01	0.0030	-	-	-	-	-	Inventive example
2	0.13	0.32	1.32	0.013	0.003	0.029	0.20	0.15	0.0028	-	-	-	-	-	Inventive example
3	0.14	0.31	1.41	0.011	0.002	0.029	0.36	0.08	0.0027	-	-	-	-	-	Inventive example
4	0.12	0.32	1.35	0.012	0.003	0.030	0.06	0.07	0.0028	Sb:0.11	-	-	-	-	Inventive example
5	0.08	0.31	1.45	0.010	0.002	0.025	0.07	0.10	0.0025	Sb:0.09 Sn:0.04	-	-	-	-	Inventive example
6	0.10	0.28	1.33	0.009	0.002	0.035	0.04	0.02	0.0030	Sb:0.11 Sn:0.03	-	Ti:0.011	-	-	Inventive example
7	0.05	0.35	1.57	0.007	0.002	0.033	0.01	0.03	0.0015	Sn:0.23	-	-	-	-	Inventive example
8	0.05	0.32	1.51	0.006	0.001	0.032	0.05	0.03	0.0041	Sb:0.01 Sn:0.15	-	Ti:0.015	-	-	Inventive example
9	0.03	0.15	1.58	0.006	0.002	0.028	0.10	0.06	0.0016	Sb:0.24	-	-	0.0007	-	Inventive example
10	0.05	0.28	1.57	0.012	0.002	0.025	0.05	0.02	0.0038	Sb:0.10 Sn:0.01	-	-	-	-	Inventive example
11	0.10	0.30	1.35	0.011	0.002	0.028	0.15	0.16	0.0035	-	Ni:0.21	-	-	-	Inventive example
12	0.12	0.25	1.05	0.011	0.003	0.031	0.04	0.07	0.0029	-	Ni:0.01 Mo:0.38 Co:0.15	-	-	-	Inventive example
13	0.08	0.29	1.15	0.008	0.003	0.029	0.45	0.18	0.0045	Sn:0.10	-	Ti:0.012	-	-	Inventive example

(continued)

Steel No.	Component (mass%)														
	C	Si	Mn	P	S	Al	W	Cr	N	Sb, Sn	Ni, Mo, Co	Nb, Ti, Zr, V	B	Ca, REM, Y	Remarks
14	0.07	0.35	0.95	0.009	0.002	0.031	0.07	0.07	0.0035	-	Mo:0.15	Nb:0.012 Zr:0.007 V: 0.04	-	-	Inventive example
15	0.11	0.32	1.35	0.011	0.003	0.028	0.06	0.02	0.0028	Sb:0.09 Sn:0.04	Ni:0.01	-	0.0007	-	Inventive example
16	0.14	0.35	1.25	0.008	0.003	0.025	0.81	0.06	0.0015	Sb:0.15	Co:0.02	Ti:0.003	0.0005	-	Inventive example
17	0.09	0.15	1.47	0.009	0.002	0.035	0.02	0.19	0.0031	-	Ni:0.04 Co:0.05	-	-	Ca:0.0018	Inventive example
18	0.08	0.25	1.45	0.011	0.003	0.025	0.15	0.10	0.0038	Sb:0.05	Mo:0.05	Ti:0.018	-	REM: 0.0030	Inventive example
19	0.11	0.29	1.42	0.009	0.003	0.029	0.05	0.07	0.0021	-	-	Zr:0.005	-	REM: 0.0010 Y: 0.01	Inventive example
20	0.12	0.32	1.38	0.013	0.002	0.031	0.12	0.03	0.0030	Sb:0.10	-	-	-	-	Inventive example
21	0.14	0.31	1.45	0.011	0.004	0.029	-	-	0.0035	-	-	-	-	-	Comparative example
22	0.13	0.30	1.43	0.012	0.004	0.031	0.08	-	0.0030	-	-	-	-	-	Comparative example
23	0.11	0.32	1.36	0.013	0.003	0.028	-	0.07	0.0031	-	-	-	-	-	Comparative example
24	0.10	0.33	1.29	0.011	0.002	0.029	0.03	-	0.0031	Sb:0.08 Sn:0.05	-	-	-	-	Comparative example
25	0.13	0.31	1.36	0.012	0.003	0.031	0.12	0.75	0.0031	-	-	-	-	-	Comparative example
26	0.12	0.32	1.25	0.012	0.003	0.383	0.21	-	0.0035	-	-	-	-	-	Comparative example

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(continued)

Steel No.	Component (mass%)														
	C	Si	Mn	P	S	Al	W	Cr	N	Sb, Sn	Ni, Mo, Co	Nb, Ti, Zr, V	B	Ca, REM, Y	Remarks
27	0.13	0.30	1.24	0.041	0.003	0.028	0.15	0.18	0.0026	-	-	-	-	-	Comparative example

Table 3

Steel No.	Mechanical properties of mother material			Impact property of weld vE (0°C) (J)	Remarks	
	Tensile properties		Impact property vE(- 20°C)(J)			
	YS(MPa)	TS(MPa)				El(%)
1	387	512	30	228	132	Inventive example
2	395	538	32	235	152	Inventive example
3	402	556	36	245	151	Inventive example
4	396	556	36	223	135	Inventive example
5	385	541	35	217	142	Inventive example
6	376	518	32	269	145	Inventive example
7	391	511	31	285	136	Inventive example
8	378	519	32	298	133	Inventive example
9	359	514	30	289	151	Inventive example
10	361	551	34	272	147	Inventive example
11	400	536	37	207	126	Inventive example
12	365	527	36	215	126	Inventive example
13	373	542	37	252	189	Inventive example
14	389	539	31	265	195	Inventive example
15	379	546	32	234	166	Inventive example
16	381	554	37	254	164	Inventive example
17	384	538	34	242	198	Inventive example
18	376	547	32	269	211	Inventive example
19	391	541	35	228	178	Inventive example
20	379	525	36	236	125	Inventive example
21	358	525	34	225	105	Comparative example
22	388	526	36	225	119	Comparative example
23	378	539	33	219	131	Comparative example
24	372	541	32	221	129	Comparative example
25	385	555	31	158	41	Comparative example
26	375	535	36	118	96	Comparative example
27	385	537	36	84	21	Comparative example

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Table 4

Steel No.	Results of exposure test (two years)			Results of exposure test (three years)			Remarks
	Zinc primer paint film and tar epoxy paint film	Tar epoxy paint film	Bare steel	Zinc primer paint film and tar epoxy paint film	Tar epoxy paint film	Bare steel	
	Area of swollen paint film (ratio to base steel: %)	Area of swollen paint film (ratio to base steel: %)	Amount of decrease in thickness (ratio to base steel: %)	Area of swollen paint film (ratio to base steel: %)	Area of swollen paint film (ratio to base steel: %)	Amount of decrease in thickness (ratio to base steel: %)	
1	46	47	43	44	39	40	Inventive example
2	36	43	42	26	32	33	Inventive example
3	40	38	38	26	25	25	Inventive example
4	39	36	36	30	35	36	Inventive example
5	30	33	34	29	33	34	Inventive example
6	42	43	41	40	36	37	Inventive example
7	45	49	48	43	42	44	Inventive example
8	40	43	40	39	35	36	Inventive example
9	34	41	38	29	33	34	Inventive example
10	40	42	39	39	35	37	Inventive example
11	33	41	40	24	34	33	Inventive example
12	31	39	39	30	38	37	Inventive example
13	35	34	33	20	21	20	Inventive example
14	40	37	37	31	36	37	Inventive example
15	40	43	36	38	34	34	Inventive example
16	30	21	19	21	17	15	Inventive example
17	30	43	44	27	44	44	Inventive example

(continued)

Steel No.	Results of exposure test (two years)			Results of exposure test (three years)			Remarks
	Zinc primer paint film and tar epoxy paint film	Tar epoxy paint film	Bare steel	Zinc primer paint film and tar epoxy paint film	Tar epoxy paint film	Bare steel	
	Area of swollen paint film (ratio to base steel: %)	Area of swollen paint film (ratio to base steel: %)	Amount of decrease in thickness (ratio to base steel: %)	Area of swollen paint film (ratio to base steel: %)	Area of swollen paint film (ratio to base steel: %)	Amount of decrease in thickness (ratio to base steel: %)	
18	33	37	37	26	31	31	Inventive example
19	48	46	45	34	39	40	Inventive example
20	73	47	48	42	33	34	Inventive example
21	100	100	100	100	100	100	Comparative example
22	75	49	49	73	43	38	Comparative example
23	62	95	98	60	92	93	Comparative example
24	57	43	41	56	40	36	Comparative example
25	35	49	48	17	41	36	Comparative example
26	135	149	162	132	148	149	Comparative example
27	36	44	42	25	39	35	Comparative example

Claims

1. Anti-corrosion steel for ship, comprising:

C of 0.03 to 0.25 mass%,
 Si of 0.05 to 0.50 mass%,
 Mn of 0.1 to 2.0 mass%,
 P of 0.025 mass% or less,
 S of 0.01 mass% or less,
 Al of 0.005 to 0.10 mass%,
 W of 0.01 to 1.0 mass%,
 Cr of 0.01 mass% or more and less than 0.20 mass%,
 N of 0.001 to 0.008 mass%, and
 the remainder including Fe and inevitable impurities.

2. The anti-corrosion steel for ship according to claim 1, **characterized by** containing:

one or two selected from Sb of 0.001 to 0.3 mass% and Sn of 0.001 to 0.3 mass% in addition to the composition.

3. The anti-corrosion steel for ship according to claim 1 or 2, **characterized by** further containing:

5 one or at least two selected from Ni of 0.005 to 0.25 mass%, Mo of 0.01 to 0.5 mass%, and Co of 0.01 to 1.0 mass% in addition to the composition.

4. The anti-corrosion steel for ship according to any one of claims 1 to 3, **characterized by** further containing:

10 one or at least two selected from Nb of 0.001 to 0.1 mass%, Ti of 0.001 to 0.1 mass%, Zr of 0.001 to 0.1 mass%, and V of 0.002 to 0.2 mass% in addition to the composition.

5. The anti-corrosion steel for ship according to any one of claims 1 to 4, **characterized by** further containing:

15 B of 0.0002 to 0.003 mass% in addition to the composition.

6. The anti-corrosion steel for ship according to any one of claims 1 to 5, **characterized by** further containing:

20 one or at least two selected from Ca of 0.0002 to 0.01 mass%, REM of 0.0002 to 0.015 mass%, and Y of 0.0001 to 0.1 mass% in addition to the composition.

7. The anti-corrosion steel for ship according to any one of claims 1 to 6, **characterized in that:**

25 an epoxy paint film is formed on a surface of the steel.

8. The anti-corrosion steel for ship according to any one of claims 1 to 6, **characterized in that:**

a zinc primer paint film is formed on a surface of the steel.

- 30 9. The anti-corrosion steel for ship according to any one of claims 1 to 6, **characterized in that:**

a zinc primer paint film and an epoxy paint film are formed on a surface of the steel.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2007/050736

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C38/00

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 2002-266052 A (Kawasaki Steel Corp.), 18 September, 2002 (18.09.02), Claims; Par. Nos. [0001], [0019], [0027] (Family: none)	1-9
A	JP 7-34196 A (Sumitomo Metal Industries, Ltd.), 03 February, 1995 (03.02.95), Claims; Par. Nos. [0001], [0024] (Family: none)	1-9

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

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Date of the actual completion of the international search
09 March, 2007 (09.03.07)Date of mailing of the international search report
20 March, 2007 (20.03.07)Name and mailing address of the ISA/
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2007/050736

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2002-332537 A (Kawasaki Steel Corp.), 22 November, 2002 (22.11.02), Claims; Par. Nos. [0001], [0020] to [0028] (Family: none)	1-9
A	JP 54-131522 A (Nippon Steel Corp.), 12 October, 1979 (12.10.79), Claims; page 2, upper right column, lines 10 to 18 (Family: none)	1-9

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REFERENCES CITED IN THE DESCRIPTION

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