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(71) Applicant: JFE Steel Corporation Tokyo 100-0011 (JP)

(72) Inventors:

 INOHARA, Yasuto Tokyo 100-0011 (JP)  SHIOTANI, Kazuhiko Tokyo 100-0011 (JP)

 KOMORI, Tsutomu Tokyo 100-0011 (JP)

 NISHIMURA, Kimihiro Tokyo 100-0011 (JP)

(74) Representative: Grünecker, Kinkeldey,

Stockmair & Schwanhäusser

Leopoldstrasse 4

80802 München (DE)

# (54) CORROSION RESISTANT STEEL FOR CRUDE OIL TANK, MANUFACTURING METHOD THEREFOR, AND CRUDE OIL TANK

(57) Provided is a steel product for a crude oil tank which possesses excellent general corrosion resistance and excellent local corrosion resistance and also exhibits such excellent corrosion resistances even when the steel product is used in a state where Zn is present in a surface of the steel product. To be more specific, provided is a corrosion resistance steel product for a crude oil tank having a composition which contains by mass% 0.001 to 0.16% C, 1.5% or less Si, 0.1 to 2.5% Mn, 0.025 or less P, 0.01% or less S, 0.005 to 0.1% Al, 0.001 to 0.008% N, 0.008 to 0.35% Cu, more than 0.1% and 0.5% or less Cr, 0.005 to 0.3% Sn, and 0.01% or less Mo, and a value of A1 defined by the following formula is set to 0 or less.

Note

 $A1=28\times[C]+2000\times[P]^2+27000\times[S]^2+0.0083\times(1/[Cu])+0.027\times$ 

 $(1/[Cr]) + 95 \times [Mo] + 0.00098 \times (1/[Sn]) - 6.$ 

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#### Description

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[Technical Field]

[0001] The present invention relates to steel products which are preferably used for forming an oil tank of a crude oil tanker and a tank for transporting or storing crude oil (hereinafter collectively referred to as "crude oil tank" as a general term), and more specifically to steel products which can reduce general corrosion which occurs in a surface of steel products which form a top part, a sidewall part or a bottom part of a crude oil tank and local corrosion which occurs in a bottom plate of the crude oil tank. Here, the steel products for a crude oil tank according to the present invention include a thick steel plate, a thin steel sheet and a shaped steel as a concept. [Background of the Invention]

**[0002]** It has been known that general corrosion occurs on steel products which are used for forming an inner surface of a crude oil tank of a tanker, particularly a back side of an upper deck and an upper part of a sidewall part of the crude oil tank. As causes of general corrosion, the followings (1) to (4) and similar causes are considered.

- (1) Formation of dew drops on a steel plate surface or alternate wetting and drying due to the temperature difference between daytime and night
- (2) Dissolution of  $O_2$ ,  $CO_2$ ,  $SO_2$  in an inert gas sealed in the inside of a crude oil tank for explosion protection (an exhaust gas from a boiler or an engine which has the representative composition of approximately 5vol%  $O_2$ , approximately 13vol%  $CO_2$ , approximately 0.01vol%  $SO_2$  and  $N_2$  as a balance) into dew condensation water
- (3) Dissolution of a corrosive gas such as H<sub>2</sub>S which is evaporated from crude oil into dew condensation water
- (4) Retention of salt water used in cleaning a crude oil tank

These causes may be estimated from a fact that dew condensation water having strong acidity, a sulfate ion and a chloride ion are detected in a search carried out in an actual dock inspection.

**[0003]** Further, H<sub>2</sub>S is oxidized using iron rust generated by corrosion as a catalyst so that elemental sulfur is generated in iron rust in layers, and these corrosion products are easily peeled off, and fall down and are deposited on a bottom part of a crude oil tank. Accordingly, in the inspection which is currently carried out every 2.5 years, the maintenance and repair of an upper part of a tank and the recovery of a deposited material on a bottom part of the tank are carried out spending a considerable amount of money.

**[0004]** On the other hand, with respect to a bottom plate of a crude oil tank of a tanker, it is considered that no corrosion occurs in steel products used for forming the bottom plate due to a corrosion inhibition function of crude oil per se and a protective coating derived from crude oil formed on an inner surface of the crude oil tank (hereinafter referred to as "oil coat"). However, it is found from recent studies that bowl-shaped local corrosion (pitting corrosion) occurs in steel products for the bottom plate of the tank. As causes of local corrosion, the followings (1) to (5) and similar causes are considered.

- (1) The presence of brine into which salts represented by sodium chloride are dissolved at high concentration
- (2) Falling down of the oil coat by excessive cleaning
- (3) High concentration of sulfide in crude oil
- (4) High concentration of  $O_2$ ,  $CO_2$ ,  $SO_2$  in an inert gas sealed in a crude oil tank for explosion protection
- (5) Participation of microorganims in the occurrence of local corrosion

However, these causes are still within a range of speculation and clear causes are not yet determined. In an analysis of dwelling water in a crude oil tank at the time of performing the dock inspection actually, chloride ion of high concentration and a sulfate ion of high concentration are detected.

**[0005]** A most effective method for suppressing the above-mentioned general corrosion and local corrosion is a method in which heavy coating is applied to a surface of steel products thus shielding the steel products from a corrosion environment. However, in a coating operation of a crude oil tank, a coating area is enormous. Further, in view of the degradation of a coating film with time, it is necessary to change the coating film once for every 10 years and hence, the inspection and the coating require a huge amount of cost. Further, it has been pointed out that the corrosion at a damaged part of heavy-coated coating film is accelerated in a crude oil tank environment, to the contrary.

**[0006]** To cope with the above-mentioned drawbacks on corrosion, there have been proposed several corrosion resistance steels which improve the corrosion resistance of steel products per se thus allowing the steel products to exhibit the corrosion resistance even in a crude oil tank environment.

For example, patent document 1 discloses a corrosion resistance steel for a cargo oil tank which improves resistance against general corrosion and local corrosion, wherein the corrosion resistance steel is formed such that proper amounts of Si, Mn, P, S and 0.05 to 3% of Ni by mass% are added to steel containing 0.01 to 0.3% of C by mass%, and Mo, Cu, Cr, W, Ca, Ti, Nb, V, B are further selectively added to the steel.

In patent document 1, there is the description that, in an environment containing  $H_2S$  where wetting and drying are alternated, when a content of Cr exceeds 0.05mass%, the general corrosion resistance and the pitting corrosion resistance are remarkably lowered so that a content of Cr is set to 0.05mass% or less.

[0007] Further, patent document 2 discloses a corrosion resistance steel for a crude oil tank which exhibits the excellent general corrosion resistance and the excellent local corrosion resistance and, further, suppresses the generation of corrosion product containing elemental sulfur, wherein the corrosion resistance steel is formed such that proper amounts of Si, Mn, P, S, 0.01 to 1.5% of Cu, 0.001 to 0.3% of Al and 0.001 to 0.01% of N by mass% are added to steel containing 0.001 to 0.2% of C by mass%, and at least one of 0.01 to 0.2% of Mo and 0.01 to 0.5% of W by mass% is added to the steel.

[0008] Further, patent document 3 discloses a corrosion resistance steel for a cargo oil tank which enhances the general corrosion resistance and the local corrosion resistance, wherein the corrosion resistance steel is formed such that proper amounts of Si, Mn, P, 0.01 to 2% of Ni, 0.05 to 2% of Cu and 0.01 to 1% of W by mass% are added to steel containing 0.01 to 0.2% of C by mass%, Cr, Al, N, O are selectively added to the steel, and addition amounts of Cu, Ni, W are defined by parameter formulae.

**[0009]** Further, patent document 4 discloses a corrosion resistance steel for a cargo oil tank which enhances the general corrosion resistance and the local corrosion resistance, wherein the corrosion resistance steel is formed such that proper amounts of Si, Mn, P, Cr, Al, 0.01 to 1% of Ni, 0.05 to 2% of Cu and 0.01 to 0.2% of Sn by mass% are added to steel containing 0.01 to 0.2% of C by mass%, and Mo, W, Ti, Zr, Sb, Ca, Mg, Nb, V, B are selectively added to the steel.

[Prior art literature]

[Patent document]

### [0010]

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[Patent document 1] JP-A-2003-082435
 [Patent document 2] JP-A-2004-204344
 [Patent document 3] JP-A-2005-325439
 [Patent document 4] JP-A-2007-270196

30 [Summary of the Invention]

[Problems that the Invention is to Solve]

**[0011]** However, when the corrosion resistance steel disclosed in the above-mentioned patent documents 1 to 4 is applied to a crude oil tank, it is hardly possible to state that the resistance against general corrosion when the corrosion resistance steel is used for forming an upper part of the crude oil tank (hereinafter referred to as "general corrosion resistance") and the resistance against local corrosion when the corrosion resistance steel is used for forming a bottom plate of the crude oil tank (hereinafter referred to as "local corrosion resistance") are always sufficient.

**[0012]** This implies that it is insufficient to merely carry out simple corrosion resistance tests which simulate respective corrosion environments to develop corrosion resistance steels which can cope with the general corrosion of a back surface of an upper deck of a crude oil tank and the local corrosion of a bottom plate of the crude oil tank respectively. This is because a corrosion test carried out in an experiment room includes more or less an element of an accelerating test and hence, some corrosion factors are omitted or there arises a case where an actual environment is not accurately reproduced. Particularly, in the development of corrosion resistance steel for a crude oil tank, it is inevitable to add a chloride ion and a sulfate ion in a test environment.

**[0013]** Further, the inventions described in patent documents 3 and 4 are directed to techniques which aim at the acquisition of both of corrosion resistance in a crude oil corrosion environment and the corrosion resistance in a salt water corrosion environment in view of a fact that salt water is loaded in a ballast tank arranged outside a cargo oil tank when crude oil is not loaded in a tanker. These techniques focus on the corrosion resistance which steel products per se have as the corrosion resistance of an outer surface of a cargo oil tank after the deterioration of a corrosion prevention coating film with respect to the salt water corrosion environment. However, the inventions described in patent document 3 and 4 pay no consideration to the enhancement of the corrosion resistance in a state where a coating film is present on a surface of steel products attributed to a synergistic effect of a corrosion resistance element which the steel products contain and Zn in a zinc primer, that is, the enhancement of the post-coating corrosion resistance.

**[0014]** However, the enhancement of the post-coating corrosion resistance which is not taken into consideration in patent documents 3 and 4 is extremely important and effective in achieving the prolongation of lifetime of a crude oil tanker use corrosion resistance steel products. However, techniques which realize the post-coating corrosion resistance are not present under current circumstances.

**[0015]** Accordingly, the present invention has been developed to overcome the above-mentioned drawbacks, and it is an object of the present invention to provide a steel product for a crude oil tank which exhibits the excellent general corrosion resistance when used for forming an inner surface of a crude oil tank and, particularly, an upper deck and a side plate of the crude oil tank, exhibits the excellent local corrosion resistance also when used for forming a bottom plate of the crude oil tank and, further, exhibits the remarkably excellent general corrosion resistance and local corrosion resistance when used in a state where Zn is present on a surface of the steel products. It is another object of the present invention to provide a method of manufacturing the steel product, and a crude oil tank which uses the steel product.

[Means for solving the Problems]

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**[0016]** Inventors of the present invention and the like, to achieve the above-mentioned object, firstly carried out the corrosion test by extracting factors participating in the general corrosion in the inside of a crude oil tank, and by combining these factors. As a result, the inventors have succeeded in the reproduction of the general corrosion which occurs in the inside of the crude oil tank, and have obtained the following finding with respect to governing factors and a corrosion mechanism of the general corrosion.

An inert gas which is sealed in a crude oil tank for explosion protection contains moisture. Accordingly, dew drops are formed on a surface of steel products which form an inner wall of the tank due to the temperature difference between daytime and night during navigation. In this dew condensation water,  $CO_2$  (carbon dioxide),  $O_2$  (oxygen),  $SO_2$  (Sulfur dioxide) which are inert gas components,  $H_2S$  (hydrogen sulfide) which is a volatile component from a crude oil and the like are dissolved thus forming a corrosive acid solution containing sulfate ion. Further, it is necessary to take a chloride ion introduced by cleaning a crude oil tank with salt water into consideration. The corrosive acid solution in which these components are dissolved is concentrated in a process where a steel plate temperature is elevated, and the general corrosion occurs in a surface of the steel plate. Further, using iron rust formed on the surface of the steel plate as a catalyst, S (sulfur) is precipitated from  $H_2S$  and a rust layer in which iron rust and sulfur are formed in layers is formed and hence, the rust layer formed on the surface of the steel plate becomes brittle and non-protective whereby the corrosion progresses continuously.

[0017] In view of the above, the inventors of the present invention and the like have investigated the influence of respective alloy elements exerted on the general corrosion of a surface of a steel plate under an environment where dew condensation water which contains sulfate ion and chloride ion are present. As a result, the inventors have confirmed that the addition of Cu, Cr, and Sn densifies a rust layer formed on the surface of the steel plate formed in an environment where the steel plate is used as steel products for a crude oil tank thus enhancing the general corrosion resistance, and the addition of W and Sb promotes the formation of the dense rust layer thus enhancing the general corrosion resistance. That is, the inventors have found that steel products for a crude oil tank which exhibits the excellent general corrosion resistance can be obtained by mainly adding Cu, Cr and Sn and further by adding proper amounts of W and Sb.

**[0018]** Next, the inventors of the present invention carried out a corrosion test by extracting factors participating in the local corrosion of a bottom plate of a crude oil tank, and by combining these factors. As a result, in the same manner as the general corrosion, the inventors have succeeded in the reproduction of the local corrosion which occurs in the bottom plate of the crude oil tank, and have obtained the following finding with respect to governing factors and a corrosion mechanism of the local corrosion.

In the bowl-shaped local corrosion which occurs in a bottom plate of an actual crude oil tank,  $O_2$  and  $O_2$  which are contained in a solution dwelling on the bottom plate act as main governing factors. To be more specific, the local corrosion occurs under an environment where  $O_2$  and  $O_2$  concentration and  $O_2$  concentration and  $O_2$  concentration and  $O_2$  concentration and  $O_2$  concentration: 2 to 8vol%,  $O_2$  concentration: 0.1 to 5vol% in a saturated state). That is, under the environment with low  $O_2$  concentration and low  $O_2$  concentration,  $O_2$  is oxidized so that the elemental sulfur is precipitated. This precipitated elemental sulfur forms a local battery between the elemental sulfur and the bottom plate of the crude oil tank thus causing the local corrosion in a surface of the steel products. This local corrosion is further promoted and grows under an acid environment where a chloride ion and a sulfate ion are present.

[0019] In view of the above, the inventors of the present invention and the like have investigated the influence of respective alloy elements exerted on the occurrence of the local corrosion under the above-mentioned environment with low  $O_2$  concentration and low  $H_2S$  concentration. As a result, the inventors have confirmed that the addition of W densifies a rust layer formed on the surface of the steel plate formed in an environment where the steel plate is used as steel products for a crude oil tank thus enhancing the local corrosion resistance, and the addition of Sn and Sb assists the formation of the dense rust layer containing W thus enhancing the local corrosion resistance. Further, the inventors have confirmed that the addition of Mo deteriorates the corrosion resistance to the contrary in an acid corrosion environment where both of a chloride ion and a sulfate ion are present simultaneously. That is, steel products for a crude oil tank which exhibits the excellent local corrosion resistance can be obtained by adding proper amounts of Sn and Sb in addition to the addition of W and, by limiting the content of Mo.

**[0020]** Based on a result of the above-mentioned finding, the inventors of the present invention have found that by properly setting contents of Cu, Cr, Sn, W and Sb, it is possible to acquire steel products for a crude oil tank which exhibits the excellent general corrosion resistance when used in an inner surface of the crude oil tank, and exhibits the excellent local corrosion resistance when used in an bottom plate of the crude oil tank, that is, exhibits the excellent corrosion resistance when used in any part of the inside of the crude oil tank.

**[0021]** The inventors of the present invention also have found that although the steel products in which the above-mentioned contents of Cu, Cr, Sn, W and Sb are properly set exhibit excellent corrosion resistance even in a non-coated state, when the steel products are used in a state where coating which contains metal Zn or a Zn compound is applied to a surface of the steel products, a lifetime of the coating can be largely prolonged and, at the same time, the general corrosion resistance and the local corrosion resistance can be remarkably enhanced. Further, the inventors have investigated the influence which the microstructure of the steel exerts on the corrosion resistance, and also have found that the corrosion resistance can be enhanced by generating 2% or more of pearlite in terms of an area rate.

The present invention has been made by conducting further studies based on the above-mentioned findings.

**[0022]** That is, the present invention provides a corrosion resistance steel product for a crude oil tank having a composition which contains 0.001 to 0.16mass% C, 1.5mass% or less Si, 0.1 to 2.5mass% Mn, 0.025mass% or less P, 0.01mass% or less S, 0.005 to 0.1mass% Al, 0.001 to 0.008mass% N, 0.008 to 0.35mass% Cu, more than 0.1mass% and 0.5mass% or less Cr, 0.005 to 0.3mass% Sn, and 0.01mass% or less Mo, and Fe and unavoidable impurities as a balance, and a value of Al defined by a following formula (1) is set to 0 or less,

 $A1=28\times[C]+2000\times[P]^2+27000\times[S]^2+0.0083\times(1/[Cu])+0.027\times$  $(1/[Cr])+95\times[Mo]+0.00098\times(1/[Sn])-6 ... (1),$ 

wherein

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[C], [P], [S], [Cu], [Cr], [Mo] and [Sn] are contents of respective elements (mass%).

**[0023]** The corrosion resistance steel product for a crude oil tank of the present invention is **characterized in that** the corrosion resistance steel product further contains, in addition to the above-mentioned component composition, 0.005 to 0.4mass% Ni, and a value of A2 defined by a following formula (2) is set to 0 or less,

$$A2=28\times[C]+2000\times[P]^2+27000\times[S]^2+0.0083\times(1/[Cu])+2\times[Ni]$$

$$+0.027\times(1/[Cr])+95\times[Mo]+0.00098\times(1/[Sn])-6 ... (2),$$

wherein

C], [P], [S], [Cu], [Ni], [Cr], [Mo] and [Sn] are contents of respective elements (mass%).

**[0024]** Further, the corrosion resistance steel product for a crude oil tank of the present invention is **characterized in that** the corrosion resistance steel product further contains, in addition to the above-mentioned component composition, one kind or two kinds selected from 0.001 to 0.5mass% W and 0.005 to 0.3mass% Sb, and a value of A3 defined by a following formula (3) is set to 0 or less,

$$A3=28\times[C]+2000\times[P]^2+27000\times[S]^2+0.0083\times(1/[Cu])+2\times[Ni]$$

$$+0.027\times(1/[Cr])+95\times[Mo]+0.00098\times(1/[Sn])+0.0019\times(1/([Sb])+[Sn])$$

$$W]))-6.5 ... (3),$$

wherein

[C], [P], [S], [Cu], [Ni], [Cr], [Mo], [Sn], [Sb] and [W] are contents of respective elements (mass%).

**[0025]** Further, the corrosion resistance steel product for a crude oil tank of the present invention is **characterized in that** the corrosion resistance steel product further contains, in addition to the above-mentioned component composition, one kind or two kinds or more selected from 0.002 to 0.1mass% Nb, 0.002 to 0.1mass% V, 0.001 to 0.1mass% Ti and 0.01mass% or less B.

**[0026]** Further, the corrosion resistance steel product for a crude oil tank of the present invention is **characterized in that** the corrosion resistance steel product further contains, in addition to the above-mentioned component composition, one kind or two kinds selected from 0.0002 to 0.005mass% Ca and 0.0005 to 0.015mass% REM.

**[0027]** Further, the corrosion resistance steel product for a crude oil tank of the present invention is **characterized** in **that** a microstructure at a position away from a surface of the steel product by 1/4 of a plate thickness contains 2 to 20% of pearlite in terms of an area rate.

[0028] Further, the corrosion resistance steel product for a crude oil tank of the present invention is **characterized** in that a coating film which contains metal Zn or a Zn compound is formed on a surface of the steel product.

[0029] Further, the corrosion resistance steel product for a crude oil tank of the present invention is **characterized** in that a content of Zn in the coating film is 1.0g/m<sup>2</sup> or more.

**[0030]** Further, the present invention provides a method of manufacturing a corrosion resistance steel product for a crude oil tank, wherein a raw steel material having the above-mentioned component composition is heated to 1000 to 1350°C and, thereafter, hot rolling is applied to the raw steel material at a rolling finish temperature of not lower than 750°C, and a rolled plate is cooled to a cooling stop temperature of not higher than 650°C and not lower than 450°C at a cooling rate of 2°C/sec or more.

[0031] Further, the present invention is directed to a crude oil tank which is characterized by using the above-mentioned steel product.

[Advantage of the Invention]

- [0032] According to the present invention, it is possible to provide, at a low cost, a steel product which causes neither the general corrosion nor the local corrosion even when the steel product is used for forming any part of a crude oil tank such as an oil tank of a crude oil tanker or a tank for transporting or storing crude oil and hence, the present invention can exhibit an industrially outstanding advantage.
- 30 [Brief Description of the Drawings]

### [0033]

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- Fig. 1 is a view for explaining a local corrosion testing device.
- Fig. 2 is a view for explaining a general corrosion testing device.

[Best mode for carrying out the Invention]

**[0034]** Reasons for limiting the component composition of a steel product for a crude oil tank according to the present invention to the above-mentioned ranges are explained.

C: 0.001 to 0.16mass%

[0035] C is an element which increases strength of a steel product. In this invention, the steel product is required to contain 0.001mass% or more of C for obtaining desired strength. On the other hand, not only C progresses the deterioration of corrosion resistance along with the increase of the content but also C deteriorates weldability and toughness of a welded heat affected zone when the content of C exceeds 0.16mass%. Accordingly, the content of C is set to a value which falls within a range from 0.001 to 0.16mass%. From a viewpoint of further enhancing strength and toughness of the steel product, the content of C is preferably set to a value which falls within a range from 0.01 to 0.15mass%. The content of C is more preferably set to a value which falls within a range from 0.05 to 0.15mass%.

Si: 1.5mass% or less

[0036] Si is an element which acts as a deoxidizing agent and increases strength of the steel product. However, the addition of Si exceeding 1.5mass% lowers toughness of steel. Accordingly, in the present invention, the content of Si is limited to a range of 1.5mass% or less. Si forms an anticorrosion coat thus contributing to enhance corrosion resistance in an acid environment and hence, from a viewpoint of improving corrosion resistance in the acid environment, the addition amount of Si is preferably set to a value which falls within a range from 0.2 to 1.5mass%, and the addition

amount of Si is more preferably set to a value which falls within a range from 0.3 to 1.5 mass%.

Mn: 0.1 to 2.5mass%

[0037] Mn is an element which increases strength of steel product. In this invention, the steel product is required to contain 0.1mass% or more of Mn for obtaining desired strength. On the other hand, the addition of Mn exceeding 2.5mass% lowers toughness and weldability of steel, and promotes the segregation thus bringing about non-uniformity of the composition of a steel plate. Accordingly, the content of Mn is set to a value which falls within a range from 0.1 to 2.5mass%. From a viewpoint of maintaining high strength of the steel product and suppressing the formation of the inclusion which lowers corrosion resistance, the content of Mn is preferably set to a value which falls within a range from 0.5 to 1.6mass%, and the content of Mn is more preferably set to a value which falls within a range from 0.8 to 1.4mass%.

P: 0.025mass% or less

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15 [0038] P is a harmful element which lowers the toughness of steel by generating segregation in a grain boundary and also lowers the corrosion resistance of steel and hence, it is desirable to reduce the content of P as much as possible. Particularly, when the content of P exceeds 0.025mass%, the central segregation is promoted thus brining about non-uniformity of the composition of a steel plate, and also the toughness of the steel plate is remarkably lowered whereby the content of P is set to 0.025mass% or less. When the content of P is decreased to less than 0.003mass%, a manufacturing cost is pushed up and hence, a lower limit of P is preferably set to approximately 0.003mass% and, from a viewpoint of enhancing the general corrosion resistance in an acid environment, the content of P is preferably set to 0.010mass% or less. The content of P is more preferably set to 0.009mass% or less.

S: 0.01mass% or less

**[0039]** S is a harmful element which becomes a start point of corrosion by forming MnS which is non-metal inclusion, and lowers local corrosion resistance and general corrosion resistance and hence, it is desirable to decrease S as much as possible. Particularly, when the content of S exceeds 0.01mass%, the remarkable lowering of local corrosion resistance and general corrosion resistance is brought about and hence, in the present invention, an upper limit of S is set to 0.01mass%. From a viewpoint of enhancing corrosion resistance, it is desirable to set the content of S to 0.0020mass% or less. However, the extreme decrease of S brings about the increase of a manufacturing cost. Accordingly, in the actual manufacture of steel products, the content of S is set to a value which falls within a range from 0.0002 to 0.0020mass%. The content of S is more preferably set to 0.0009mass% or less.

Al: 0.005 to 0.01mass%

**[0040]** Al is an element which acts as a deoxidizer and, in this invention, the steel product is required to contain 0.005mass% or more of Al. On the other hand, when the additional amount of Al exceeds 0.1mass%, toughness of steel is lowered. Accordingly, the content of Al is set to a value which falls within a range from 0.005 to 0.1mass%. The content of Al is preferably set to a value which falls within a range from 0.01 to 0.05mass%. The content of Al is more preferably set to a value which falls within a range from 0.02 to 0.04mass%.

N: 0.001 to 0.008mass%

[0041] To enhance toughness of steel and also to enhance mechanical properties of a weld joint part, the addition of 0.001 mass% or more of N is necessary. However, when the addition content of N exceeds 0.008mass%, solid solution N is increased and hence, toughness of the joint part is remarkably lowered depending on a welding condition. Accordingly, the content of N is set to a value which falls within a range from 0.001 to 0.008mass%. The content of N is preferably set to a value which falls within a range from 0.002 to 0.005mass%, and the content of N is more preferably set to a value which falls within a range from 0.002 to 0.004mass%.

Cu: 0.008 to 0.35mass%

[0042] Cu forms an anticorrosion coat and performs the action of suppressing the general corrosion, and is an inevitable element to be added in the present invention. However, when the content of Cu is less than 0.008mass%, the above-mentioned advantageous effects cannot be acquired. On the other hand, when Cu is added in combination with Sn, the general corrosion resistance is remarkably enhanced. However, when the content of Cu exceeds 0.35mass%, hot workability is lowered thus damaging the manufacturing property. Accordingly, the addition content of Cu is set to a

value which falls within a range from 0.008 to 0.35mass%. Since the advantageous effect brought about by the addition of Cu is saturated along with the increase of an addition amount and hence, from a viewpoint of cost-effectiveness, the content of Cu is preferably set to a value which falls within a range from 0.008 to 0.15mass%. The content of Cu is more preferably set to a value which falls within a range from 0.01 to 0.14mass%.

Cr: more than 0.1mass% and 0.5mass% or less

[0043] Cr forms a protective coating on a surface of a steel product together with Cu thus performing the function of enhancing strength of a steel product in addition to the function of enhancing the general corrosion resistance in an acid environment and hence, Cu is an inevitable element to be added in the present invention. Particularly, in an acid environment which contains a sulfate ion and a chloride ion, Cr forms an oxide layer which covers a surface of a steel product thus giving rise to an advantageous effect that a general corrosion rate is lowered. Further, Cr densifies a rust layer together with Cu and hence, a Zn compound can be held in the rust layer for a long time even in a state where zinc primer coating is applied to the surface of the steel product whereby Cr largely contributes to the enhancement of corrosion resistance including post-coating corrosion resistance. Further, due to an effect of enhancing corrosion resistance acquired by the addition of Cr, an addition amount of Cu can be suppressed and hence, it is possible to acquire an advantageous effect that lowering of hot workability which occurs under the co-existence of Cu and Sn can be alleviated. However, when the addition content of Cr is 0.1mass% or less, the above-mentioned advantageous effects brought about the addition of Cr cannot be acquired, while when the addition content of Cr exceeds 0.5mass%, the above-mentioned advantageous effects are saturated, and a cost is pushed up and weldability is deteriorated. Accordingly, the additional content of Cr is set to a value which falls within a range more than 0.1mass% and 0.5mass% or less. The content of Cr is preferably set to a value which falls within a range from 0.11 to 0.3mass%. The content of Cr is more preferably set to a value which falls within a range from 0.12 to 0.2mass%.

Sn: 0.005 to 0.3mass%

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[0044] Sn, due to a combined effect with Cu or due to a combined effect with Cu and W when W is added to steel as described later, performs the action of suppressing general corrosion as well as local corrosion under an acid environment by forming a dense rust layer, and is an inevitable element to be added in the present invention. However, when the addition content of Sn is less than 0.005mass%, the above-mentioned addition effect cannot be obtained, while when the addition content exceeds 0.3mass%, hot workability and toughness are deteriorated. Accordingly, the content of Sn is set to a value which falls within a range from 0.005 to 0.3mass%. The content of Sn is preferably set to a value which falls within a range from 0.02 to 0.1mass%. The content of Sn is more preferably set to a value which falls within a range from 0.03 to 0.09mass%.

Mo: 0.01mass% or less

**[0045]** Mo is, in general, considered to be an element which performs the same action as W thus enhancing corrosion resistance. However, inventors of the present invention have newly found that while W forms an insoluble salt under an acid salt water environment, Mo forms a salt having resolving property under an acid salt water environment and does not perform a barrier effect and, particularly, when the content of Mo is increased exceeding 0.01mass%, corrosion resistance in an acid salt water environment is deteriorated to the contrary. Accordingly, in the present invention, the content of Mo is limited to 0.01 mass% or less. The content of Mo is preferably set to 0.008mass% or less, and the content of Mo is more preferably set to 0.005mass% or less.

**[0046]** The above-mentioned elements are basic components of the steel product of the present invention. However, to impart both the excellent general corrosion resistance and the excellent local corrosion resistance to the steel product of the present invention, besides that the above-mentioned components fall within the above-mentioned composition ranges, it is necessary that the steel product contains the above-mentioned components such that a value of Al defined by the following formula (1) is set to 0 or less. Further, the value of Al is preferably -1 or less.

50 Note

$$A1=28\times[C]+2000\times[P]^2+27000\times[S]^2+0.0083\times(1/[Cu])+0.027\times$$
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$$(1/[Cr])+95\times[Mo]+0.00098\times(1/[Sn])-6 ... (1),$$

wherein

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[C], [P], [S], [Cu], [Cr], [Mo] and [Sn] are contents of

respective elements (mass%). The above-mentioned formula (1) is an experimental formula expressing indexes of corrosion resistance which summarize influences of the respective elements exerted on general corrosion resistance and local corrosion resistance obtained in a corrosion test carried out in the present invention. It is found that when a value of the above-mentioned AI exceeds 0, either one or both of general corrosion resistance and local corrosion resistance cannot be secured. The above-mentioned formula (1) shows that, with respect to the influence of the respective elements exerted on corrosion resistances, the more an addition amount of the element is increased, the more general corrosion resistance and local corrosion resistance are lowered with respect to the elements of primary and secondary terms, while the more an addition amount of the element is increased, the more general corrosion resistance and local corrosion resistance are enhanced with respect to the elements of inverse-numbered terms. That is, C and Mo are elements which lower corrosion resistance influencing the corrosion resistance at a rate of two powers of content, and Cu, Cr and Sn are elements which enhance corrosion resistance.

**[0047]** In addition to the above-mentioned basic components, Ni can be added to the steel product of the present invention within the following range.

Ni: 0.005 to 0.4mass%

[0048] Ni performs the action of suppressing the deterioration of hot workability in combination with Cu when added to the steel product. However, when the addition content of Ni is less than 0.005mass%, the above-mentioned effect cannot be obtained, while when the addition amount of Ni exceeds 0.4mass%, a cost is pushed up. Accordingly, the content of Ni is preferably set to a value which falls within a range from 0.005 to 0.4mass%. From a viewpoint of cost-effectiveness, the content of Ni is more preferably set to a value which falls within a range from 0.005 to 0.1mass%. The content of Ni is still more preferably set to a value which falls within a range from 0.005 to 0.1mass%.

**[0049]** When Ni is added to the steel product, the steel product is required to contain the respective components such that a value of A2 defined by the following formula (2) is set to 0 or less in place of the value of the above-mentioned Al. Further, the value of A2 is preferably -1 or less.

30 As can be understood from the formula (2), Ni is an element which lowers corrosion resistance. Note

$$A2=28\times[C]+2000\times[P]^2+27000\times[S]^2+0.0083\times(1/[Cu])+2\times[Ni]$$
 
$$+0.027\times(1/[Cr])+95\times[Mo]+0.00098\times(1/[Sn])-6 ... (2),$$

wherein

40 [C], [P], [S], [Cu], [Ni], [Cr], [Mo] and [Sn] are contents of respective elements (mass%).

**[0050]** In addition to the above-mentioned contents, one kind or two kinds selected from Sb and W can be added to the steel product of the present invention within the following ranges.

45 Sb: 0.005 to 0.3mass%

**[0051]** In the same manner as Sn, Sb, due to a combined effect with Cu or a combined effect with Cu and W when W is added to steel product as described later, performs the action of suppressing corrosion under an acid environment by forming a dense rust layer, and can be added when it is necessary to further enhance this property. However, when the addition content of Sb is less than 0.005mass%, such an effect cannot be obtained, while when the addition amount of Sb exceeds 0.3mass%, the effect is saturated, and workability is lowered. Accordingly, when Sb is added to steel product, the content of Sb is preferably set to a value which falls within a range from 0.005 to 0.3mass%. The content of Sb is more preferably set to a value which falls within a range from 0.02 to 0.15mass%. The content of Sb is still more preferably set to a value which falls within a range from 0.03 to 0.09mass%.

W: 0.001 to 0.5mass%

[0052] With respect to W, a  $WO_4^{2-}$  ion formed in a corrosion environment exhibits a barrier effect against an anion

such as a chloride ion, and W forms  $FeWO_4$  having insolubility thus suppressing progress of corrosion. W also has an effect of densifying a rust layer formed on a surface of a steel plate. Further, W has, due to such chemical and physical effects, an effect of suppressing progress of local corrosion and general corrosion in a corrosion environment where  $H_2S$  and  $CI^-$  are present. However, when the addition content of W is less than 0.001mass%, a sufficient addition effect cannot be acquired, while when the addition content of W exceeds 0.5mass%, not only such effect is saturated but also a cost is pushed up. Accordingly, when W is added to the steel product, the content of W is preferably set to a value which falls within a range from 0.001 to 0.5mass%. The content of W is more preferably set to a value which falls within a range from 0.02 to 0.1mass%. The content of W is further preferably set to a value which falls within a range from 0.03 to 0.09mass%.

**[0053]** When Sb and/or W are added to the steel product in addition to the above-mentioned Ni, the steel product is required to contain the respective elements such that a value of A3 defined by the following formula (3) is set to 0 or less in place of the value of the above-mentioned A1 or A2. Further, the value of A3 is preferably -1 or less. As can be understood from the formula (3), Sb and W are elements which enhance corrosion resistance.

Note

$$A3=28\times[C]+2000\times[P]^2+27000\times[S]^2+0.0083\times(1/[Cu])+2\times[Ni]$$

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$$+0.027 \times (1/[Cr]) + 95 \times [Mo] + 0.00098 \times (1/[Sn]) + 0.0019 (1/([Sb]+[W])) - 6.5 \dots (3),$$

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wherein

[C], [P], [S], [Cu], [Ni], [Cr], [Mo], [Sn], [Sb] and [W] are contents of respective elements (mass%).

**[0054]** Further, to enhance strength and toughness of the steel product of the present invention, one kind or two kinds or more selected from Nb, V, Ti and B can be added to the steel product within the following ranges in addition to the above-mentioned components.

Nb: 0.002 to 0.1mass%

**[0055]** Nb is an element which is added aiming at the enhancement of strength and toughness of steel. However, when the addition content of Nb is less than 0.002mass%, such an effect is not acquired, while when the addition content of Nb exceeds 0.1mass%, the effect is saturated. Accordingly, when Nb is added to the steel product, the addition amount of Nb is preferably set to a value which falls within a range from 0.002 to 0.1mass%. The addition amount of Nb is more preferably set to a value which falls within a range from 0.004 to 0.05mass%. The addition amount of Nb is further preferably set to a value which falls within a range from 0.005 to 0.01mass%.

V: 0.002 to 0.1mass%

**[0056]** V is an element which is added aiming at the enhancement of strength of steel. However, when the addition content of V is less than 0.002mass%, strength enhancement effect is not acquired, while when the addition content of V exceeds 0.1mass%, the toughness of steel is lowered. Accordingly, when V is added to the steel product, the addition amount of V is preferably set to a value which falls within a range from 0.002 to 0.1mass%. The addition amount of V is more preferably set to a value which falls within a range from 0.003 to 0.05mass%. The addition amount of V is further preferably set to a value which falls within a range from 0.004 to 0.01mass%.

50 Ti: 0.001 to 0.1mass%

**[0057]** Ti is an element which is added aiming at the enhancement of strength and toughness of steel. However, when the addition content of Ti is less than 0.001mass%, such an effect is not acquired, while when the addition content of Ti exceeds 0.1mass%, the effect is saturated. Accordingly, when Ti is added to the steel product, the addition amount of Ti is preferably set to a value which falls within a range from 0.001 to 0.1mass%. The addition amount of Ti is further preferably set to a value which falls within a range from 0.005 to 0.03mass%. The addition amount of Ti is further preferably set to a value which falls within a range from 0.006 to 0.02mass%.

#### B: 0.01mass% or less

**[0058]** B is an element which is added aiming at the enhancement of strength of steel, and such effect can be acquired by adding 0.0003mass% or more of B to the steel product. However, when the addition content of B exceeds 0.01mass%, the toughness of steel is lowered. Accordingly, when B is added to the steel product, the addition amount of B is preferably set to 0.01mass% or less. The addition amount of B is more preferably set to a value which falls within a range from 0.0003 to 0.002mass%. The addition amount of B is further preferably set to a value which falls within a range from 0.0003 to 0.0015mass%.

**[0059]** Further, to enhance ductility and toughness of the steel product of the present invention, one kind or two kinds selected from Ca and REM can be added to the steel product within the following ranges in addition to the abovementioned components.

Ca: 0.0002 to 0.005mass%

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[0060] Ca has an effect of enhancing corrosion resistance of steel product in a coated state as well as an effect of enhancing ductility and toughness of steel product due to morphological control of inclusion and hence, Ca can be added to the steel product aiming at enhancement of these properties. However, when the addition content of Ca is less than 0.0002mass%, such an effect is not acquired, while when the addition content of Ca exceeds 0.005mass%, the toughness of the steel product is lowered. Accordingly, when Ca is added to the steel product, the addition amount of Ca is preferably set to a value which falls within a range from 0.0002 to 0.005mass%. From a viewpoint of enhancing the corrosion resistance, the addition amount of Ca is more preferably set to a value which falls within a range from 0.001 to 0.005mass%. The addition amount of Ca is further preferably set to a value which falls within a range from 0.001 to 0.003mass%.

5 REM: 0.0005 to 0.015mass%

[0061] REM (Rare Earth Metal) means elements of rare earths whose atomic numbers are 57 to 71 and, in general, the addition of REM can be performed by adding misch metal which is a mixture containing La, Ce, Pr, Nd or the like to the steel product. REM performs the action of enhancing ductility and toughness of the steel product by controlling a morphology of the inclusion. However, when the addition content of REM is less than 0.0005mass%, such effects cannot be acquired, while when the addition content of REM exceeds 0.015mass%, the toughness of the steel product is lowered. Accordingly, when REM is added to steel product, the addition amount of REM is preferably set to a value which falls within a range from 0.0005 to 0.015mass%. From a viewpoint of enhancing the corrosion resistance, the addition amount of REM is more preferably set to a value which falls within a range from 0.005 to 0.015mass%. The addition amount of REM is further preferably set to a value which falls within a range from 0.005 to 0.01mass%.

**[0062]** The balance of the steel product of the present invention other than the above-mentioned components is constituted of Fe and unavoidable impurities. However, the steel product of the present invention does not exclude the inclusion of other elements provided that contents of these elements fall within ranges in which the other elements do not adversely influence the above-mentioned manner of operation and advantageous effects of the present invention. For example, when the other element is O, the steel product may contain 0.008% or less of O.

**[0063]** Next, the microstructure of a steel product for a crude oil tank of the present invention is explained. In the steel product of the present invention, the microstructure at a position away from a surface of the steel product by 1/4 of a plate thickness t is preferably formed of a composite structure constituted of ferrite, pearlite and bainite transformation, and may preferably contain 2 to 20% of pearlite in terms of an area rate.

In general, as a method of controlling strength of steel having the same component composition, various kinds of structure control methods are used. Among these structure control methods, water cooling after hot rolling is one of the most-popularly-used methods. In the steel product having the component composition of the present invention, when slow cooling is applied to the steel product after hot rolling, the microstructure constituted of ferrite and pearlite is formed. On the other hand, when quenching treatment which is represented by water cooling is performed, the above-mentioned pearlite is transformed into the bainite structure having higher strength. Particularly, the higher a cooling rate or the lower a cooling stop temperature becomes, the higher a rate of the bainite structure becomes so that the two-phase structure constituted of ferrite and bainite is obtained eventually.

**[0064]** However, the bainite structure is the structure where cementite is finely dispersed and hence, the bainite structure has the property of accelerating corrosion in an acid environment. In view of the above, by leaving a fixed amount of pearlite structure in the steel product thus suppressing the fine dispersion of cementite, corrosion resistance can be enhanced. The corrosion resistance enhancing effect acquired by leaving pearlite explicitly appears when an area rate of pearlite is 2% or more. On the other hand, when the area rate of pearlite structure exceeds 20%, toughness is lowered so that such an area rate is not preferable. Accordingly, to allow the steel product of the present invention to

acquire the more excellent corrosion resistance, it is preferable to control the area rate of pearlite in the microstructure to a value which falls within a range from 2 to 20%. Here, the reason a measuring position of the above-mentioned microstructure is set at the position away from the surface of the steel product by 1/4 of the plate thickness of the steel product is that, in a steel product having a large plate thickness such as a steel product for shipbuilding, the microstructure at the position away from the surface of the steel product by 1/4 of the plate thickness can represent the microstructure over the whole plate thickness and, further, even when a worked surface of the steel product is exposed to a corrosion environment, general corrosion resistance is satisfied from a surface layer to a plate thickness center portion of the steel product over the whole surface. The corrosion resistance steel product for a crude oil tank of the present invention which has the microstructure has strength with yield stress of approximately 315MPa or more and tensile strength of approximately 440MPa or more. Provided that the steel product can acquire desired strength, the presence of the bainite structure is unnecessary.

[0065] Next, a method of manufacturing steel product for a crude oil tank of the present invention is explained.

The steel product of the present invention can be manufactured using a raw steel material having component compositions thereof controlled within the above-mentioned ranges of the present invention by a method substantially equal to a method of manufacturing a conventional steel product. For example, in a secondary refining furnace such as a steel converter, an electric furnace or vacuum degassing equipment, besides C, Si, Mn, P and S which are five main elements, contents of Cu, Cr, Sn and Mo are adjusted within ranges of the present invention and, when necessary, other alloy elements are added to the raw steel material, and the raw steel material is melted to form molten steel compatible to the present invention. Thereafter, the molten steel is formed into steel slab by a continuous casting method, an ingot-making and ingot-rolling method or the like, and the steel slab is directly subjected to hot rolling or is cooled and is subjected to hot rolling by reheating.

**[0066]** With respect to a condition for carrying out the above-mentioned hot rolling, from a viewpoint of allowing the steel product to secure corrosion resistance and mechanical properties, it is necessary to control the microstructure by selecting a proper rolling temperature and a proper reduction ratio. To be more specific, it is necessary to heat a raw steel material having the component composition adjusted to the above-mentioned proper ranges at a temperature of 1000 to 1350°C, to apply hot rolling to the raw steel material at a finishing temperature of not lower than 750°C after heating, and to cool down the hot-rolled steel plate to a cooling stop temperature of not higher than 650°C and not lower than 450°C at 2°C/sec or more.

30 Slab heating temperature: 1000 to 1350°C

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**[0067]** When the heating temperature is below 1000°C, the deformation resistance is large and hence, hot rolling becomes difficult. On the other hand, when the heating temperature exceeds 1350°C, such heating generates flaws on a surface of the rolled steel plate, or a scale loss or a fuel basic unit is increased. The slab heating temperature is preferably set to a value which falls within a range from 1100 to 1300°C.

Hot roll finishing temperature: not lower than 750°C

**[0068]** It is necessary to set the hot roll finishing temperature to not lower than 750°C. When the hot roll finishing temperature is below 750°C, a standby time until a temperature of the steel product reaches a predetermined rolling temperature takes place and hence, rolling efficiency is lowered or a rolling force is increased due to the increase of the deformation resistance thus making rolling difficult.

[0069] Cooling rate after hot rolling: 2°C/sec or more, cooling stop temperature: not higher than 650°C and not lower than 450°C

With respect to a cooling rate after hot rolling, it is necessary to cool a hot-rolled steel plate at a cooling rate of 2°C/sec or more. This is because when the cooling rate is less than 2°C/sec, grains of ferrite become coarse so that a yield stress is lowered. On the other hand, although an upper limit of the cooling rate is not necessarily limited, it is sufficient that the cooling rate is not higher than approximately 80°C/sec by which normal water cooling is obtained.

Further, it is necessary to set the cooling stop temperature to not higher than 650°C and not lower than 450°C. When the cooling stop temperature exceeds 650°C, grains of ferrite become coarse so that a yield stress is lowered, while when the cooling stop temperature is below 450°C, a structural fraction of pearlite becomes less than 2%.

[0070] In general, a steel product used for a crude oil tank of a tanker or the like is used after enhancing local corrosion resistance and general corrosion resistance by applying coating such as primer which contains metal Zn or a Zn compound (hereinafter collectively referred to as "zinc primer" as a general term). Since zinc primer coating is applied to the steel product after shotblasting is applied to a surface of the steel product, depending on a surface state of a steel plate such as the degree of roughness, there may be a case where a background cannot be completely covered with a zinc primer coating, and it is necessary for the zinc primer coating to have a coating film thickness of a predetermined amount or more ( $15\mu$  or more, for example) for completely covering the whole surface of the steel product.

In this respect, the steel product for a crude oil tank of the present invention manufactured by the above-mentioned method using the raw steel material having the above-mentioned component composition is characterized in that the steel product exhibits excellent corrosion resistance (general corrosion resistance, local corrosion resistance) not only in a non-coated state but also after coating. Particularly, with respect to the steel product for a crude oil tank of the present invention, a coating amount of the primer which contains metal Zn or a Zn compound is set to 1.0g/m<sup>2</sup> or more in terms of a Zn content and hence, the local corrosion resistance and the general corrosion resistance can be remarkably enhanced. Further, by setting the coating amount of the primer to 2.5g/m<sup>2</sup> or more, the steel product for a crude oil tank of the present invention can acquire the more excellent local corrosion resistance and the more excellent general corrosion resistance. Although there is no upper limit for the zinc primer coating amount from a viewpoint of local corrosion resistance and general corrosion resistance, cutting property and weldability are lowered when a thickness of a coating film of zinc primer is increased and hence, it is preferable to set an upper limit of the thickness of the zinc primer to 100 µm. [0071] Although the relationship between the coating thickness of the zinc primer and the Zn content in the surface of the steel product depends on the Zn content in the zinc primer, in general, provided that the zinc primer has an average coating thickness of 15 µm or more, the zinc primer can cover the whole surface of the steel product so that the zinc primer can secure a coating amount of 1.0g/m<sup>2</sup> or more in terms of Zn content irrespective of a kind of the zinc primer. The Zn content in the surface of the steel plate can be obtained by cutting away a plurality of (for example, 10) small pieces having a size of 30mm square from the steel product, and by dissolving and collecting all coating film or a rust layer formed on a surface of the small piece, and by analyzing an amount of Zn contained in the recovered coating film or a rust layer.

### [Embodiment 1]

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[0072] Steels having component compositions shown in Table 1-1 to Table 1-4 are formed as molten steel using a converter or the like, the molten steel is formed into slabs having a thickness of 200mm by a continuous casting method, these slabs are heated at a temperature of 1200°C, the slabs are subjected to hot rolling with a finish rolling completion temperature of 800°C thus forming hot-rolled steel plates having a plate thickness of 25mm and, thereafter, the hot-rolled steel plates are cooled down to 580°C at a cooling rate of 30°C/sec thus manufacturing steel plates No. 1 to 35. With respect to these steel plates, an area rate of pearlite is measured by observing the microstructure at a position away from a surface of the steel plate by 1/4 of a plate thickness, and it is confirmed that the area rate of pearlite in the microstructure is 2% or more with respect to all these steel plates.

Further, with respect to the steel plates No. 1 and 8 shown in Table 1, the steel plates which differ in an area rate of pearlite in the microstructure are manufactured by changing a cooling rate and a cooling stop temperature after hot rolling. **[0073]** Next, specimens each having a length of 50mm, a width of 50mm and a thickness of 5mm and adopting a plane at the position away from a surface of the steel plate by 1/4 of a plate thickness as a testing surface are sampled from respective steel plates obtained in the above-mentioned manner, and shotblasting is applied to the surface. Then, corrosion test specimens having four kinds of surface conditions in total consisting of a specimen in a non-coated state with only shotblasting, and three kinds of specimens to which a zinc primer is applied at a thickness level of 5 to 10μm, a thickness level of 15 to 25μm and a thickness level of 50 to 70μm respectively are prepared. Thereafter, a sludge containing a crude oil content which is sampled from an actual tanker is uniformly applied to the testing surfaces of the specimens each having an area of 50mm x 50mm except for a center portion of 5mmφ which becomes a starting point of local corrosion. A content (coating amount) per unit area of Zn is proportional to a thickness of the zinc primer provided that a coating state is uniform, and when the thickness of the zinc primer is 15μm, 1.0g/m² or more can be secured in terms of a Zn coating amount irrespective of a kind of the zinc primer in general.

[0074] Next, the above-mentioned specimens are served in a local corrosion test in which the specimens are immersed in a test liquid in a testing device having the structure shown in Fig. 1 for one month. The testing device has the duplicate structure constituted of a corrosion test bath 2 and a constant-temperature bath 3, wherein a test liquid 6 which can cause local corrosion substantially equal to local corrosion which occurs in a bottom plate of an actual crude oil tank is poured into the corrosion test bath 2. As the test liquid 6, a solution which is prepared by introducing and dissolving a mixed gas 4 adjusted at a concentration ratio of CO<sub>2</sub>:13vol% + O<sub>2</sub>:5vol% + SO<sub>2</sub>: 0.01vol% + H<sub>2</sub>S:0.3vol% into a mother liquid is used, wherein the mother liquid is formed of a 10mass% NaCl aqueous solution containing 5000mass ppm of sulfate ion. An adjustable gas which is a balance of the mixed gas 4 is formed of an inert nitrogen gas. In the abovementioned testing device, the mixed gas 4 is continuously supplied to the test liquid 6 and hence, the test liquid 6 is constantly stirred. Further, a temperature of the test liquid 6 is held at a temperature of 40°C by adjusting a temperature of water 7 filled into a constant-temperature bath 3.

**[0075]** After the above-mentioned corrosion test is completed, rust formed on the surface of the specimen is removed, the corrosion configuration is observed with naked eyes, a depth of occurred local corrosion is measured using a depth meter, and local corrosion resistance is evaluated in accordance with following criteria.

<Evaluation of local corrosion resistance>

### [0076]

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AA @: no occurrence of local corrosion

A O: depth of local corrosion being less than 0.5mm

B  $\triangle$ : depth of local corrosion being 0.5mm or more and less than 1mm

C X: depth of local corrosion being 1mm or more

[0077] A result of the above-mentioned local corrosion test is shown in Table 2 and Table 3. As can be understood from Table 2, with respect to the steel plates of the present invention examples No. 1 to 21 compatible to the present invention, irrespective of the presence or non-presence of coating of the zinc primer, AA ⊚ or A ○ is given as the evaluation of local corrosion resistance. Even when local corrosion occurs in a non-coated state, a maximum depth of the local corrosion is suppressed to less than 0.5mm and hence, the steel plates of the present invention examples No. 1 to 21 possess favorable local corrosion resistance. Particularly, with respect to the steel plates to which the zinc primer having a thickness of 15μm or more is applied by coating, that is, with respect to the steel plates having a uniform coating state of the zinc primer and a Zn content of 1.0g/m² or more, all of steel plates No. 3 to 21 are given AA ⊚ as the evaluation of corrosion resistance so that it is confirmed that the local corrosion resistance is remarkably enhanced due to coating of the zinc primer.

On the other hand, the steel plates of the comparison examples No. 22 to 35 which do not satisfy the condition of the present invention, that is, the steel plate where at least one of contents of Cu, Cr, Sn is below the range of the present invention, the steel plate where contents of P, S, Mo exceed the range of the present invention or the steel plate where any of indexes of corrosion resistance A1 to A3 exceeds 0 is given C X or B  $\triangle$  as the evaluation of local corrosion resistance not only when the steel plate is not coated with the zinc primer but also when steel plate is coated with the zinc primer. That is, the steel plates of the comparison examples exhibit poor local corrosion resistance in a non-coated state, and exhibit the extremely small improvement of local corrosion resistance even when the steel plates are coated with the zinc primer.

Further, Table 3 shows a result of the evaluation of local corrosion resistance in a non-coated state in the same manner as the above using steel plates among which an area rate of pearlite in the microstructure is changed. It is confirmed from Table 3 that compared to the steel plates having the microstructure which is constituted of only bainite containing no pearlite, the steel plates having the microstructure which contains 2% or more of pearlite in terms of an area rate have tendency of enhancing the local corrosion resistance.

### [Embodiment 2]

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[0078] Rectangular specimens each having a length of 50mm, a width of 25mm and a thickness of 4mm and adopting a plane at the position away from a surface of the steel product by 1/4 of a plate thickness as a testing surface are sampled from respective steel plates No. 1 to 35 obtained in the embodiment 1, and shotblasting is applied to the surface and, thereafter, in the same manner as the embodiment 1, corrosion test specimens having four kinds of surface states in total consisting of a specimen in a non-coated state with only shotblasting, and three kinds of specimens to which a zinc primer is applied at a thickness level (proportional to a content per unit area of Zn) of 5 to  $10\mu$ m, a thickness level of 15 to  $25\mu$ m and a thickness level of 50 to  $70\mu$ m respectively are prepared. X-shaped cutting which reaches a surface of the steel product is formed on the testing surface of the specimen to which zinc primer is applied by coating for accelerating corrosion, and this portion is set as a simulated damaged portion. A damage of the coating is 1.0% in terms of an area rate.

[0079] Next, the above-mentioned specimens are served in a general corrosion test in which a testing device shown in Fig. 2 which can simulates a corrosion environment in a crude oil tank is used. The corrosion testing device is constituted of a corrosion test bath 12 and a temperature control plate 13. Water 16 is filled in the corrosion test bath 12 for keeping a saturated vapor pressure, and a temperature in the corrosion test bath 12 is held at 30°C. Further, the inside of the corrosion test bath is, for simulating a corrosion environment in a crude oil tank, filled with a mixed gas containing 13vol% of  $CO_2$ , 5vol% of  $O_2$ , 0.01vol% of  $SO_2$ , and 0.01vol% of  $H_2S$  and a balance of  $N_2$  under a saturated vapor pressure (dew point: 30°C). The specimen is mounted on a lower part of the temperature control plate mounted on an upper portion of the corrosion test bath. General corrosion due to dew condensation water is simulated using a heater and a cooling device in such a manner that 1 cycle (8 hours) consisting of 1 hour at 25°C, 5 hours at 50°C, temperature elevation time of 1 hour and temperature lowering time of 1 hour is carried out for 28 days. To impart a sulfate ion and a chloride ion to a surface (testing surface) of a specimen,  $500\mu$ L of an aqueous solution into which sodium sulfate and sodium chloride corresponding to 1000mass ppm of sulfate ion and 10000mass ppm of chloride ion are mixed is applied, and the aqueous solution is dried, and the specimen is used in the test. Further, after starting the test, a sulfate ion and a

chloride ion are supplied for every week.

**[0080]** After the above-mentioned corrosion test is completed, with respect to the specimen in a non-coated state, rust formed on the surface of the specimen is removed, a reduction amount of plate thickness due to corrosion is obtained based on a change in mass before and after the test, the reduction amount of plate thickness is converted into a corrosion plate thickness par 1 year, and general corrosion resistance is evaluated in accordance with the following criteria.

<Evaluation of general corrosion resistance of non-coated product>

### [0081]

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- A O: corrosion rate being less than 0.2mm/year
- B △: corrosion rate being 0.2mm/year or more and less than 0.8mm/year
- C X: corrosion rate being 0.8mm/year or more

**[0082]** Further, with respect to the primer coated product, an area rate of rust which progresses on a surface and below a coating film of each specimen is measured, and general corrosion resistance is evaluated in accordance with the following criteria.

<Evaluation of general corrosion resistance of primer-coated product>

### [0083]

A O: rust area rate being less than 25%

B  $\triangle$ : rust area rate being 25% or more and less than 50%

C X: rust area rate being 50% or more

**[0084]** A result of the above-mentioned general corrosion test is shown in Table 4 and Table 5. As can be understood from Table 4, with respect to the steel plates of the present invention examples No. 1 to 21 compatible to the present invention, all non-coated products are given  $A \bigcirc$  in the evaluation of general corrosion resistance so that steel plates have favorable general corrosion resistance. All products which are coated with the zinc primer are also given  $A \bigcirc$  in the evaluation of general corrosion resistance. That is, it is confirmed that the steel plates of the present invention examples possess the favorable general corrosion resistance in a non-coated state and, also possesses the more favorable general corrosion resistance due to coating of the zinc primer.

On the other hand, the steel plates No. 22 to 35 of the comparison examples are, not only with respect to a case where the steel plate is not coated with the zinc primer but also with respect to a case where the steel plate is coated with the zinc primer, given C X or B  $\triangle$  in the evaluation of general corrosion resistance and hence, it is understood that general corrosion resistance is deteriorated in all cases.

Further, Table 5 shows a result of the evaluation of general corrosion resistance which is obtained in accordance with criteria substantially equal to the above-mentioned criteria by carrying out a general corrosion test in a non-coated state using steel plates obtained in the embodiment 1 where an area rate of pearlite in the microstructure is changed. From Table 5, it is understood that the steel plate in which an area rate of pearlite is 2% or more has tendency of improving general corrosion resistance in the same manner as local corrosion resistance.

[Industrial applicability]

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**[0085]** The technique of the present invention is not limited to steel products for a crude oil tank such as an oil tank of a crude oil tanker or a tank for transporting or storing crude oil, and the technique of the present invention is preferably applicable to steel products in other fields where the steel products are used in similar corrosion environments including a case where primer coating or normal coating is used in combination.

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[Description of reference numerals and signs]

### [0086]

55 1, 11: test specimen

2, 12: corrosion test bath

3: constant-temperature bath

4, 14: introduced gas

5, 15: discharged gas6, 16: test liquid7: water

13: temperature control plate

[0087] [Table 1-1]

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Table 1-1

	steel				chemic	cal compor	nents (ma	ıss%) (con	tinued)				remarks
10	plate No.	С	Si	Mn	Р	S	sol.Al	N	Cu	Cr	Sn	Мо	
15	1	0.06	0.32	1.42	0.009	0.0019	0.032	0.0023	0.067	0.14	0.035	-	present invention example
	2	0.14	0.35	1.03	0.017	0.0016	0.035	0.0019	0.089	0.13	0.032	-	present invention example
20	3	0.05	0.25	1.49	0.012	0.0015	0.032	0.0022	0.086	0.17	0.029	-	present invention example
25	4	0.13	0.28	0.95	0.011	0.0016	0.029	0.0024	0.077	0.13	0.032	-	present invention example
	5	0.07	0.31	1.33	0.017	0.0010	0.033	0.0022	0.091	0.19	0.043	-	present invention example
30	6	0.14	0.33	0.99	0.008	0.0014	0.033	0.0026	0.066	0.11	0.033	-	present invention example
35	7	0.15	0.34	1.00	0.008	0.0013	0.037	0.0034	0.012	0.14	0.025	-	present invention example
	8	0.14	0.40	1.02	0.009	0.0016	0.033	0.0024	0.081	0.11	0.021	-	present invention example
40	9	0.06	0.33	1.39	0.010	0.0016	0.031	0.0026	0.054	0.13	0.036	-	present invention example
45	10	0.06	0.31	1.42	0.010	0.0012	0.036	0.0026	0.075	0.12	0.031	-	present invention example
	11	0.06	0.33	1.44	0.012	0.0019	0.037	0.0027	0.082	0.14	0.030	-	present invention example
50	12	0.06	0.33	1.46	0.007	0.0016	0.035	0.0024	0.010	0.15	0.032	-	present invention example
55	13	0.14	0.32	1.00	0.007	0.0018	0.034	0.0030	0.120	0.15	0.028	-	present invention example

(continued)

steel				chemi	cal compor	nents (ma	iss%) (con	tinued)				remarks
plate No.	С	Si	Mn	Р	S	sol.Al	N	Cu	Cr	Sn	Мо	
14	0.06	0.34	1.45	0.008	0.0018	0.035	0.0026	0.029	0.17	0.029	-	present invention example
15	0.15	0.31	0.96	0.006	0.0018	0.035	0.0026	0.057	0.16	0.028	-	present invention example
16	0.14	0.36	0.96	0.007	0.0008	0.036	0.0032	0.009	0.21	0.037	-	present invention example
17	0.06	0.25	1.38	0.006	0.0009	0.031	0.0031	0.140	0.14	0.032	-	present invention example
18	0.14	0.35	0.95	0.006	0.0009	0.036	0.0029	0.092	0.14	0.030	-	present invention example

[0088] [Table 1-2]

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Table 1-2

						Table 1-2				
	steel plate		chemi	cal com	oonents (mass	s%)	corrosion	resistance ir	ndex value	remarks
	No.	Ni	Sb	W	Nb,V,Ti,B	Ca,REM	A1	A2	A3	Temarks
30	1	-	-	-	-	-	-3.7	-	-	present invention example
35	2	-	-	-	-	-1.1	-	-	-	present invention example
40	3	0.092	-	-	-	-	-	-3.8	-	present invention example
40	4	0.049	0.06	-	-	-	-	-	-2.1	present invention example
45	5	0.089	-	0.05	-	-	-	-	-3.5	present invention example
50	6	0.082	0.06	0.06	-	-	-	-	-1.8	present invention example
	7	-	0.05	-	-	-	-	-	-1.2	present invention example
55	8	-	-	0.08	-	-	-	-	-1.9	present invention example

(continued)

	steel plate		chemi	cal com	ponents (mass	s%)	corrosion	resistance i	ndex value	romarka
	No.	Ni	Sb	W	Nb,V,Ti,B	Ca,REM	A1	A2	A3	remarks
5	9	-	0.06	0.07	-	-	-	-	-4.1	present invention example
10	10	0.034	0.06	0.07	Nb:0.012	1	-	-	-4.1	present invention example
15	11	-	0.11	0.08	Nb:0.007, V:0.004	-	-	-	-4.1	present invention example
, 6	12	-	0.04	0.10	V:0.006, Ti:0.012	-	-	-	-3.6	present invention example
20	13	-	0.04	0.05	Nb:0.008, Ti:0.010	-	-	-	-2.1	present invention example
25	14	0.053	0.10	0.04	Ti:0.013, B:0.0009	-	-	-	-4.0	present invention example
	15	-	0.06	0.05	B:0.0011	-	-	-	-1.8	present invention example
30	16	-	0.07	0.06	1	Ca:0.0020	-	-	-1.4	present invention example
35	17	0.068	0.05	0.06	-	Ca:0.0023	-	-	-4.3	present invention example
	18	0.001	0.05	0.06	Nb:0.008	Ca:0.0022	-	-	-2.2	present invention example

[0089] [Table 1-3]

( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( )	Tellialks	present invention example	present invention example	present invention example	comparison example													
(continued)	Mo	nd -	- pro	nd -	-	-	-	-	-	00 -	-	-	00 -	-	0.05 co	0.06	-	-
	Sn	0.031	0.036	0.037	0.001	0.042	0.001	0.035	0.001	0.026	0.037	0.032	0.032	0.001	0.036	0.049	0.033 -	0.028
	స	0.13	0.14	0.17	0.02	0.16	0.18	0.16	0.15	0.05		0.14	0.11	0.01	0.14	0.15	0.14	0.13
	Cu	0.086	0.093	0.052	0.001	0.030	0.081	0.002	0.003	0.009	0.006 0.21	0.007	0.003	0.100	0.066	0.043	690.0	0.086
chemical components (mass%)	z	0.0023	0.0025	0.0027	0.0036	0.0022	0.0024	0.0024	0.0025	0.0028	0.003	0.0031	0.0029	0.0025	0.0026	0.0028	0.0022	0.0029
mponent	sol.Al	0.031	0.031	0.036	0.035	0.036	0.033	0.036	0.031	0.033	0.035	0.031	0.032	0.034	0.034	0.035	0.034	0.036
hemical co	S	0.0008	0.0007	0.0006	0.0020	0.0036	0.0019	0.0016	0.0017	0.0019	0.0008	0.0007	0.0016	0.0013	0.0013	0.0006	6000.0	0.0120
O	۵	0.007	0.007	0.007	0.018	0.022	0.009	0.010	0.007	0.018	0.007	0.008	0.009	0.020	900.0	0.008	0.026	0.012
	Mn	1.01	1.37	1.00	1.15	1.14	1.33	0.99	1.06	1.42	1.03	1.51	0.97	1.37	1.02	1.32	0.95	1.43
	·is	0.33	0.34	0.33	0.35	0.35	0.33	0.33	0.32	0.36	0.36	0.22	0.29	0.33	0.36	0.32	0.31	0.34
	ပ	0.14	90.0	0.14	0.14	0.15	90.0	0.15	0.14	0.07	0.13	0.05	0.15	0.08	0.14	90.0	0.14	90.0
	steer prate No.	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
					•													

## [0090] [Table 1-4]

Table 1-4

5	steel plate		chemi	cal comp	oonents (mass	s%)	corrosion i	resistance ir	ndex value	remarks
	No.	Ni	Sb	W	Nb,V,Ti,B	Ca, REM	A1	A2	A3	Terriarks
10	19	0.042	0.06	0.05	Ti:0.011	Ca:0.0026	ı	ı		present invention example
10	20	0.053	0.06	0.06	V:0.004, Ti:0.012	Ca:0.0022	1	-		present invention example
15	21	0.039	0.05	0.05	Ti:0.010	REM: 0.0019	ı	ı		present invention example
	22	ı	ı	1	ı	-	9.3	1		comparison example
20	23	0.011	ı	1	-	-	1	0.2		comparison example
	24	-	ı	1	-	-	-2.8	-		comparison example
25	25	-	-	-	-	-	<u>2.8</u>	-		comparison example
	26	0.033	0.05	0.06	Nb:0.009, Ti:0.010	-	-	-		comparison example
30	27	0.100	0.04	0.05	ı	-	ı	ı		comparison example
	28	0.078	ı	0.06	-	Ca:0.0025	ı	1		comparison example
35	29	0.068	0.04	0.06	Ti:0.012	Ca:0.0023	-	-		comparison example
	30	-	0.05	0.05	Nb:0.012, Ti:0.011	-	-	-		comparison example
40	31	-	0.06	0.05	-	-	-	-		comparison example
	32	-	0.04	0.06	-	-	-	-		comparison example
45	33	0.044	0.06	0.05	Nb:0.008, V:0.006, Ti:0.010	Ca:0.0019	-	-		comparison example
	34	0.057	0.05	0.05	Ti:0.011	Ca:0.0020	-	-		comparison example
50	35	-	0.05	0.05	-	-	-	-		comparison example

[0091] [Table 2]

Table 2

romarko	roduct	mer-coated p	zinc-pri		
- remarks	5-25 50-70	kness (μm) 1	average thic	non-coated product	steel plate No.
present invention examp			5-10		
present invention examp	AA ⊚	<b>A</b> O	A O	ΑO	1
present invention examp	AA ⊚	<b>A</b> O	A O	ΑO	2
present invention examp	AA ⊚	AA ⊚	A O	A O	3
present invention examp	AA ⊚	AA ⊚	A O	ΑO	4
present invention examp	AA ⊚	AA ⊚	A O	A O	5
present invention examp	AA ⊚	AA ⊚	ΑO	A O	6
present invention examp	AA ⊚	AA ⊚	A O	ΑO	7
present invention examp	AA ⊚	AA ⊚	AA ⊚	<b>A</b> O	8
present invention examp	AA ⊚	AA ⊚	AA ⊚	A O	9
present invention examp	AA ⊚	AA ⊚	A O	A O	10
present invention examp	AA ⊚	AA ⊚	<b>A</b> O	A O	11
present invention examp	AA ⊚	AA ⊚	<b>A</b> O	A O	12
present invention examp	AA ⊚	AA ⊚	A O	A O	13
present invention examp	AA ⊚	AA ⊚	<b>A</b> O	<b>A</b> O	14
present invention examp	AA ⊚	AA ⊚	A O	A O	15
present invention examp	AA ⊚	AA ⊚	AA ⊚	A O	16
present invention examp	AA ⊚	AA ⊚	AA ⊚	A O	17
present invention examp	AA ⊚	AA ⊚	AA ⊚	A O	18
present invention examp	AA ⊚	AA ⊚	AA ⊚	ΑO	19
present invention examp	AA ⊚	AA ⊚	AA ⊚	<b>A</b> O	20
present invention examp	AA ⊚	AA ⊚	AA ⊚	ΑO	21
comparison example	СХ	СХ	СХ	CX	22
comparison example	В∆	В∆	В∆	CX	23
comparison example	В∆	В∆	СХ	CX	24
comparison example	СХ	СХ	СХ	CX	25
comparison example	В∆	В∆	В∆	CX	26
comparison example	В∆	В∆	В∆	CX	27
comparison example	В△	В∆	В△	СХ	28
comparison example	СХ	СХ	СХ	СХ	29
comparison example	В∆	В∆	В∆	СX	30
comparison example	В△	В∆	В△	СХ	31
comparison example	СХ	СХ	СХ	СХ	32
comparison example	В△	СХ	СХ	СХ	33
comparison example	В∆	СХ	СХ	CX	34

### (continued)

		zinc-pri	mer-coated p	roduct	remarks
steel plate No.	non-coated product	average thic	kness (μm) 1	5-25 50-70	remarks
		5-10			present invention example
35	CX	СХ	СХ	В△	comparison example

<Evaluation of local corrosion resistance>

AA : no occurrence of local corrosion

A  $\bigcirc$ : depth of local corrosion less than 0.5mm

B  $\triangle$ : depth of local corrosion 0.5mm or more and less than 1mm

C X: depth of local corrosion 1 mm or more

### [0092] [Table 3]

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### Table 3

		l .	on of local resistance	remarks
	steel plate No.	1	8	
	less than 2%	В 🛆	A ()	comparison example of claim 6
pearlite	2% or more and less than 5%	A O	A ()	present invention example
area rate	6% or more and less than 10%	A O	A O	present invention example
	11% or more	A O	A O	present invention example

<Evaluation of local corrosion resistance>

AA ©: no occurrence of local corrosion

A O: depth of local corrosion less than 0.5mm

В Δ: depth of local corrosion 0.5mm or more and less than 1.0mm

С X: depth of local corrosion 1.0mm or more

### [0093] [Table 4]

			Table 4		
		2	zinc-primer-coated produ	ıct	remarks
steel plate No.	non-coated product		average		Temarks
		5-10	thickness(µm) 15-25	50-70	present invention example
1	A O	A O	A O	A O	present invention example
2	A O	A O	A O	A O	present invention example
3	A O	A O	A O	A O	present invention example
4	A O	A O	A O	A O	present invention example
5	A O	A O	A O	A O	present invention example
6	A O	A O	<b>A</b> O	ΑO	present invention example
7	A O	A O	A O	ΑO	present invention example
8	A O	A O	A O	A O	present invention example
9	A O	A O	A O	ΑO	present invention example
10	A O	A O	A O	A O	present invention example

(continued)

		2	zinc-primer-coated produ	remarks	
steel plate No.	non-coated product		average		
		5-10	thickness(μm) 15-25	50-70	present invention ex
11	АО	A O	<b>A</b> O	ΑO	present invention ex
12	АО	A O	<b>A</b> O	A O	present invention ex
13	A O	A O	A O	A O	present invention ex
14	A O	A O	A O	A O	present invention ex
15	A O	A O	A O	A O	present invention ex
16	A O	A O	A O	A O	present invention ex
17	A O	A O	A O	A O	present invention ex
18	A O	A O	A O	A O	present invention ex
19	<b>A</b> O	A O	<b>A</b> O	A O	present invention ex
20	<b>A</b> O	A O	A O	A O	present invention ex
21	<b>A</b> O	A O	A O	<b>A</b> O	present invention ex
22	CX	СХ	CX	СХ	comparison example
23	CX	СХ	CX	В∆	comparison example
24	CX	В∆	В△	В∆	comparison example
25	СХ	СХ	CX	В∆	comparison example
26	CX	СХ	CX	В∆	comparison example
27	CX	В∆	В∆	В∆	comparison example
28	CX	С	CX	В∆	comparison example
29	СХ	В∆	В△	В∆	comparison example
30	СХ	СХ	В∆	В∆	comparison example
31	CX	СХ	В△	В∆	comparison example
32	СХ	СХ	CX	В∆	comparison example
33	CX	СХ	В∆	В∆	comparison example
34	CX	СХ	В△	В∆	comparison example
35	СХ	СХ	В∆	В△	comparison example

[0094] [Table 5]

<Evaluation of general corrosion resistance of primer-coated product>

A  $\bigcirc$ :rust area rate being less than 25%

C X:rust area rate 50% or more

B  $\triangle$ :rust area rate 25% or more and less than 50%

Table 5

Evaluation of local corrosion resistance remarks steel plate No. 8 less than 2% Δ comparison example of claim 6 В В Δ 2% or more and less than 5% A O A O present invention example pearlite area rate 6% or more and less than 10% A OA Opresent invention example 11% or more A O A O present invention example

<Evaluation of general corrosion resistance of non-coated product>

A : corrosion rate less than 0.2mm/year

B Δ: corrosion rate 0.2mm/year or more and less than 0.8mm/year

C X: corrosion rate 0.8mm/year or more

#### 20 Claims

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1. A corrosion resistance steel product for a crude oil tank having a composition which contains 0.001 to 0.16mass% C, 1.5mass% or less Si, 0.1 to 2.5mass% Mn, 0.025masts% or less P, 0.01mass% or less S, 0.005 to 0.1mass% Al, 0.001 to 0.008mass% N, 0.008 to 0.35mass% Cu, more than 0.1mass% and 0.5mass% or less Cr, 0.005 to 0.3mass% Sn, and 0.01mass% or less Mo, and Fe and unavoidable impurities as a balance, and a value of A1 defined by a following formula (1) is set to 0 or less.
Note

$$A1=28\times[C]+2000\times[P]^2+27000\times[S]^2+0.0083\times(1/[Cu])+0.027\times$$
 $(1/[Cr])+95\times[Mo]+0.00098\times(1/[Sn])-6 \dots (1),$ 

35 wherein

[C], [P], [S], [Cu], [Cr], [Mo] and [Sn] are contents of respective elements (mass%).

2. The corrosion resistance steel product for a crude oil tank according to claim 1, wherein the corrosion resistance steel product further contains, in addition to the above-mentioned component composition, 0.005 to 0.4mass% Ni, and a value of A2 defined by a following formula (2) is set to 0 or less.

Note

$$A2=28\times[C]+2000\times[P]^{2}+27000\times[S]^{2}+0.0083\times(1/[Cu])+2\times[Ni]$$

$$+0.027\times(1/[Cr])+95\times[Mo]+0.00098\times(1/[Sn])-6 ... (2),$$

wherein

[C], [P], [S], [Cu], [Ni], [Cr], [Mo] and [Sn] are contents of respective elements (mass%).

3. The corrosion resistance steel product for a crude oil tank according to claim 1 or 2; wherein the corrosion resistance steel product further contains, in addition to the above-mentioned component composition, one kind or two kinds selected from 0.001 to 0.5mass% W and 0.005 to 0.3mass% Sb, and a value of A3 defined by a following formula (3) is set to 0 or less.
Note

wherein

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[C], [P], [S], [Cu], [Ni], [Cr], [Mo], [Sn], [Sb] and [W] are contents of respective elements (mass%).

- **4.** The corrosion resistance steel product for a crude oil tank according to any one of claims 1 to 3, wherein the corrosion resistance steel product further contains, in addition to the above-mentioned component composition, one kind or two kinds or more selected from 0.002 to 0.1mass% Nb, 0.002 to 0.1mass% V, 0.001 to 0.1mass% Ti and 0.01mass% or less B.
- **5.** The corrosion resistance steel product for a crude oil tank according to any one of claims 1 to 4, wherein the corrosion resistance steel product further contains, in addition to the above-mentioned component composition, one kind or two kinds selected from 0.0002 to 0.005mass% Ca and 0.0005 to 0.015mass% REM.
- **6.** The corrosion resistance steel product for a crude oil tank according to any one of claims 1 to 5, wherein a microstructure of the steel product at a position away from a surface of the steel product by 1/4 of a plate thickness contains 2 to 20% of pearlite in terms of an area rate.
- 7. The corrosion resistance steel product for a crude oil tank according to any one of claims 1 to 6, wherein a coating film which contains metal Zn or a Zn compound is formed on a surface of the steel product.
  - **8.** The corrosion resistance steel product for a crude oil tank according to claim 7, wherein a content of Zn in the coating film is 1.0g/m² or more.
  - **9.** A method of manufacturing a corrosion resistance steel product for a crude oil tank, wherein a raw steel material having the component composition according to any one of claims 1 to 5 is heated to 1000 to 1350°C and, thereafter, hot rolling is applied to the raw steel material at a rolling finish temperature of not lower than 750°C, and a rolled plate is cooled to a cooling stop temperature of not higher than 650°C and not lower than 450°C at a cooling rate of 2°C/sec or more.
  - 10. A crude oil tank which is **characterized by** using the steel product according to any of claims 1 to 8.

FIG.1

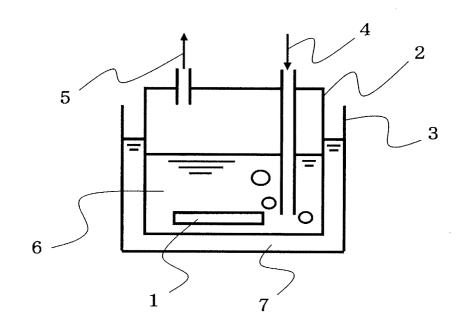
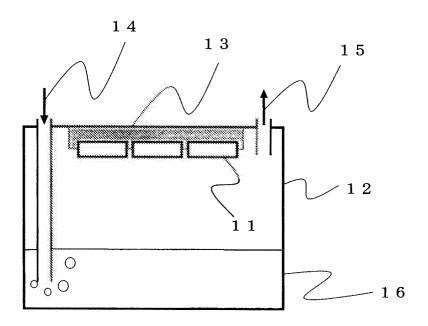


FIG.2



#### INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/051550

<ul> <li>A. CLASSIFICATION OF SUBJE</li> </ul>	CT MATTER
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C22C38/00(2006.01)i, C21D8/02(2006.01)i, C22C38/38(2006.01)i, C22C38/60 (2006.01)i

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

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) C22C38/00, C21D8/02, C22C38/38, C22C38/60

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 Kokai Jitsuyo Shinan Koho 1971-2010 Toroku Jitsuyo Shinan Koho 1994-2010

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

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

Further documents are listed in the continuation of Box C.

Special categories of cited documents:

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
А	JP 2007-291494 A (JFE Steel Corp.), 08 November 2007 (08.11.2007), & EP 2009125 A1	1-10
A	JP 2008-274379 A (Kobe Steel, Ltd.), 13 November 2008 (13.11.2008), (Family: none)	1-10
A	JP 2001-214236 A (Nippon Steel Corp.), 07 August 2001 (07.08.2001), (Family: none)	1-10
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