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(54) DUPLEX STAINLESS STEEL MATERIAL AND DUPLEX STAINLESS STEEL TUBE

(57) The present invention pertains to a duplex stainless steel material including a ferrite phase and an austenite phase. The present invention is characterized in that: the steel material contains, as metal component composition, at least one X-group element selected from 0.01 to 0.50 mass% of V, 0.0001 to 0.0500 mass% of Ti, 0.0005 to 0.0500 mass% of Nb, and 0.01 to 0.50 mass% of Ta, the steel material has composite inclusions or has composite inclusions and inclusions; each of the inclusions includes at least one of an oxide, a sulfide, and an oxysulfide; each of the composite inclusions includes one of the inclusions as a nucleus and includes an outer shell existing around the nucleus and having a carbide or a nitride containing Cr and the at least one X-group element, and the proportion of the number of the composite inclusions with respect to the total number of the inclusions is 30% or more.

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Description

Technical Field

[0001] The present invention relates to a duplex stainless steel material and a duplex stainless steel tube.

Background Art

[0002] A stainless steel material is a material spontaneously forming a stable surface film mainly including Cr oxides referred to as a passive film in a corrosive environment to exhibit corrosion resistance. Particularly, a duplex stainless steel material including a ferrite phase and an austenite phase has excellent strength properties compared with austenitic stainless steel or ferritic stainless steel and has good pitting corrosion resistance and stress corrosion cracking resistance. Due to such features, a duplex stainless steel material is used as structural materials in seawater environments such as umbilical tubes, seawater desalination plants, and LNG (Liquefied Natural Gas) vaporizers, as well as structural materials for oil well tubes and various chemical plants.

[0003] However, in a case where the use environment contains a large amount of corrosive substances such as chlorides, hydrogen sulfide, and carbon dioxide, local corrosion, a so-called pitting corrosion, sometimes occurs in the duplex stainless steel material starting from inclusions and defects in the passive film of the duplex stainless steel material. Further, in structural crevices of the pipes, flanges, and the like of the duplex stainless steel material, corrosive substances such as chloride ions are concentrated inside the crevices to result in a severer corrosive environment and, further, oxygen concentration cells are formed between the outside and the inside of the crevices, which sometimes further promote local corrosion inside the crevices to generate a so-called crevice corrosion. Further, local corrosion such as pitting corrosion and crevice corrosion sometimes forms origins of stress corrosion cracking.

[0004] As a countermeasure to cope with such a problem, Patent Literature 1, for example, discloses a duplex stainless steel with improved corrosion resistance by defining the PREW value to be 40 or more through control of the content of Cr, Mo, N, and W. Also, Patent Literature 2 discloses a duplex stainless steel excellent in corrosion resistance and hot workability by control of the content of B, T, and the like in addition to control of the content of Cr, Mo, W, and N.

[0005] Also, Non-Patent Literature 1 experimentally shows that, in stainless steel, MnS in the in-steel inclusions forms origins of local corrosion (pitting corrosion). Further, according to the technique disclosed in Patent Literature 3, an amount of S is reduced to 3 ppm or less by using a CaO crucible and $CaO\text{-}CaF_2\text{-}Al_2O_3$-based slags in a vacuum melting furnace in order to decrease in the steel sulfide-based inclusions that give adverse effects on the hot workability and the corrosion resistance.

[0006] Also, Patent Literature 4 discloses a method for producing a stainless steel slab having an austenite-ferrite duplex phase excellent in hot workability with controlled form of the ferrite phase by finely dispersing composite nonmetallic inclusions of Ti-based nitride and Mg-based oxide from the surface layer of the slab down to 10 mm depth in an arbitrary cross-section.

[0007] Also, Patent Literature 5 discloses a method for producing a ferrite-based stainless steel with improved corrosion resistance by preventing pitting corrosion starting from the inclusions and by miniaturizing the structure of the slab through finely dispersing composite nonmetallic inclusions in which Ti-based oxide or nitride is generated using an Mg-based inclusion as a nucleus.

[0008] Also, Patent Literature 6 discloses a method for producing a low alloy steel excellent in pitting corrosion resistance without inducing sulfide stress cracking starting from pitting corrosion by preventing the pitting corrosion starting from inclusions through finely dispersing the inclusions having an outer shell of Ti and/or Nb carbonitride around a nucleus of Al-Ca-based oxysulfide.

[0009] Also, Patent Literature 7 discloses a method for producing a duplex stainless steel excellent in local corrosion resistance in which Ta-containing sulfide-oxide-based composite inclusions having a major diameter of 1 μm or more are present in a number of 500 or less per 1 mm^2 of a cross-section perpendicular to a working direction, and the content of Ta in the sulfide-oxide-based composite inclusions is defined to be 5 atom% or more, so that the sulfide-based inclusions contained in usual stainless steel are modified to Ta-containing sulfide-oxide-based composite inclusions.

[0010] However, according to the techniques disclosed in Patent Literatures 1 to 7, the passive film tends to be unstable because the continuity of the passive film decreases at an interface between the ferrite phase and the austenite phase or at an interface between the matrix metal and the inclusions such as oxides or sulfides that are unavoidably formed in the steel. For this reason, there has been room for making studies on the inclusions that cause local corrosion.

Citation List

Patent Literature

[0011]

Patent Literature 1: Japanese Unexamined Patent Publication No. H05(1993)-132741
Patent Literature 2: Japanese Unexamined Patent Publication No. H08(1996)-170153
Patent Literature 3: Japanese Unexamined Patent Publication No. H03(1991)-291358
Patent Literature 4: Japanese Unexamined Patent Publication No. 2002-69592
Patent Literature 5: Japanese Unexamined Patent Publication No. 2000-212704
Patent Literature 6: Japanese Patent No. 3864921
Patent Literature 7: Japanese Unexamined Patent Publication No. 2015-110828

Non-Patent Literature

[0012] Non-Patent Literature 1: Izumi MUTO and others, "FERRUM" Vol. 17(2012), No. 12, pp. 858-863

Summary of Invention

[0013] The present invention has been made in view of such circumstances, and a principal object thereof is to provide a duplex stainless steel material and a duplex stainless steel tube exhibiting excellent corrosion resistance.

[0014] Among the inventions disclosed in the specification of the present application, a summary of representative inventions will be briefly described as follows. In other words, a duplex stainless steel material according to one aspect of the present invention includes a ferrite phase and an austenite phase, in which the duplex stainless steel material contains, as metal component composition, at least one X-group element selected from 0.01 to 0.50 mass% of V, 0.0001 to 0.0500 mass% of Ti, 0.0005 to 0.0500 mass% of Nb, and 0.01 to 0.50 mass% of Ta; the duplex stainless steel material has composite inclusions or has composite inclusions and inclusions; each of the inclusions includes at least one of an oxide, a sulfide, and an oxysulfide; each of the composite inclusions includes one of the inclusions as a nucleus and includes an outer shell existing around the nucleus and having a carbide or a nitride containing Cr and the at least one X-group element; and a proportion of a number of the composite inclusions with respect to a total number of the inclusions is 30% or more.

[0015] Also, a duplex stainless copper tube according to another aspect of the present invention comprises the duplex stainless steel material described above.

[0016] With the duplex stainless steel material and the duplex stainless steel tube according to the present invention, excellent corrosion resistance can be exhibited.

Brief Description of Drawings

[0017]

FIG. 1 is a schematic enlarged sectional view illustrating a composite inclusion and an inclusion of a duplex stainless steel material according to the present invention.
FIG. 2 is a schematic enlarged descriptive view illustrating the composite inclusion in an A-region of FIG. 1 in the duplex stainless steel material according to the present invention.
FIG. 3 is a schematic enlarged descriptive view illustrating the inclusion in a B-region of FIG. 1 in the duplex stainless steel material according to the present invention.
FIG. 4 is a schematic enlarged descriptive view illustrating a form of the composite inclusion in the duplex stainless steel material according to the present invention.
FIG. 5 is a descriptive view showing a difference between a process of a heat treatment in a preferable method for producing a duplex stainless steel material according to the present invention and a process of a heat treatment in a method for producing a duplex stainless steel material according to the prior art.
FIG. 6 is a graph diagram showing a relationship between a pitting potential and an inclusion covering rate by which the inclusion is covered with an outer shell.
FIG. 7 is a graph diagram showing a relationship between a pitting potential and a Ta content in the metal components of the outer shell by classifying the duplex stainless steel materials according to the present invention into two types depending on a value of PRE.
FIG. 8 is a graph diagram showing a relationship between a pitting potential and a Ta/Ti ratio by classifying the

duplex stainless steel materials according to the present invention into two types depending on the value of PRE.

Description of Embodiments

<Duplex stainless steel material>

[0018] A duplex stainless steel material and a duplex stainless steel tube according to an embodiment of the present invention will be described. Here, composite inclusions 20 and core inclusions 10 will be described with reference to FIGS. 1 to 3 as appropriate.

[0019] The duplex stainless steel material according to the present embodiment is a duplex stainless steel material including a ferrite phase and an austenite phase. This duplex stainless steel material contains the basic metal component composition and contains Cr and at least one element selected from V, Ti, Nb, and Ta in predetermined amounts. Here, in the present embodiment, V, Ti, Nb, and Ta are comprehensively referred to as "X-group elements". Further, the duplex stainless steel material has composite inclusions 20, where each of the composite inclusions 20 includes, as a nucleus, an inclusion 10 including at least one of oxides, sulfides, and oxysulfides and includes an outer shell 15 existing around the nucleus and having a carbide or a nitride containing Cr and at least one of the aforementioned X-group elements, and the proportion of the number of the composite inclusions 20 with respect to the total number of the inclusions 10 containing an oxide, sulfide, or oxysulfide is controlled to be 30% or more.

[0020] Here, when the duplex stainless steel material contains a predetermined amount of Ta among the X-group elements, it is preferable that the Ta content in the metal components of the carbide or nitride of the outer shell 15 is 5 atom% or more. Also, when the duplex stainless steel material contains Ta and Ti, it is preferable that the Ta content is 25 times or more as large as the Ti content in terms of mass%. Further, as one example of the basic metal component composition, the duplex stainless steel material preferably contains C, Si, Mn, S, Ni, Mo, N, Cr, and O in predetermined amounts, with the balance being Fe and unavoidable impurities. Also, the duplex stainless steel material preferably further contains one or two selected from Mg and Al in predetermined amounts. Furthermore, in the duplex stainless steel material, it is possible to adopt a constitution in which the metal component composition further contains Ca in a predetermined amount, a constitution in which the metal component composition further contains one or both of Co and Cu in predetermined amounts, or a constitution in which the metal component composition further contains B in a predetermined amount.

[0021] Hereafter, each constitution of the duplex stainless steel material will be described.

(Steel material structure)

[0022] The duplex stainless steel material according to the present embodiment includes two phases of a ferrite phase and an austenite phase. In the duplex stainless steel material including the ferrite phase and the austenite phase, ferrite phase stabilizing elements such as Cr and Mo tend to be concentrated in the ferrite phase, and austenite phase stabilizing elements such as Ni and N tend to be concentrated in the austenite phase. At this time, when the area ratio of the ferrite phase is less than 30% or more than 70%, difference in the concentration of the elements contributing to the corrosion resistance such as Cr, Mo, Ni, and N between the ferrite phase and austenite phase is excessively large. For this reason, unless the area ratio of the ferrite phase is within the aforesaid range in the duplex stainless steel material, the ferrite phase or the austenite phase whichever is inferior in the corrosion resistance tends to be selectively corroded to deteriorate the corrosion resistance. Accordingly, in the duplex stainless steel material, it is also recommended to optimize the area ratio between the ferrite phase and the austenite phase, and the area ratio of the ferrite phase is preferably 30 to 70% and more preferably 40 to 60% from the viewpoint of the corrosion resistance. The area ratio of the ferrite phase described above can be optimized by adjusting the contents of the ferrite phase stabilizing elements and the austenite phase stabilizing elements.

[0023] Further, in the duplex stainless steel material according to the present embodiment, a different phase such as a σ-phase is also allowable in addition to the ferrite phase and the austenite phase to such an extent that various characteristics such as corrosion resistance and mechanical properties are not impaired. A sum of the area ratios of the ferrite phase and the austenite phase relative to the whole phases of the steel material is preferably defined to be 95% or more, and more preferably 97% or more.

(Inclusions in steel material)

[0024] The duplex stainless steel material of the present embodiment contains Cr and at least one X-group element selected from the X-group consisting of V, Ti, Nb, and Ta in predetermined amounts together with the basic metal component composition. Further, the duplex stainless steel material has composite inclusions 20, where each of the composite inclusions 20 includes a core inclusion 10 including at least one of oxides, sulfides, and oxysulfides and

includes an outer shell 15 existing around the core inclusion 10 and having a carbide or a nitride containing Cr and at least one X-group element, and the proportion of the number of the composite inclusions 20 with respect to the total number of the inclusions 10 containing an oxide, sulfide, or oxysulfide is controlled to be 30% or more. For this reason, even when pitting corrosion occurs in oxide, sulfide, and oxysulfide in the composite inclusion 20, development of the pitting corrosion is suppressed by the outer shell 15 of the carbide or nitride of Cr and the X-group element excellent in corrosion resistance. In the duplex stainless steel material, the proportion of the number of the composite inclusions 20 with respect to the total number of the inclusions 10 can be adjusted to 30% or more, that is, [composite inclusions 20] / [inclusions 10] $\times$ 100 can be adjusted to 30% or more, by performing hot working (hot forging) and a solid solution forming heat treatment at a predetermined temperature for a predetermined period of time on an ingot that has been subjected to adjustment of the metal component composition to a constitution shown in the present embodiment, as will be described later.

(Oxide-sulfide)

[0025] In the duplex stainless steel of the present embodiment, the oxide is preferably controlled to be an Al-Mg-based oxide as much as possible from the viewpoint of the corrosion resistance and the rate of covering the inclusion 10 with the outer shell 15. When the amount of addition of Mg is insufficient, the oxide will be an Al-Ca-based oxide that may possibly be dissolved in an oxidizing atmosphere. On the other hand, when the amount of addition of Mg is in excess, an Mg oxide inferior in corrosion resistance is deposited in a large amount, so that the corrosion resistance of the steel material decreases. By setting the amount of addition of Mg to be within a range defined in the present invention, the oxide can be controlled to be an Al-Mg oxide excellent in corrosion resistance, and also, since the outer shell 15 of nitride is provided, the pitting corrosion starting from the inclusion 10 can be reduced.

[0026] Also, when a sulfide of Mn is deposited as the inclusion 10, the outer shell 15 of nitride is destroyed by deformation of the sulfide of Mn during the working, so that an improvement in corrosion resistance by the outer shell 15 of nitride cannot be expected. For this reason, the sulfide is preferably controlled to be a sulfide of Ca as much as possible by addition of Ca.

[0027] Next, a numerical value range of the metal component composition constituting one example of the duplex stainless steel material as well as the reason for limiting to the range will be described. First, the X-group elements and Cr will be described, and later, the basic metal component composition will be described.

(X-group elements: 0.01 to 0.50 mass% of V, 0.0001 to 0.0500 mass% of Ti, 0.0005 to 0.0500 mass% of Nb, and 0.01 to 0.50 mass% of Ta)

[0028] The X-group element that is at least one element selected from V, Ti, Nb, and Ta produces, likewise Cr, an effect of forming a composite inclusion 20 having an outer shell 15 of carbide or nitride of the X-group element around a nucleus, which is an inclusion 10 made of at least one of oxide, sulfide, and oxysulfide, by bonding with C and N. Further, Ta among the X-group elements can cover the inclusion 10 of oxide, sulfide, or oxysulfide, which gives an adverse effect on the corrosion resistance, with the outer shell 15 which is a carbonitride layer containing Ta having higher corrosion resistance. Accordingly, Ta is an element that improves the corrosion resistance.

[0029] Due to the reason given above, the upper limit and the lower limit for the X-group elements are defined as follows. That is, the V content is defined to be 0.01 mass% or more, and preferably 0.05 mass% or more. Also, the Ti content is defined to be 0.0001 mass% or more, preferably 0.0003 mass% or more, and more preferably 0.0010 mass% or more. Further, the Nb content is defined to be 0.0005 mass% or more, and preferably 0.0010 mass% or more. The Ta content is defined to be 0.01 mass% or more, preferably 0.02 mass% or more, and more preferably 0.03 mass% or more.

[0030] Also, the V content and the Ta content are each defined to be 0.50 mass% or less, preferably 0.40 mass% or less, and more preferably 0.30 mass% or less. Further, the Ti content and the Nb content are each defined to be 0.0500 mass% or less, preferably 0.0400 mass% or less, more preferably 0.0300 mass% or less, still more preferably 0.0200 mass% or less, and further more preferably 0.0050 mass% or less. Also, a sum of the contents of V, Ti, Nb, and Ta is preferably 0.02 to 1.00 mass% in consideration of the corrosion resistance and the hot workability.

[0031] Also, when Ta is contained in a range of 0.01 to 0.50 mass% as the X-group element, it is possible to adopt a constitution in which the outer shell 15 contains Ta in an amount satisfying the following formula (1):

$$([Ta] / [M]total) \times 100 \geq 5 \text{ ..... formula (1)}$$

where [Ta] represents the number of Ta atoms contained in the outer shell 15, and [M]total represents the total number of atoms of the metal elements contained in the outer shell 15.

[0032] When the Ta content (atom%) satisfies the formula (1), the corrosion resistance of the outer shell 15 of carbide or nitride is improved, thereby producing a higher effect of suppressing the development of pitting corrosion and improving the corrosion resistance of the steel material. Here, in order that the content of Ta in the outer shell 15 satisfies the formula (1), Ta needs to be added in a range of 0.01 to 0.50 mass%, and predetermined production conditions described later need to be satisfied.

[0033] Also, in the present embodiment, the inclusion 10 is more desirably controlled to be an Mg-Al-based oxide excellent in corrosion resistance.

[0034] Also, when 0.01 to 0.50 mass% of Ta and 0.0001 to 0.0500 mass% of Ti are contained as the X-group elements, it is possible to adopt a constitution in which the (Ta mass% / Ti mass%) ratio satisfies the following formula (2).

$$\text{Ta mass\% / Ti mass\%} \geq 25 \quad \text{..... formula (2)}$$

[0035] When the (Ta mass% / Ti mass%) ratio satisfies the formula (2), the Ta-containing carbide or nitride constituting the outer shell 15 more readily covers the inclusion 10, thereby producing a higher effect of suppressing the development of pitting corrosion and improving the corrosion resistance of the steel material.

[0036] Next, one example of the basic metal component composition in the steel material will be described. Here, the basic metal component composition is preferably defined to be within the following range in consideration of the performance such as workability that is needed for the material to become a product, and the conditions, production costs, and the like to turn the metal structure into a duplex structure.

(C: 0.100 mass% or less)

[0037] When C is contained in an excessive amount, the hot workability decreases. When C is contained in a predetermined amount or less, unnecessary carbide is not generated, thereby producing an effect of suppressing decrease in the corrosion resistance. For this reason, the C content is defined to be 0.100 mass% or less. Here, the C content is preferably as small as possible, so that the C content is preferably defined to be 0.080 mass% or less, more preferably 0.060 mass%. Also, it is possible to adopt a constitution in which C is not contained in the steel material, that is, the C content may be 0 mass%.

(Si: 0.10 to 2.00 mass%)

[0038] Si is an essential element for deoxidization and stabilization of the ferrite phase. In order to obtain such effects, the Si content is defined to be 0.10 mass% or more, preferably 0.15 mass% or more, and more preferably 0.20 mass% or more. However, Si contained in an excessive amount decreases the workability, so that the Si content is defined to be 2.00 mass% or less, preferably 1.50 mass% or less, and more preferably 1.00 mass% or less.

(Mn: 0.10 to 3.00 mass%)

[0039] Mn, likewise Si, has a deoxidization effect and further, Mn is an essential element for ensuring strength. In order to obtain such effects, the Mn content is defined to be 0.10 mass% or more, preferably 0.15 mass% or more, and more preferably 0.20 mass% or more. However, Mn contained in an excessive amount invites toughness deterioration or deterioration of the corrosion resistance, so that the Mn content is defined to be 3.00 mass% or less, preferably 2.50 mass% or less, and more preferably 2.00 mass% or less.

(S: 0.0100 mass% or less)

[0040] S, likewise P, is an element that is unavoidably mingled as an impurity and is bonded with Mn or the like to form a sulfide inclusion 10, thereby deteriorating the corrosion resistance or hot workability. Further, S contained in an excessive amount invites insufficient covering of the sulfide inclusion 10 with the outer shell 15 containing the X-group element, thereby decreasing the corrosion resistance. For this reason, the S content is defined to be 0.0100 mass% or less, preferably 0.0050 mass% or less, and more preferably 0.0030 mass% or less. Here, as described in the Background Art, the S content is preferably as low as possible, and it is possible to adopt a constitution in which S is not contained in the steel material, that is, the S content may be 0 mass%. However, since an excessive decrease in the S content, for example, a decrease of 3 ppm or less, increases the production costs, the lower limit of the S content is about 0.0004 mass%.

(Ni: 1.0 to 10.0 mass%)

[0041] Ni is an essential element for improving the corrosion resistance and has a marked effect in suppressing the local corrosion particularly in a chloride environment. Further, Ni is also effective in improving the low-temperature toughness and further is an essential element for stabilizing the austenite phase. In order to obtain such effects, the Ni content is defined to be 1.0 mass% or more, preferably 2.0 mass% or more, and more preferably 3.0 mass% or more. However, Ni contained in an excessive amount increases the austenite phase too much and decreases the strength. Accordingly, the Ni content is defined to be 10.0 mass% or less, preferably 9.5 mass% or less, and more preferably 9.0 mass% or less.

(Mo: 0.05 to 6.00 mass%)

[0042] Mo is an element that has an effect of forming molybdic acid during the dissolution to improve the local corrosion resistance due to an inhibitor effect, thereby improving the corrosion resistance. Further, Mo is an element that stabilizes the ferrite phase and has an effect of improving the pitting corrosion resistance and the cracking resistance of the steel material. In order to obtain such effects, the Mo content is defined to be 0.05 mass% or more, preferably 0.50 mass% or more, and more preferably 1.00 mass% or more. However, since Mo contained in an excessive amount promotes formation of an intermetallic compound such as the σ-phase to decrease the corrosion resistance and the hot workability, the Mo content is defined to be 6.00 mass% or less, preferably 5.50 mass% or less, and more preferably 5.00 mass% or less.

(N: 0.10 to 0.50 mass%)

[0043] N is an element that intensely stabilizes the austenite phase and has an effect of improving the corrosion resistance without increasing the sensitivity to σ-phase formation. Further, since N is an element that is also effective in strengthening the steel, N is positively used in the present embodiment. Here, when the N content is small, the role of N that is important in stabilizing the austenite phase may not be fulfilled, thereby raising a fear that the corrosion resistance may decrease. In order to obtain such effects, the N content is defined to be 0.10 mass% or more, preferably 0.15 mass% or more, and more preferably 0.20 mass% or more. However, N contained in an excessive amount forms a coarse nitride to decrease the toughness. Also, N contained in an excessive amount deteriorates the hot workability and generates broken edges and surface defects during the forging and rolling. For this reason, the N content is defined to be 0.50 mass% or less, preferably 0.45 mass% or less, and more preferably 0.40 mass% or less.

(Cr: 20.0 to 28.0 mass%)

[0044] Cr has an effect of being bonded with C and N to form an outer shell 15 of carbide or nitride together with the X-group element consisting of at least one of V, Ti, Nb, and Ta described above around a nucleus which is an inclusion 10 made of at least one of oxide, sulfide, and oxysulfide, thereby forming a composite inclusion 20 having the outer shell 15 around the inclusion 10. For this reason, Cr has an effect of improving the pitting corrosion resistance. Also, Cr is a main component of the passive film and is a fundamental element that causes the stainless steel material to exhibit the corrosion resistance. Further, Cr is an element that stabilizes the ferrite phase. In order to obtain such effects, the Cr content is defined to be 20.0 mass% or more, preferably 21.0 mass% or more, and more preferably 21.5 mass% or more. However, Cr contained in an excessive amount forms a coarse carbide or nitride to deteriorate the toughness. For this reason, the Cr content is defined to be 28.0 mass% or less, preferably 27.5 mass% or less, and more preferably 27.0 mass% or less.

[0045] Also, together with the basic metal component composition, a selective metal component composition such as the following may be contained, and hereafter, one example of the selective metal component composition will be described.

(Al: 0.001 to 0.050 mass%)

[0046] Al is a deoxidization element and is an essential element for decreasing the O amount and the S amount during the melting. Also, Al is an essential element together with Mg for forming an Mg-Al oxide that is comparatively excellent in corrosion resistance among the oxide inclusions. In order to obtain such effects, the Al content is defined to be 0.001 mass% or more, preferably 0.003 mass% or more, and more preferably 0.005 mass% or more. However, Al contained in an excessive amount forms a coarse oxide inclusion 10 to give adverse effects on the pitting corrosion resistance, so that the Al content is defined to be 0.050 mass% or less, preferably 0.040 mass% or less, and more preferably 0.030 mass% or less.

(Mg: 0.0001 to 0.0200 mass%)

[0047] Mg is an essential element together with Al for forming an Mg-Al oxide that is comparatively excellent in corrosion resistance among the oxide inclusions. Further, Mg is an element that is bonded with S or O in the steel to suppress segregation of these inclusions at the grain boundary, thereby improving the hot workability. In order to obtain such effects, the Mg content is defined to be 0.0001 mass% or more, and preferably 0.0003 mass% or more. However, Mg contained in an excessive amount stabilizes the Mg-based oxide that is inferior in the corrosion resistance, thereby deteriorating the corrosion resistance. For this reason, the Mg content is defined to be 0.0200 mass% or less, preferably 0.0150 mass% or less, and more preferably 0.0100 mass% or less.

(Ca: 0.0001 to 0.0200 mass%)

[0048] Ca is an element that is bonded with S contained as an impurity in the steel to form CaS by suppressing formation of MnS that is liable to be an origin of local corrosion, thereby improving the local corrosion resistance. Also, Ca is an element that is bonded with S or O in the steel to suppress segregation of these inclusions at the grain boundary, thereby improving the hot workability. In order to obtain such effects, the Ca content is defined to be 0.0001 mass% or more, and preferably 0.0003 mass% or more. However, Ca contained in an excessive amount invites increase in the oxide inclusions to deteriorate the corrosion resistance and the workability. For this reason, the Ca content is defined to be 0.0200 mass% or less, and preferably 0.0100 mass% or less.

(Co: 0.1 to 2.0 mass%, Cu: 0.1 to 2.0 mass%)

[0049] Co and Cu are elements that improve the corrosion resistance and stabilize the austenite phase. In order to obtain such effects, the Co content and the Cu content are each defined to be 0.1 mass% or more, and preferably 0.2 mass% or more, when Co or Cu is contained. However, when these elements are contained in an excessive amount, the hot workability is deteriorated, so that the Co content and the Cu content are each defined to be 2.0 mass% or less, and preferably 1.5 mass% or less. Here, either one or both of Co and Cu contained in the aforementioned predetermined amount produces an effect of improving the corrosion resistance and stabilizing the austenite phase.

(B: 0.0005 to 0.0100 mass%)

[0050] B has an effect in improving the corrosion resistance and the hot workability. In order to obtain such effects, the B content is defined to be 0.0005 mass% or more, and preferably 0.0010 mass% or more, when B is contained. Since B is an arbitrary component, the B content may be defined to be 0 mass%. On the other hand, B contained in an excessive amount may generate cracks during the hot working or may be bonded with N in the steel to form BN, thereby raising a fear that the concentration of N contributing to the corrosion resistance may decrease to deteriorate the corrosion resistance. For this reason, the B content is defined to be 0.0100 mass% or less, preferably 0.0050 mass% or less, and more preferably 0.0020 mass% or less.

(Fe and unavoidable impurities)

[0051] The basic components of the component composition constituting the duplex stainless steel material are as described above, and the balance components are Fe and unavoidable impurities. Here, examples of the unavoidable impurities include P and O.

(P: 0.05 mass% or less)

[0052] P is an element that is unavoidably mingled as an impurity, is harmful to the corrosion resistance, and deteriorates the weldability and the workability. For this reason, the P content is defined to be 0.05 mass% or less. Here, the P content is preferably as low as possible, and is preferably 0.04 mass% or less, and more preferably 0.03 mass% or less. Here, it is possible to adopt a constitution in which P is not contained in the steel material, that is, the P content may be 0 mass%; however, since excessive decrease in the P content increases the production costs, the lower limit of the P content in practical operation is about 0.01 mass%.

(O: 0.030 mass% or less)

[0053] O is an impurity that is mingled during the melting, and is an element that is bonded with a deoxidization element such as Si or Al to deposit as an oxide in the steel, thereby deteriorating the workability and the corrosion resistance of

the duplex stainless steel material. Further, when O is contained in an excessive amount, oxides or oxysulfides deposit in a large number, thereby deteriorating the corrosion resistance and the hot workability. For this reason, the O content is defined to be 0.030 mass% or less, preferably 0.028 mass% or less, and more preferably 0.024 mass% or less. Here, the O content is preferably as low as possible; however, excessive decrease in the O content leads to increase in the costs, so that the lower limit of the O content is about 0.0005 mass%.

[0054] The unavoidable impurities are impurities that are unavoidably mingled during the melting and are contained within a range that does not deteriorate various characteristics of the steel material. Further, in addition to the aforementioned components, other elements may be positively contained into the component composition of the steel material within a range that does not give a bad influence on the effects of the steel material according to the present invention. Here, unlike the prior art, there is no need to add W into the duplex stainless steel material of the present application, thereby suppressing increase in the costs and being economically advantageous.

[0055] The above is a description of one example of a basic metal component composition that is suitable for a super duplex stainless steel material in which a calculation result of PRE = [Cr] + 3.3[Mo] + 16[N] is 40 or more and a standard duplex stainless steel material in which a calculation result of PRE is 30 or more and less than 40.

[0056] One example of a basic metal component composition that is suitable for a lean duplex stainless steel material in which a calculation result of PRE is less than 30 is as follows.

[0057] That is, the lean duplex stainless steel material is such that the metal component composition contains 0.100 mass% or less of C, 0.10 to 2.00 mass% of Si, 0.10 to 3.00 mass% of Mn, 0.0100 mass% or less of S, 3.0 to 7.0 mass% of Ni, 0.05 to 1.00 mass% of Mo, 0.05 to 0.20 mass% of N, 20.0 to 25.0 mass% of Cr, and 0.030 mass% or less of O, with a balance being Fe and unavoidable impurities.

[0058] The lean duplex stainless steel material is different from the super duplex stainless steel material and the standard duplex stainless steel material in that the metal component composition contains 3.0 to 7.0 mass% of Ni, 0.05 to 1.00 mass% of Mo, 0.05 to 0.20 mass% of N, and 20.0 to 25.0 mass% of Cr; however, the effect of each component and the significance of defining the content are the same, and the description thereof will be a duplicated one, so that the description of these will be omitted. Here, in the lean duplex stainless steel material, the Ni content is preferably defined to be 3.5 mass% or more and 6.5 mass% or less. The Mo content is preferably defined to be 0.10 mass% or more and 0.95 mass% or less. The N content is preferably defined to be 0.10 mass% or more and 0.15 mass% or less. The Cr content is preferably defined to be 20.5 mass% or more and 24.5 mass% or less.

[0059] Referring to FIGS. 1 to 4, in the duplex stainless steel material having the above constitution, that is, in the super duplex stainless steel material, the standard duplex stainless steel material, and the lean duplex stainless steel material, development of the pitting corrosion is prevented because the number of composite inclusions 20 each of which the outer shell 15 is formed around the inclusion 10 is 30% or more of the number of inclusions 10. From FIG. 4, it will be understood that, in a state in which a pitting corrosion hole is about to develop in a part of the inclusion 10, the development of the pitting corrosion hole is prevented because the outer shell 15 is formed. In other words, in the duplex stainless steel material, the larger the number of composite inclusions 20 each provided with the outer shell 15 around the inclusion 10 is, the more the development of the pitting corrosion hole is prevented, so that excellent corrosion resistance can be exhibited even in a severe corrosive environment. Here, it is most preferable that the outer shell 15 completely covers the surrounding of the inclusion 10 functioning as a nucleus; however, it is sufficient that the outer shell 15 covers the inclusion 10 within a range of 30% or more, preferably within a range of 40% or more, more preferably within a range of 60% or more, still more preferably within a range of 80% or more, and most preferably by 100%. The outer shell 15 may be made of a single layer or multiple layers.

<Method for producing duplex stainless steel material>

[0060] Next, a method for producing the duplex stainless steel material according to the present embodiment will be described.

[0061] The duplex stainless steel material according to the present embodiment can be produced by employing production equipment and production methods used for mass production of usual stainless steel. In order to decrease O as an impurity in the steel, deoxidization is carried out by adding a comparatively larger amount of elements, such as Si and Al, having a large affinity to O, and further, the oxide inclusion 10 is removed by performing secondary refining such as vacuum degassing or argon gas stirring for a longer period of time or for plural times.

[0062] For example, after a molten steel melted by a converter or an electric furnace is subjected to adjustment of components by performing refining using the AOD (Argon Oxygen Decarburization) method, the VOD (Vacuum Oxygen Decarburization) method, or the like, the molten steel is cast into a steel ingot by a casting method such as the continuous casting method or the ingot making method. The obtained steel ingot is subjected to hot working in a temperature region of about 900°C to 1300°C, and then subjected to cold working into a desired size and shape. Further, the total working ratio of the cross-section of the original steel ingot / the cross-section after the working is defined to be about 10 to 50 as usual.

[0063] In the present embodiment, the number of composite inclusions 20 and the number of inclusions 10 are adjusted by controlling the temperature during the hot working and controlling the total heat treatment time of the heat treatment immediately before the hot working and the heat treatment during the hot working. In other words, for the duplex stainless steel material, a heat treatment in a temperature region of about 900°C to 1300°C is performed for 3 hours or more, preferably 5 hours or more, and more preferably 10 hours or more, in order that the proportion of the number of composite inclusions 20 each having an outer shell 15 around an inclusion 10 with respect to the total number of the inclusions 10 may be 30% or more. Here, the longer the heat treatment time is, the better it is. However, when the heat treatment time is excessively long, the productivity may be worsened, so that the heat treatment time is preferably 100 hours or less.

[0064] Here, in conventional production of duplex stainless steel materials, the heat treatment time immediately before the hot working and during the hot working has been generally controlled to be one hour or less, because a shorter period of time is better in view of productivity. The present embodiment obtains a state in which the proportion of the number of composite inclusions 20 with respect to the total number of inclusions 10 is 30% or more, by daringly defining the heat treatment time to be within the aforementioned range so as to achieve a heat treatment time that is considerably longer than usual.

[0065] Here, FIG. 5 gives an illustration for understanding the difference between a process of the heat treatment in a preferable method of producing a duplex stainless steel material according to the present embodiment and a process of the heat treatment in a conventional method of producing a duplex stainless steel material. Referring to FIG. 5, the hot forging time in the preferable method of producing a duplex stainless steel material according to the present embodiment is defined to be 3 hours or more, while the hot forging time in the conventional method of producing a duplex stainless steel material is defined to be one hour.

[0066] For the duplex stainless steel material according to the present embodiment, it is preferable that a solid solution forming heat treatment and rapid cooling are carried out in accordance with the needs in order to eliminate deposits that are harmful to mechanical properties. The lower limit value of the temperature of the solid solution forming heat treatment is preferably 1000°C or higher, and the upper limit value thereof is preferably 1200°C or lower, more preferably 1100°C or lower, and still more preferably 1080°C or lower. The holding time is preferably 1 to 30 minutes. By defining the heat treatment temperature to be 1000°C or higher to 1200°C or lower, the proportion of the number of composite inclusions 20 each having an outer shell 15 around an inclusion 10 with respect to the total number of the inclusions 10 comes to be 30% or more. Further, by defining the heat treatment temperature to be 1000°C or higher and 1080°C or lower, the aforementioned proportion comes to be 70% or more.

[0067] The rapid cooling is preferably applied at a cooling rate of 10°C/sec or more. Further, pickling can be applied in accordance with the needs for surface conditioning such as scale removal.

<Duplex stainless steel tube>

[0068] An embodiment of a duplex stainless steel tube according to the present embodiment will be described. The duplex stainless steel tube includes the duplex stainless steel material described above. Therefore, as described above, the duplex stainless steel tube according to the present embodiment exhibits excellent corrosion resistance. For this reason, the duplex stainless steel tube according to the present embodiment can be used as structural materials in seawater environments such as umbilical tubes, seawater desalination plants, and LNG vaporizers, as well as structural materials for oil well tubes and various chemical plants. The duplex stainless steel tube according to the present embodiment can be produced by employing production equipment and production methods used for mass production of usual stainless steel tubes. For example, the steel tube can be formed into a desired size by extrusion tube production or Mannesmann tube production using a round rod as a starting material, or by welding tube production using a sheet material as a starting material and welding the seam after fabrication. The size of the duplex stainless steel tube can be appropriately determined in accordance with the oil well tubes, chemical plants, umbilical tubes, and the like in which the steel tube is used. Also, the duplex stainless steel tube can be set to have an appropriate size as a structural material for seawater desalination plants, LNG vaporizers, and the like.

[0069] Here, when the welding tube production is employed or when two or more duplex stainless steel tubes are joined by welding, the welding may be performed by using a technique that is generally used in stainless steels, for example, by using an appropriate method from among various kinds of arc welding such as TIG, MIG, SAW, and shielded metal arc as well as electron beam welding, laser welding, and electric resistance welding.

[0070] While the present specification discloses various modes of techniques as described above, principal techniques among these will be summarized as follows.

[0071] A duplex stainless steel material according to one aspect of the present invention includes a ferrite phase and an austenite phase, in which the duplex stainless steel material contains, as metal component composition, at least one X-group element selected from 0.01 to 0.50 mass% of V, 0.0001 to 0.0500 mass% of Ti, 0.0005 to 0.0500 mass% of Nb, and 0.01 to 0.50 mass% of Ta; the duplex stainless steel material has composite inclusions or has composite inclusions and inclusions; each of the inclusions includes at least one of an oxide, a sulfide, and an oxysulfide; each of

the composite inclusions includes one of the inclusions as a nucleus and includes an outer shell existing around the nucleus and having a carbide or a nitride containing Cr and the at least one X-group element; and a proportion of a number of the composite inclusions with respect to a total number of the inclusions is 30% or more.

[0072] Owing to the above constitution, the duplex stainless steel material contains Cr and a predetermined amount of at least one element selected from V, Ti, Nb, and Ta, which are X-group elements, in the outer shell formed around the inclusion, whereby the corrosion resistance is improved. The elements V, Ti, Nb, and Ta have an effect of being bonded with C and N to form a carbide or nitride at an interface between the steel and the inclusion of an oxide, sulfide, or oxysulfide. Further, Ta has an effect of forming a covering layer of carbonitride that is more excellent in corrosion resistance.

[0073] Also, the duplex stainless steel material may contain 0.01 to 0.50 mass% of Ta as the metal component composition, and the outer shell may contain Ta in an amount satisfying formula (1) below:

$$([Ta] / [M]total) \times 100 \geq 5 \text{ ..... formula (1)}$$

where, [Ta] represents a number of Ta atoms contained in the outer shell, and [M]total represents a total number of atoms of metal elements contained in the outer shell.

[0074] Owing to the above constitution, the duplex stainless steel material has a higher effect of suppressing development of the pitting corrosion to improve the corrosion resistance of the steel material because the corrosion resistance of the outer shell of carbide or nitride is improved.

[0075] Also, the duplex stainless steel material may contain 0.01 to 0.50 mass% of Ta and 0.0001 to 0.0500 mass% of Ti as the metal component composition, and a (Ta mass% / Ti mass%) ratio may satisfy formula (2) below:

$$\text{Ta mass\% / Ti mass\%} \geq 25 \text{ ..... formula (2).}$$

[0076] Owing to the above constitution, the carbide or nitride containing Ta can cover the inclusion more readily in the duplex stainless steel material, thereby giving a higher effect of suppressing development of the pitting corrosion to improve the corrosion resistance of the steel material

[0077] Further, the duplex stainless steel material may contain 0.0001 to 0.0200 mass% of Mg and 0.001 to 0.050 mass% of Al as the metal component composition, and the nucleus in each of the composite inclusions may contain an oxide of Mg and Al.

[0078] Owing to the above constitution, the duplex stainless steel material has improved corrosion resistance because each of the inclusions and the nucleus in each of the composite inclusions contain Mg and Al that influence the corrosion resistance.

[0079] Also, it is preferable that the duplex stainless steel material contains, as the metal component composition, 0.100 mass% or less of C, 0.10 to 2.00 mass% of Si, 0.10 to 3.00 mass% of Mn, 0.0100 mass% or less of S, 1.0 to 10.0 mass% of Ni, 0.05 to 6.00 mass% of Mo, 0.10 to 0.50 mass% of N, 20.0 to 28.0 mass% of Cr, and 0.030 mass% or less of O, with a balance being Fe and unavoidable impurities.

[0080] Also, it is preferable that the duplex stainless steel material contains, as the metal component composition, 0.100 mass% or less of C, 0.10 to 2.00 mass% of Si, 0.10 to 3.00 mass% of Mn, 0.0100 mass% or less of S, 3.0 to 7.0 mass% of Ni, 0.05 to 1.00 mass% of Mo, 0.05 to 0.20 mass% of N, 20.0 to 25.0 mass% of Cr, and 0.030 mass% or less of O, with a balance being Fe and unavoidable impurities.

[0081] Owing to these constitutions, the duplex stainless steel material can obtain a duplex structure of the austenite phase and the ferrite phase because of containing predetermined amount of C, Si, Mn, S, Ni, Mo, N, Cr, and O as the metal component composition. C, when contained in a predetermined amount or less, produces an effect of suppressing decrease in the corrosion resistance because unnecessary carbide is not formed. Si and Mn have an effect for deoxidization. S, when contained in a predetermined amount or less, produces an effect of suppressing decrease in the corrosion resistance and the hot workability. Also, S may be a cause of forming MnS that deteriorates the corrosion resistance and the toughness. Cr, Mo, and N have an effect in improving the pitting corrosion resistance. Ni has an effect in improving the corrosion resistance and stabilizing the austenite phase. Also, since the O content is defined to be a predetermined amount or less, the corrosion resistance and the hot workability are less likely to decrease.

[0082] It is possible to adopt a constitution in which the duplex stainless steel material further contains 0.0001 to 0.0200 mass% of Ca as the metal component composition of the steel material, a constitution in which the duplex stainless steel material further contains at least one selected from the group consisting of 0.1 to 2.0 mass% of Co and 0.1 to 2.0 mass% of Cu as the metal component composition of the steel material, or a constitution in which the duplex stainless steel material further contains 0.0005 to 0.0100 mass% of B as the metal component composition of the steel material.

[0083] Owing to the above constitution, the duplex stainless steel material further contains a predetermined amount

of one of Ca, Co, Cu, and B, thereby improving the corrosion resistance. Ca is bonded with S or O in the steel to suppress segregation at the grain boundary, thereby improving the corrosion resistance and the hot workability. Co and Cu have an effect in improving the corrosion resistance and stabilizing the austenite phase. In the duplex stainless steel material, B has an effect in improving the hot workability.

[0084] A duplex stainless steel tube according to another aspect of the present invention has a constitution of including the aforementioned duplex stainless steel material.

[0085] Owing to the above constitution, in the duplex stainless steel tube, the inclusions that form origins of local corrosion are modified because the steel tube is constituted of the duplex stainless steel material, whereby the corrosion resistance is improved, and the stress corrosion cracking resistance at the welded part is improved.

Examples

[0086] Hereafter, the duplex stainless steel material according to the present invention will be described in further detail by way of Examples. Here, the duplex stainless steel material according to the present invention is not limited to the following examples. In the following examples, Tables 1 to 6 show the metal component composition of the duplex stainless steel materials and the evaluation results.

[0087] (Preparation of super duplex stainless steel material and standard duplex stainless steel material)

[0088] With use of a small melting furnace having a capacity of 53 kg, steel having component composition shown in Tables 2 and 4 was melted and cast with use of a square mold of about 120 square × about 350 mm. Here, in the component composition sections of Tables 2 and 4, the blank section (-) indicates that the relevant component is not contained, with the balance being Fe and unavoidable impurities. The one shown by "-" in relation to "Ta/Ti" in Tables 2 and 4 indicates that the calculation of "Ta/Ti" was not appropriate in the present embodiment because at least one of Ta and Ti was not contained. Also, for each steel, the calculation result of PRE = [Cr] + 3.3[Mo] + 16[N] is shown in Tables 1 and 3. The blank section (-) in Tables 1 and 3 indicates that the element to be analyzed was not detected as a result of EDX analysis of the outer shell of the composite inclusion.

[0089] As a steel material, here, a solidified steel ingot was heated up to 900 to 1300°C, subjected to hot forging at that temperature, and thereafter cut. Immediately before the hot forging and during the hot forging, a heat treatment in a temperature region of about 900 to 1300°C was carried out for 3 hours or more. Subsequently, the resultant was subjected to a solid solution forming heat treatment of holding at 1 100°C for 3 minutes and cooled with water at a cooling rate of 12°C/sec, followed by cutting to finish the resultant into a steel material of 300 × 120 × 50 mm. The steel materials prepared as described above were defined as steel material Nos. A1 to 6, A9 to 20, B2, and B5 to 8.

[0090] Also, the cast steel material was solidified and, in addition, the solidified steel ingot was heated up to 900 to 1300°C and subjected to hot forging at that temperature. Immediately before the hot forging and during the hot forging, a heat treatment in a temperature region of about 900 to 1300°C was carried out for 3 hours or more. Subsequently, the resultant was subjected to a solid solution forming heat treatment of holding at 1050°C for 3 minutes and cooled with water at a cooling rate of 12°C/sec, followed by cutting to finish the resultant into a steel material of 300 × 120 × 50 mm. The steel materials prepared as described above were defined as steel material Nos. A7, A8, A21, and A22.

[0091] Also, the cast steel material was solidified and, in addition, the solidified steel ingot was heated up to 900 to 1300°C and subjected to hot forging at that temperature. Immediately before the hot forging and during the hot forging, a heat treatment in a temperature region of about 900 to 1300°C was carried out for one hour. Subsequently, the resultant was subjected to a solid solution forming heat treatment of holding at 1100°C for 3 minutes and cooled with water at a cooling rate of 12°C/sec, followed by cutting to finish the resultant into a steel material of 300 × 120 × 50 mm. In this manner, steel material Nos. B1, B3, and B4 were prepared.

(Preparation of lean duplex stainless steel material)

[0092] Further, with use of a small melting furnace (capacity of 20 kg / 1 ch), steel having component composition shown in Table 6 was melted and cast with use of a cylindrical mold (main body: ϕ110 × about 200 mm) (steel material Nos. A23 to A27 and B9 to B11). Here, in the component composition sections of Table 6, the blank section (-) indicates that the relevant component is not contained, with a balance being Fe and unavoidable impurities. Also, for each steel, the calculation result of PRE = [Cr] + 3.3[Mo] + 16[N] is shown in Table 5. The blank section (-) in Table 5 indicates that the element to be analyzed was not detected as a result of EDX analysis of the outer shell of the composite inclusion.

[0093] Here, the lean duplex stainless steel materials are different from the super duplex stainless steel materials and the standard duplex stainless steel materials in the capacity of the melting furnace and the shape and size of the cast product; however, these differences do not affect the performance as a steel material.

[0094] As a steel material, here, a solidified steel ingot was heated up to 1300°C, subjected to hot forging at that temperature (forging temperature: 1000 to 1300°C), and thereafter cut. At that time, a heat treatment in a temperature region of about 1000 to 1300°C was carried out for 3 hours or more. Subsequently, the resultant was subjected to a

solid solution forming heat treatment of holding at 1100°C for 30 minutes and cooled with water at a cooling rate of 12°C/sec, followed by cutting to form a steel material of 20 × 50 × 150 mm, which was then subjected to cold rolling and held at 1100°C for 5 minutes for the purpose of removing the strain and deposits, and thereafter cooled with water at a cooling rate of 12°C/sec to form samples for evaluation (steel material Nos. A23 to A27, B10, and B11).

[0095] Also, a solidified steel ingot was heated up to 1300°C, subjected to hot forging at that temperature (forging temperature: 1000 to 1300°C), and thereafter cut. Unlike the above-described one, a heat treatment for a long period of time was not performed, and the resultant was subjected to a solid solution forming heat treatment of holding at 1100°C for 30 minutes and cooled with water at a cooling rate of 12°C/sec, followed by cutting to form a steel material of 20 × 50 × 150 mm, which was then subjected to cold rolling and held at 1100°C for 5 minutes, and thereafter subjected to a finishing heat treatment of cooling with water at a cooling rate of 12°C/sec to form a sample for evaluation. (Steel material No. B9)

(Collection of sample and observation of structure)

[0096] Then, with use of a sample of 20 mm × 30 mm × 2 mmt collected from the steel material in a direction parallel to the working direction, the inclusions and the pitting corrosion resistance were evaluated by the following procedure. The results are shown in Tables 1,3, and 5.

[0097] Also, the sample was buried in a resin and processed so that the cross-section perpendicular to the working direction of the sample would be exposed, and mirror surface polishing was carried out. Further, with respect to the steel material Nos. A1 to A22 and B1 to B8, electrolytic etching was carried out in an aqueous solution of oxalic acid, followed by observation with an optical microscope at a magnification of 100 times, so as to observe the structure of each sample. With respect to the steel material Nos. A23 to A27 and B9 to B11, electrolytic etching was carried out in an aqueous solution of KOH, followed by observation with an optical microscope at a magnification of 100 times, so as to observe the structure of each sample. As a result, any of the samples was found out to include two phases of the ferrite phase and the austenite phase.

(Evaluation of inclusions and composite inclusions)

(Evaluation of core inclusions)

[0098] The sample was buried in a resin and processed so that the cross-section perpendicular to the working direction of the sample would be exposed, and mirror surface polishing was carried out. The surface subjected to the mirror surface polishing was observed with use of an electron beam microprobe X-ray analyzer (ElectronProbe X-ray Micro Analyzer: EPMA, trade name "JXA-8500F" manufactured by JEOL Ltd. DATUM Solution Business Operations, and the component composition was quantitatively analyzed with respect to the oxide inclusions having a minor diameter of 1 μm or more.

[0099] At this time, with respect to the steel material Nos. A1 to A22 and B1 to B8, the area of observation was defined to be 100 mm^2, and the component composition at the central part of the oxide inclusions was quantitatively analyzed by wavelength dispersion spectroscopy of characteristic X-ray.

[0100] Also, with respect to the steel material Nos. A23 to A27 and B9 to B11, the area of observation was defined to be 600 mm^2, and the component composition at the central part of the oxide inclusions was quantitatively analyzed by wavelength dispersion spectroscopy of characteristic X-ray.

[0101] The elements to be analyzed were defined to be Ca, Al, Si, Ti, Mg, Mn, Na, K, Cr, S, and O, and, with use of already known substances, a relationship between the X-ray intensity of each element and the element concentration was determined in advance as a calibration line. Further, the amount of the elements contained in each sample was quantitated based on the X-ray intensity obtained from the oxide inclusions to be analyzed and the calibration line, and an arithmetic average of the obtained results was calculated to determine the average composition of the inclusions.

[0102] Among the quantitation results obtained in this manner, the inclusions in which the O content was 5 mass% or more were determined as being "oxides", and the inclusions in which the S content was 0.5 mass% or more were determined as being "sulfides". Also, among the inclusions in which the S content was 0.5 mass% or more, the inclusions in which the Ca content was 1.0 mass% or more were determined as being "Ca-based sulfides".

[0103] At this time, when a plurality of elements were observed from one inclusion, the composition of oxides was calculated by converting into a single oxide of each element from the ratio of the X-ray intensities showing the presence of these elements. In the present embodiment, those subjected to mass conversion as the single oxides were averaged to determine the average composition of the oxides.

[0104] With respect to the average composition of the oxides determined in the above-described manner, the inclusions in which the content of MgO was 20 mass% or more were determined as being "Mg-based oxides"; the inclusions in which the content of MgO and the content of Al_2O_3 were each 20 mass% or more were determined as being "Mg, Al-

based oxides"; and the inclusions in which the content of Al_2O_3 and the content of CaO were each 20 mass% or more were determined as being "Ca, Al-based oxides". Here, the inclusions being both "Ca-based sulfides" and "Ca, Al-based oxides" were determined as being "Ca, Al-based oxysulfides"

[0105] Also, with respect to the average composition of the oxides determined in the above-described manner, the inclusions in which the O content was 5 mass% or more, the S content was 0.5 mass% or more, the Ca content was 1.0 mass% or more, and the content of MgO and the content of Al_2O_3 were each 20 mass% or more were determined as being "Mg, Ca, Al-based oxysulfides".

[0106] Further, with respect to the average composition of the oxides determined in the above-described manner, the inclusions in which the O content was 5 mass% or more, the S content was 0.5 mass% or more, the Ca content was 1.0 mass% or more, and the content of MgO was 20 mass% or more were determined as being "Mg, Ca-based oxysulfides".

(Evaluation of composite inclusion)

[0107] With respect to the steel material Nos. A1 to A22 and B1 to B8, from among the oxides, sulfides, or oxysulfides (that is, the inclusions) that were present in the observation area of 100 mm^2, five of them were selected sequentially in the order starting from the one having the largest size and analyzed.

[0108] Also, with respect to the steel material Nos. A23 to A27 and B9 to B11, from among the oxides, sulfides, or oxysulfides (that is, the inclusions) that were present in the observation area of 600 mm^2, five of them were selected sequentially in the order starting from the one having the largest size and analyzed.

[0109] Although not all of the inclusions were analyzed, it is considered that inclusions having a smaller size than the selected inclusions described above are also generated by a mechanism similar to that of the selected inclusions having a larger size, and it is confirmed that these have a similar composition and distribution of shape.

[0110] In other words, it is considered that in the oxides, sulfides, or oxysulfides of all sizes, inclusions having a predetermined composition and distribution of shape are generated. Here, whether the sizes of the oxides, sulfides, or oxysulfides were large or small was determined based on the area of the oxides, sulfides, or oxysulfides appearing on the above observation surface.

[0111] Thereafter, by the FIB method (Focused Ion Beam, converging ion beam processing method), the oxides, sulfides, or oxysulfides serving as an object were made into thin pieces having a thickness such that TEM observation of the oxides, sulfides, and oxysulfides could be made. As the apparatus, a converging ion beam processing observation apparatus FB2000A manufactured by Hitachi, Ltd. was used with an acceleration voltage of 30 kV and with use of Ga as an ion source.

[0112] Thereafter, the inclusions made into thin pieces were subjected to TEM observation. As the apparatus, a field emission transmission electron microscope JEM-2010F manufactured by JEOL Ltd. was used. With use of an EDX (Energy Dispersive X-ray spectrometry) analyzing apparatus Vantage manufactured by Noran Co., Ltd., EDX analysis was performed on the interface between the steel and the oxides, sulfides, or oxysulfides.

[0113] The elements to be analyzed by EDX were defined to be Ca, Al, Ti, V, Mg, Mn, Na, K, Cr, Nb, Ta, S, and O, and phases in which one or more of Cr, V, Ti, Nb, and Ta were detected and a total concentration of Cr, V, Ti, Nb, and Ta was 30 mass% or more were selected.

[0114] Further, the selected phases were subjected to identification analysis by electron beam diffraction, and those exhibiting a cubic crystal structure were determined as being a carbide or nitride. At this time, when the carbide or nitride was generated within a range of 60% or more of the interface between the steel and the oxides, sulfides, or oxysulfides as an object, that is, the surrounding on the aforementioned circumference, it was determined that a composite inclusion was present having an inclusion of oxide, sulfide, or oxysulfide as a nucleus and having an outer shell of carbide or nitride around this nucleus.

[0115] Further, among the measured five oxides, sulfides, or oxysulfides, the proportion of the number of oxides, sulfides, or oxysulfides in which the above carbide or nitride was generated was measured.

[0116] The results are shown in Tables 1, 3, and 5 as an inclusion covering rate (%).

(Evaluation of corrosion resistance)

[0117] Evaluation of corrosion resistance was carried out with reference to the method described in JIS G 0577:2014 "Methods of pitting potential measurement for stainless steel". After wet polishing the sample surface with SiC #600 polishing paper and supersonically cleaning the surface, conduction wires were attached to the sample by spot welding, and a portion other than the test surface of the sample surface (10 mm $\times$ 10 mm) was covered with an epoxy resin or silicone resin.

[0118] With respect to the super duplex stainless steel materials having PRE of 40 or more, after immersing the sample in an aqueous solution of 20% NaCl kept at 80°C for 10 minutes, anode polarization was performed at a sweeping rate

of 20 mV/min, and a potential when a current density exceeded 0.1 mA/cm^2 was taken as pitting potential (VC '100) (steel material Nos. A9 to A22 and B3 to B8).

[0119] Further, with respect to the standard duplex stainless steel materials having PRE of 30 or more and less than 40 and the lean duplex stainless steel materials having PRE less than 30, after immersing the sample in an artificial sea water solution kept at 80°C for 10 minutes, anode polarization was performed at a sweeping rate of 20 mV/min, and a potential when a current density exceeded 0.1 mA/cm^2 was taken as pitting potential (VC '100) (steel material Nos. A1 to A8, A23 to A27, B1, B2, and B9 to B11).

[0120] Regarding evaluation of the pitting corrosion resistance, with respect to the super duplex stainless steel materials and the standard duplex stainless steel materials, those in which the pitting potential was 900 mV (vs. SCE (saturated calomel electrode)) or more were evaluated as AAAA. Also, those in which the pitting potential was 750 mV (vs. SCE) or more and less than 900 mV (vs. SCE) were evaluated as AAA. Also, those in which the pitting potential was 600 mV (vs. SCE) or more and less than 750 mV (vs. SCE) were evaluated as AA. Those in which the pitting potential was 550 mV (vs. SCE) or more and less than 600 mV (vs. SCE) were evaluated as A. Also, those in which the pitting potential was less than 550 mV (vs. SCE) were evaluated as B.

[0121] With respect to the lean duplex stainless steel materials, those in which the pitting potential was 250 mV (vs. SCE) or more were evaluated as A. Also, those in which the pitting potential was less than 250 mV (vs. SCE) were evaluated as B.

[0122] The results are shown together with the pitting potential in Tables 1, 3, and 5.

[0123] Here, in each evaluation, the evaluation criterion differs among the duplex stainless steel materials that are the super duplex stainless steel materials having PRE of 40 or more, the standard duplex stainless steel materials having PRE of 30 or more and less than 40, and the lean duplex stainless steel materials having PRE less than 30, so that the evaluation results are separately provided. For this reason, Tables 1 and 2 are for the standard duplex stainless steel materials having PRE of 30 or more and less than 40; Tables 3 and 4 are for the super duplex stainless steel materials having PRE of 40 or more; and Tables 5 and 6 are for the lean duplex stainless steel materials having PRE less than 30.

[0124] Also, FIG. 6 shows a graph with the longitudinal axis representing the pitting potential (mV) and the lateral axis representing the inclusion covering rate by which the inclusions are covered by the outer shells, that is, the proportion (%) of the number of the composite inclusions with respect to the total number of the inclusions. FIG. 7 shows a graph with the longitudinal axis representing the pitting potential (mV) and the lateral axis representing the Ta content in the metal components in the outer shells, that is, the Ta content (atom%) in the covering inclusions. FIG. 8 shows a graph with the longitudinal axis representing the pitting potential (mV) and the lateral axis representing the Ta mass% / Ti mass%. Here, "mV" in FIGS. 6 to 8 denotes "mV (vs. SCE)". Also, in FIGS. 6 to 8, "super" denotes the super duplex stainless steel materials, and "Std." and "standard" denote the standard duplex stainless steel materials.

[0125] As shown in FIG. 6, even when the value of PRE is 40 or more, the value of the pitting potential does not exceed 550 mV when the inclusion covering rate of the duplex stainless steel materials is less than 30%.

[0126] Also, as shown in FIG. 7, it will be understood that, when Ta which is an X-group element is contained at 5 atom% or more in the covering inclusions in the aforementioned formula (1), the pitting potential exceeds 900 mV in the case of the super duplex stainless steel materials having the value of PRE being 40 or more, and the pitting potential exceeds 700 mV in the case of the standard duplex stainless steel materials having the value of PRE being 30 or more and less than 40.

[0127] Further, as shown in FIG. 8, it will be understood that, when the contents of Ta and Ti are 25 or more in the aforementioned formula (2), the pitting potential exceeds 900 mV in the case of the super duplex stainless steel materials having the value of PRE being 40 or more, and the pitting potential exceeds 700 mV in the case of the standard duplex stainless steel materials having the value of PRE being 30 or more and less than 40.

[Table 1]

Steel material No.	PRE	Heat treatment time (H)	Solid solution forming heat treatment temperature (°C)	Type of elements in nucleus (inclusion)	Type of elements in outer shell	Inclusion covering rate (%)	Ta content (atom%) in metal components in outer shell	Pitting potential (mV (vs. SCE))	Corrosion resistance evaluation
A1	36.1	3	1100	Mg,Ca,Al based oxysulfide	Ta,Ti,Nb,Cr	40	0.2	615	AA
A2	36.4	8.5	1100	Mg,Ca,Al based oxysulfide	V,Ti,Nb,Cr	40	0	620	AA
A3	35.8	73	1100	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Nb,Cr	60	3.1	695	AA
A4	36.1	73	1100	Ca,Al based oxysulfide	Ta,Ti,Nb,Cr	40	0.2	580	A
A5	35.4	73	1100	Mg,Ca based oxysulfide	Ta,V,Ti,Cr	60	0.1	673	AA
A6	35.6	73	1100	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Cr	60	6.5	750	AAA
A7	35.7	73	1050	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Cr	80	0.1	681	AA
A8	35.4	73	1050	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Cr	100	6.6	786	AAA
B1	35.8	1	1100	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Nb,Cr	20	1.9	362	B
B2	38.2	73	1100	Mg,Ca,Al based oxysulfide	-	0	0	65	B

[Table 2]

Steel material No.	Component composition (mass%) Balance: Fe and unavoidable impurities Underline shows that the material is out of the definition of the present invention.																				
	C	Si	Mn	P	S	Al	Ni	Cr	Mo	N	Mg	Ca	O	Co	Cu	Ta	V	Ti	Nb	B	Ta/Ti
A1	0.020	0.40	1.71	0.021	0.0010	0.013	5.2	22.7	3.21	0.17	0.0005	0.0007	0.003	0.4	-	0.08	-	0.0320	0.0210	-	2.5
A2	0.020	0.41	1.69	0.021	0.0011	0.002	5.2	22.8	3.21	0.19	0.0003	0.0008	0.004	-	0.5	-	0.12	0.0290	0.0320	0.0010	-
A3	0.020	0.40	1.67	0.022	0.0012	0.002	5.2	22.8	3.22	0.15	0.0003	0.0008	0.003	0.2	0.2	0.05	0.11	0.0400	0.0040	0.0011	1.3
A4	0.020	0.40	1.71	0.021	0.0010	0.025	5.2	22.7	3.21	0.17	0.0001	0.0007	0.003	0.4	-	0.08	-	0.0320	0.0180	-	2.5
A5	0.019	0.40	0.51	0.007	0.0017	0.002	5.1	22.3	3.20	0.16	0.0018	0.0006	0.002	-	0.7	0.09	0.30	0.0430	-	-	2.1
A6	0.018	0.41	1.52	0.030	0.0011	0.015	5.3	22.2	3.19	0.18	0.0006	0.0005	0.003	-	-	0.10	0.10	0.0010	-	0.0010	100.0
A7	0.020	0.42	0.55	0.011	0.0016	0.005	5.0	22.6	3.20	0.16	0.0008	0.0006	0.002	0.4	0.6	0.09	0.23	0.0390	0.0050	0.0010	2.3
A8	0.021	0.44	1.86	0.023	0.0015	0.016	5.4	22.2	3.26	0.15	0.0009	0.0004	0.004	-	-	0.11	0.16	0.0009	-	0.0011	122.2
B1	0.020	0.41	0.55	0.019	0.0013	0.010	5.1	22.4	3.22	0.17	0.0010	0.0010	0.003	0.2	0.7	0.06	0.12	0.0020	0.1230	0.0020	30.0
B2	0.026	0.31	0.50	0.018	0.0007	0.013	6.6	24.7	3.90	0.04	0.0006	0.0007	0.006	-	0.3	0.01	0.09	0.0020	0.0010	0.0009	5.0

[Table 3]

Steel material No.	PRE	Heat treatment time (H)	Solid solution forming heat treatment temperature (°C)	Type of elements in nucleus (inclusion)	Type of elements in outer shell	Inclusion covering rate (%)	Ta content (atom%) in metal components in outer shell	Pitting potential (mV (vs. SCE))	Corrosion resistance evaluation
A9	40.1	3	1100	Mg,Ca,Al based oxysulfide	Ta,V,Nb,Cr	40	0.2	683	AA
A10	42.4	8.5	1100	Mg,Ca,Al based oxysulfide	Ta,Ti,Nb,Cr	60	1.5	749	AA
A11	41.4	73	1100	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Nb,Cr	60	3.2	812	AAA
A12	41.0	73	1100	Mg,Ca,Al based oxysulfide	Ta,Cr	60	6.8	920	AAAA
A13	40.5	73	1100	Mg,Ca,Al based oxysulfide	V,Cr	40	0	686	AA
A14	40.5	73	1100	Mg,Ca,Al based oxysulfide	Ti,Cr	40	0	697	AA
A15	42.4	73	1100	Mg,Ca,Al based oxysulfide	Nb,Cr	40	0	673	AA
A16	41.8	73	1100	Ca,Al based oxysulfide	Ti,V,Cr	40	0	590	A
A17	42.0	73	1100	Mg,Ca based oxysulfide	V,Ti,Nb,Cr	60	0	695	AA
A18	42.6	73	1100	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Cr	60	7	942	AAAA
A19	42.5	73	1100	Ca,Al based oxysulfide	Ta,V,Ti,Cr	60	6	921	AAAA
A20	42.1	73	1100	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Cr	60	5.1	915	AAAA
A21	41.1	73	1050	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Cr	80	3.4	831	AAA

(continued)

Steel material No.	PRE	Heat treatment time (H)	Solid solution forming heat treatment temperature (°C)	Type of elements in nucleus (inclusion)	Type of elements in outer shell	Inclusion covering rate (%)	Ta content (atom%) in metal components in outer shell	Pitting potential (mV (vs. SCE))	Corrosion resistance evaluation
A22	40.8	73	1050	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Cr	100	6.3	958	AAAA
B3	42.7	1	1100	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Nb,Cr	20	1.8	500	B
B4	41.8	1	1100	Mg,Ca,Al based oxysulfide	V,Ti,Nb,Cr	20	0	437	B
B5	42.2	73	1100	Mg,Ca,Al based oxysulfide	-	0	0	93	B
B6	42.7	73	1100	Mg,Ca,Al based oxysulfide	-	0	0	96	B
B7	44.1	73	1100	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Cr	20	0.1	167	B
B8	42.6	73	1100	Mg,Ca,Al based oxysulfide	Ta,V,Ti, Cr	20	0.6	251	B

[Table 4]

Steel material No.	Component composition (mass%) Balance: Fe and unavoidable impurities Underline shows that the material is out of the definition of the present invention.																				
	C	Si	Mn	P	S	Al	Ni	Cr	Mo	N	Mg	Ca	O	Co	Cu	Ta	V	Ti	Nb	B	Ta/Ti
A9	0.022	0.29	0.50	0.021	0.0024	0.017	6.5	25.2	3.21	0.27	0.0003	0.0006	0.001	-	0.2	0.09	0.11	-	0.0320	-	-
A10	0.019	0.33	0.49	0.017	0.0008	0.011	6.7	24.5	4.10	0.27	0.0008	0.0012	0.005	-	0.6	0.07	-	0.0030	0.0014	0.0020	23.3
A11	0.027	0.32	0.52	0.013	0.0006	0.013	6.5	24.4	3.90	0.26	0.0003	0.0006	0.004	0.2	0.2	0.06	0.11	0.0290	0.0040	0.0010	2.1
A12	0.024	0.31	0.69	0.025	0.0005	0.015	6.0	24.6	3.77	0.25	0.0003	0.0008	0.003	-	0.2	0.11	-	-	-	-	-
A13	0.023	0.38	0.90	0.026	0.0010	0.016	6.1	24.5	3.60	0.26	0.0005	0.0013	0.004	-	0.3	-	0.12	-	-	-	-
A14	0.019	0.40	0.87	0.030	0.0012	0.013	6.3	25.0	3.10	0.33	0.0006	0.0011	0.005	0.2	-	-	-	0.0350	-	0.0015	-
A15	0.021	0.37	0.86	0.016	0.0020	0.012	6.2	24.6	3.90	0.31	0.0010	0.0001	0.003	0.2	-	-	-	-	0.0310	0.0023	-
A16	0.014	0.31	0.69	0.024	0.0005	0.028	6.6	25.0	3.77	0.27	0.0001	0.0016	0.003	-	0.3	-	0.10	0.0080	-	0.0022	-
A17	0.020	0.34	0.47	0.021	0.0006	0.001	6.3	24.5	3.90	0.29	0.0019	0.0010	0.007	0.2	0.2	-	0.16	0.0300	0.0240	0.0012	-
A18	0.029	0.36	0.51	0.022	0.0004	0.015	7.0	24.4	4.02	0.31	0.0006	0.0006	0.003	-	0.2	0.11	0.11	0.0010	-	0.0025	110.0
A19	0.025	0.37	0.50	0.020	0.0005	0.014	6.9	24.5	4.06	0.30	0.0001	0.0015	0.003	-	-	0.10	0.10	0.0010	-	0.0020	100.0
A20	0.015	0.39	0.53	0.023	0.0008	0.002	7.0	25.1	3.90	0.26	0.0005	0.0005	0.006	-	0.3	0.11	0.11	0.0040	-	-	27.5
A21	0.026	0.33	0.65	0.028	0.0011	0.016	6.3	24.1	3.80	0.28	0.0008	0.0005	0.003	-	0.2	0.06	0.11	0.0380	-	0.0018	1.6
A22	0.028	0.31	0.82	0.023	0.0008	0.023	6.9	24.3	3.62	0.29	0.0007	0.0006	0.002	-	0.3	0.11	0.12	0.0003	0.0032	0.0019	366.7
B3	0.021	0.31	0.51	0.013	0.0008	0.012	6.2	24.4	4.20	0.28	0.0003	0.0006	0.008	0.4	0.2	0.03	0.16	0.0010	0.0018	0.0019	30.0
B4	0.023	0.33	0.52	0.016	0.0009	0.011	7.5	24.3	4.01	0.27	0.0009	0.0007	0.008	0.2	0.2	-	0.11	0.0040	0.0013	-	-
B5	0.028	0.34	0.49	0.017	0.0011	0.016	7.4	24.9	3.80	0.30	0.0007	0.0007	0.008	0.2	-	-	-	-	-	-	-
B6	0.021	0.35	0.47	0.021	0.0023	0.012	6.4	24.5	4.29	0.27	0.0006	0.0008	0.006	0.4	-	-	-	-	-	0.0010	-
B7	0.025	0.36	0.48	0.021	0.0120	0.016	6.1	24.3	4.50	0.31	0.0003	0.0013	0.007	-	0.3	0.05	0.12	0.0280	-	-	1.8
B8	0.018	0.34	0.52	0.018	0.0009	0.015	7.2	25.1	4.05	0.27	0.0004	0.0006	0.031	0.2	-	0.05	0.11	0.0050	-	0.0013	10.0

[Table 5]

Steel material No.	PRE	Heat treatment time (H)	Solid solution forming heat treatment temperature (°C)	Type of elements in nucleus (inclusion)	Type of elements in outer shell	Inclusion covering rate (%)	Ta content (atom%) in metal components in outer shell	Pitting potential (mV (vs. SCE))	Corrosion resistance evaluation
A23	25.7	73	1100	Mg,Ca,Al based oxysulfide	Ti,Cr	60	0	264	A
A24	26.4	73	1100	Mg,Ca,Al based oxysulfide	Ta,Ti,Nb,Cr	40	4.1	271	A
A25	26.3	8	1100	Mg,Ca,Al based oxysulfide	Ta,V,Cr	40	3.2	261	A
A26	26.4	73	1100	Mg,Ca,Al based oxysulfide	Ta,V,Ti,Cr	60	6.9	312	A
A27	26.4	73	1100	Mg,Ca,Al based oxysulfide	V,Nb,Cr	60	4.2	272	A
B9	25.9	1	1100	Mg,Ca,Al based oxysulfide	-	20	0	98	B
B10	25.0	73	1100	Mg,Ca,Al based oxysulfide	Ti,Nb,Cr	20	0	88	B
B11	26.6	73	1100	Mg,Ca,Al based oxysulfide	-	0	0	115	B

[Table 6]

Steel material No.	Component composition (mass%) Balance: Fe and unavoidable impurities Underline shows that the material is out of the definition of the present invention.																			
	C	Si	Mn	P	S	Al	Ni	Cr	Mo	N	Mg	Ca	O	Co	Cu	Ta	V	Ti	Nb	B	Ta/Ti
A23	0.018	0.50	1.29	0.020	0.0009	0.013	4.8	23.2	0.18	0.12	0.0012	0.0004	0.003	-	0.5	-	-	0.0034	-	0.0022	-
A24	0.021	0.52	1.43	0.019	0.0007	0.010	4.3	22.9	0.45	0.13	0.0009	0.0007	0.003	-	-	0.04	-	0.0019	0.0015	-	21.1
A25	0.020	0.37	1.67	0.022	0.0011	0.009	4.5	23.4	0.33	0.11	0.0007	0.0006	0.003	-	0.2	0.05	0.09	-	-	0.0018	-
A26	0.020	0.48	1.51	0.017	0.0009	0.015	4.8	23.1	0.37	0.13	0.0005	0.0008	0.004	-	-	0.06	0.11	0.0015	-	0.0019	40.0
A27	0.022	0.47	1.49	0.020	0.0006	0.011	4.6	23.4	0.34	0.12	0.0011	0.0006	0.004	0.1	-	-	0.03	-	0.0024	-	-
B9	0.019	0.51	1.72	0.019	0.0008	0.012	4.6	23.4	0.24	0.11	0.0009	0.0006	0.003	-	-	0.05	0.08	0.0011	-	-	45.5
B10	0.022	0.52	1.27	0.019	0.0006	0.014	4.3	23.3	0.45	0.01	0.0007	0.0009	0.002	-	-	-	-	0.0031	0.0013	-	-
B11	0.016	0.50	1.47	0.022	0.0009	0.008	4.2	23.5	0.37	0.12	0.0007	0.0006	0.004	0.1	0.3	-	-	-	-	0.0015	-

[0128] Also, from the results of Tables 1 and 2, Tables 3 and 4, and Tables 5 and 6, it will be understood that the examples satisfying the requirements of the present invention, that is, the steel material Nos. A1 to A8, A9 to A22, and A23 to A27, all have excellent pitting corrosion resistance.

[0129] In contrast, the comparative examples that do not satisfy the requirements of the present invention, that is, the steel material Nos. B1, B2, B3 to B8, and B9 to B11, have the following inconvenience.

[0130] In the comparative examples (steel material Nos. B1, B3, B4, and B9), the heat treatment in a temperature region of about 1000 to 1300°C was not carried out for 3 hours or more. For this reason, the proportion of the number of composite inclusions each containing Cr and at least one X-group element and having an outer shell of a carbide or nitride of at least one X-group element around a nucleus which is an inclusion of at least one of the oxides, sulfides, and oxysulfides ("inclusion covering rate" in Tables 1, 3, and 5) was less than 30%, so that the criterion of the corrosion resistance was not satisfied. Also, in the steel material No. B1, the value of Nb exceeded a predetermined range, so that the value of the pitting potential was smaller even when compared with the steel material Nos. B3 and B4.

[0131] In the comparative examples (steel material Nos. B5, B6, and B11), the content of the X-group elements of Ta, V, Nb, and Ti is less than the lower limit of the present invention. Also, in the comparative examples (steel material Nos. B5, B6, and B11), the proportion of the number of composite inclusions each containing Cr and at least one X-group element and having an outer shell of a carbide or nitride of at least one X-group element around a nucleus which is an inclusion of at least one of the oxides, sulfides, and oxysulfides (inclusion covering rate) was less than 30%, so that the criterion of the corrosion resistance was not satisfied.

[0132] In the comparative example (steel material No. B2), the content of N was small, so that the proportion of the number of composite inclusions each containing Cr and at least one X-group element and having an outer shell of a carbide or nitride of at least one X-group element around a nucleus which is an inclusion of at least one of the oxides, sulfides, and oxysulfides (inclusion covering rate) was less than 30%, so that the criterion of the corrosion resistance was not satisfied.

[0133] In the comparative example (steel material No. B7), the content of S was large, so that the proportion of the number of composite inclusions each containing Cr and at least one X-group element and having an outer shell of a carbide or nitride of at least one X-group element around a nucleus which is an inclusion of at least one of the oxides, sulfides, and oxysulfides (inclusion covering rate) was less than 30%, so that the criterion of the corrosion resistance was not satisfied.

[0134] In the comparative example (steel material No. B8), the content of O was large, so that the proportion of the number of composite inclusions each containing Cr and at least one X-group element and having an outer shell of a carbide or nitride of at least one X-group element around a nucleus which is an inclusion of at least one of the oxides, sulfides, and oxysulfides (inclusion covering rate) was less than 30%, so that the criterion of the corrosion resistance was not satisfied.

[0135] In the comparative example (steel material No. B10), the content of N was small, so that the proportion of the number of composite inclusions each containing Cr and at least one X-group element and having an outer shell of a carbide or nitride of at least one X-group element around a nucleus which is an inclusion of at least one of the oxides, sulfides, and oxysulfides (inclusion covering rate) was less than 30%, so that the criterion of the corrosion resistance was not satisfied.

[0136] This application is based on Japanese Patent Application No. 2015-225214 filed on November 17, 2015 and Japanese Patent Application No. 2016-170298 filed on August 31, 2016, the contents of which are incorporated herein for reference.

[0137] While the present invention has been fully and appropriately described in the above by way of embodiments with reference to the drawings and others in order to express the present invention, it is to be recognized that those

skilled in the art can easily change and/or modify the embodiments described above. Therefore, it is to be interpreted that the changes or modifications made by those skilled in the art are encompassed within the scope of the claims unless those changes or modifications are at a level that departs from the scope of the claims described in the claims of the present application.

Industrial Applicability

[0138] The present invention has a wide range of industrial applicability in the technical field of duplex stainless steel materials and duplex stainless copper tubes.

Claims

1. A duplex stainless steel material comprising a ferrite phase and an austenite phase,
wherein
the duplex stainless steel material contains, as metal component composition, at least one X-group element selected from 0.01 to 0.50 mass% of V, 0.0001 to 0.0500 mass% of Ti, 0.0005 to 0.0500 mass% of Nb, and 0.01 to 0.50 mass% of Ta;
the duplex stainless steel material has composite inclusions or has composite inclusions and inclusions;
each of the inclusions includes at least one of an oxide, a sulfide, and an oxysulfide; each of the composite inclusions includes one of the inclusions as a nucleus and includes an outer shell existing around the nucleus and having a carbide or a nitride containing Cr and the at least one X-group element; and
a proportion of a number of the composite inclusions with respect to a total number of the inclusions is 30% or more.

2. The duplex stainless steel material according to claim 1, wherein the duplex stainless steel material contains 0.01 to 0.50 mass% of Ta as the metal component composition, and the outer shell contains Ta in an amount satisfying formula (1) below:

$$([Ta] / [M]total) \times 100 \geq 5 \text{ ..... formula (1)}$$

where [Ta] represents a number of Ta atoms contained in the outer shell, and [M]total represents a total number of atoms of metal elements contained in the outer shell.

3. The duplex stainless steel material according to claim 1 or 2, wherein the duplex stainless steel material contains 0.01 to 0.50 mass% of Ta and 0.0001 to 0.0500 mass% of Ti as the metal component composition, and a (Ta mass% / Ti mass%) ratio satisfies formula (2) below:

$$\text{Ta mass\% / Ti mass\%} \geq 25 \text{ ..... formula (2).}$$

4. The duplex stainless steel material according to claim 1, wherein the duplex stainless steel material contains 0.0001 to 0.0200 mass% of Mg and 0.001 to 0.050 mass% of Al as the metal component composition, and the nucleus in each of the composite inclusions contains an oxide of Mg and Al.

5. The duplex stainless steel material according to claim 1, wherein the metal component composition of the duplex stainless steel material is:

0.100 mass% or less of C,
0.10 to 2.00 mass% of Si,
0.10 to 3.00 mass% of Mn,
0.0100 mass% or less of S,
1.0 to 10.0 mass% of Ni,
0.05 to 6.00 mass% of Mo,
0.10 to 0.50 mass% of N,
20.0 to 28.0 mass% of Cr, and
0.030 mass% or less of O,

with a balance being Fe and unavoidable impurities.

6. The duplex stainless steel material according to claim 1, wherein the metal component composition of the duplex stainless steel material is:

0.100 mass% or less of C,
0.10 to 2.00 mass% of Si,
0.10 to 3.00 mass% of Mn,
0.0100 mass% or less of S,
3.0 to 7.0 mass% of Ni,
0.05 to 1.00 mass% of Mo,
0.05 to 0.20 mass% of N,
20.0 to 25.0 mass% of Cr, and
0.030 mass% or less of O,

with a balance being Fe and unavoidable impurities.

7. The duplex stainless steel material according to claim 5 or 6, further containing 0.0001 to 0.0200 mass% of Ca as the metal component composition.

8. The duplex stainless steel material according to claim 5 or 6, further containing at least one selected from the group consisting of 0.1 to 2.0 mass% of Co and 0.1 to 2.0 mass% of Cu as the metal component composition.

9. The duplex stainless steel material according to claim 5 or 6, further containing 0.0005 to 0.0100 mass% of B as the metal component composition.

10. A duplex stainless steel tube comprising the duplex stainless steel material according to claim 1.

FIG.1

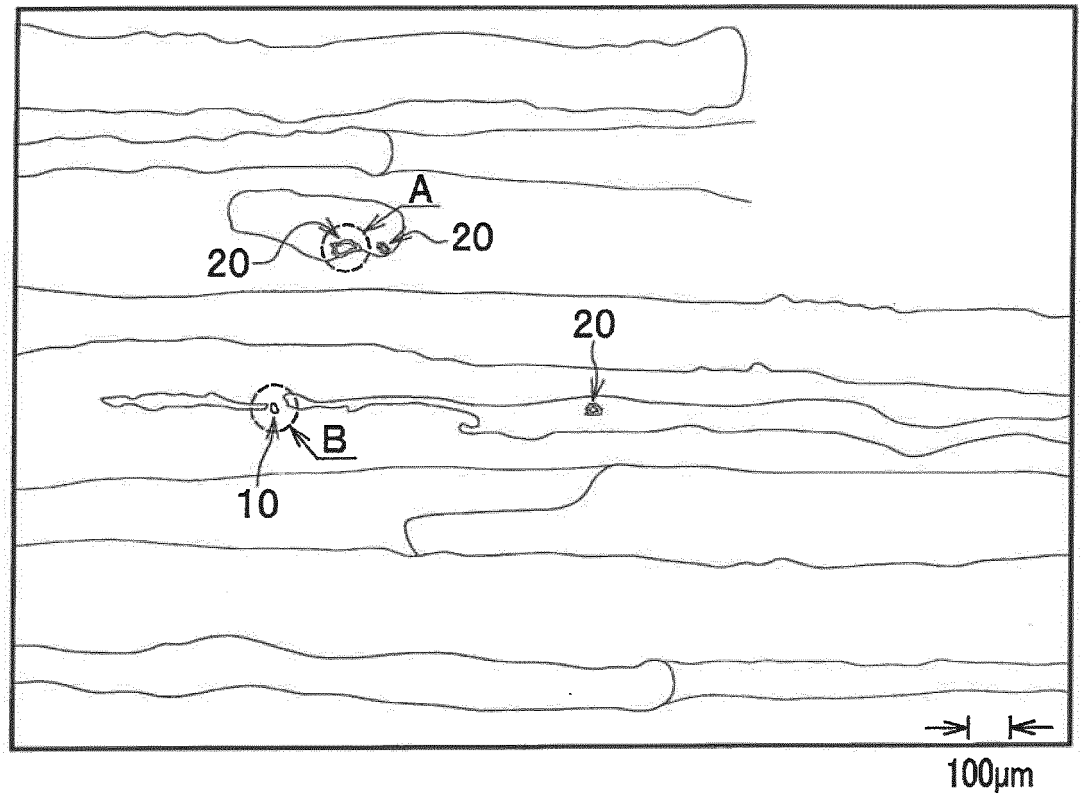


FIG.2

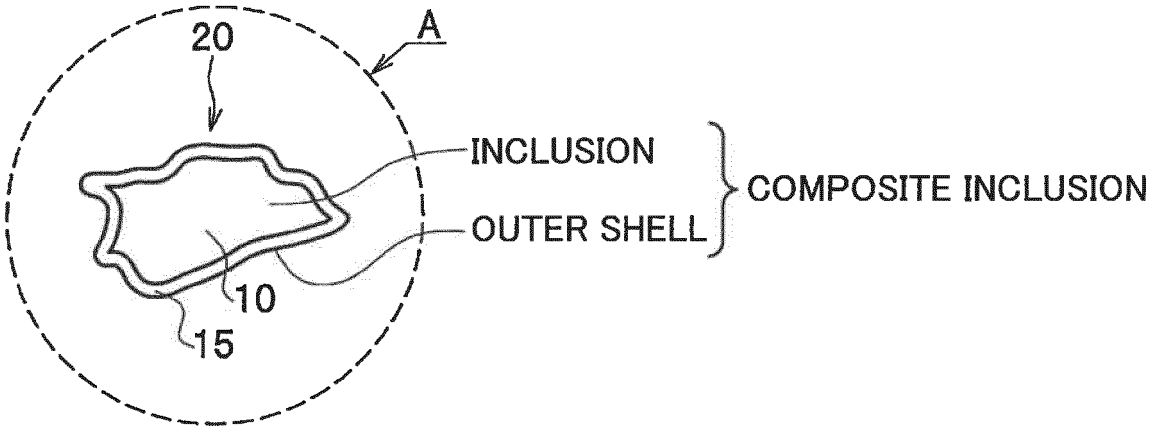


FIG.3

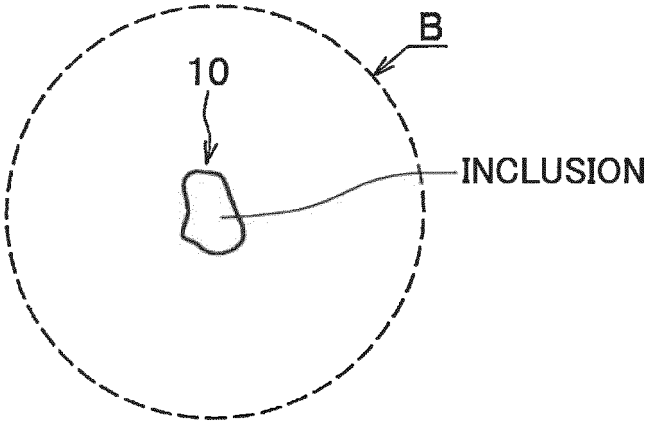


FIG.4

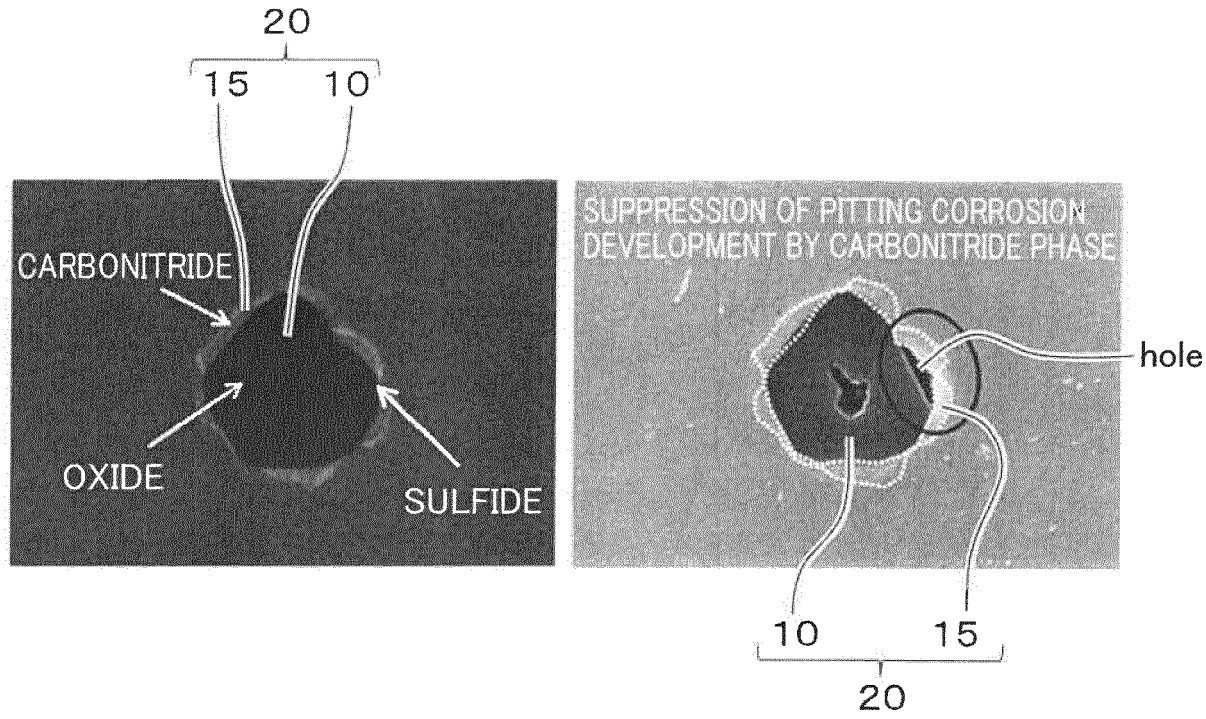

20
15
10
CARBONITRIDE
OXIDE
SULFIDE
SUPPRESSION OF PITTING CORROSION DEVELOPMENT BY CARBONITRIDE PHASE
hole
10
15
20

FIG.5

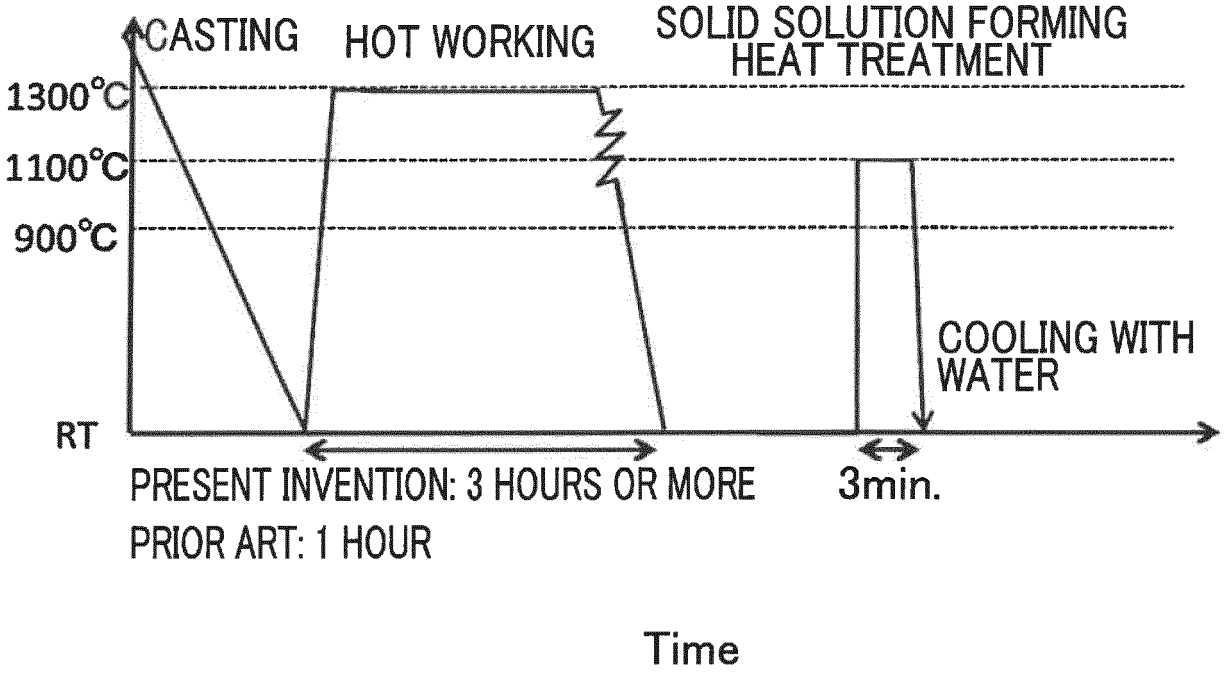

CASTING
HOT WORKING
SOLID SOLUTION FORMING HEAT TREATMENT
1300°C
1100°C
900°C
RT
COOLING WITH WATER
PRESENT INVENTION: 3 HOURS OR MORE
PRIOR ART: 1 HOUR
3min.
Time

FIG.6

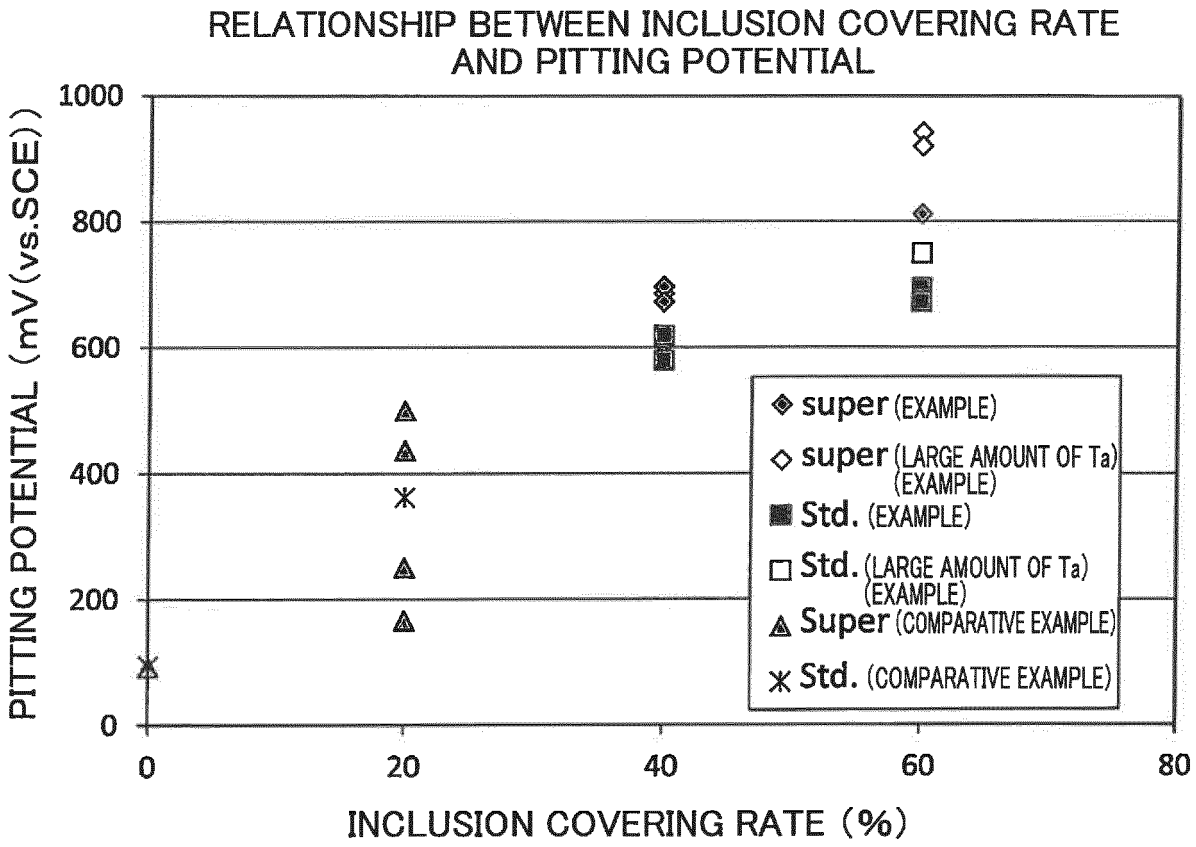

RELATIONSHIP BETWEEN INCLUSION COVERING RATE AND PITTING POTENTIAL
PITTING POTENTIAL (mV(vs.SCE))
1000
800
600
400
200
0
0
20
40
60
80
INCLUSION COVERING RATE (%)
super (EXAMPLE)
super (LARGE AMOUNT OF Ta) (EXAMPLE)
Std. (EXAMPLE)
Std. (LARGE AMOUNT OF Ta) (EXAMPLE)
Super (COMPARATIVE EXAMPLE)
Std. (COMPARATIVE EXAMPLE)

FIG.7

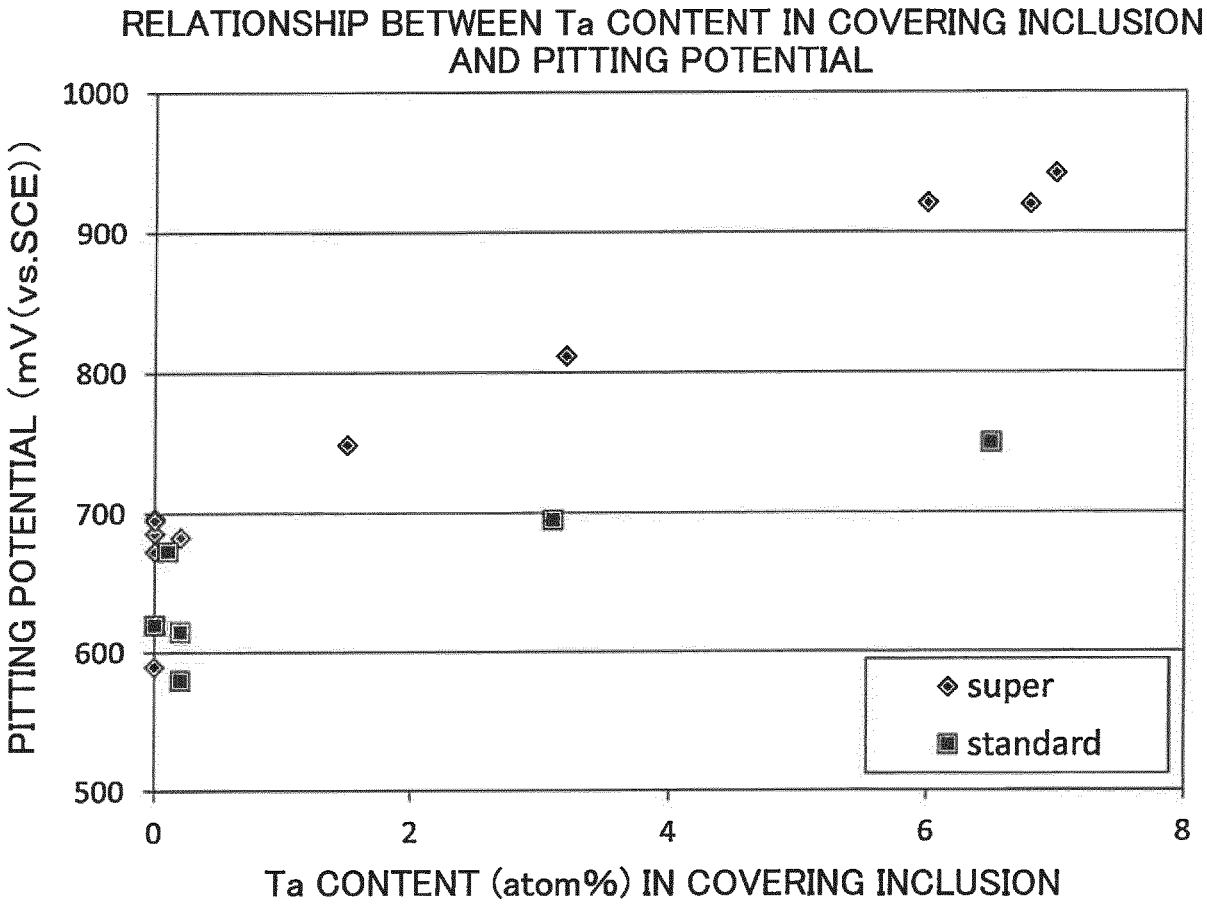
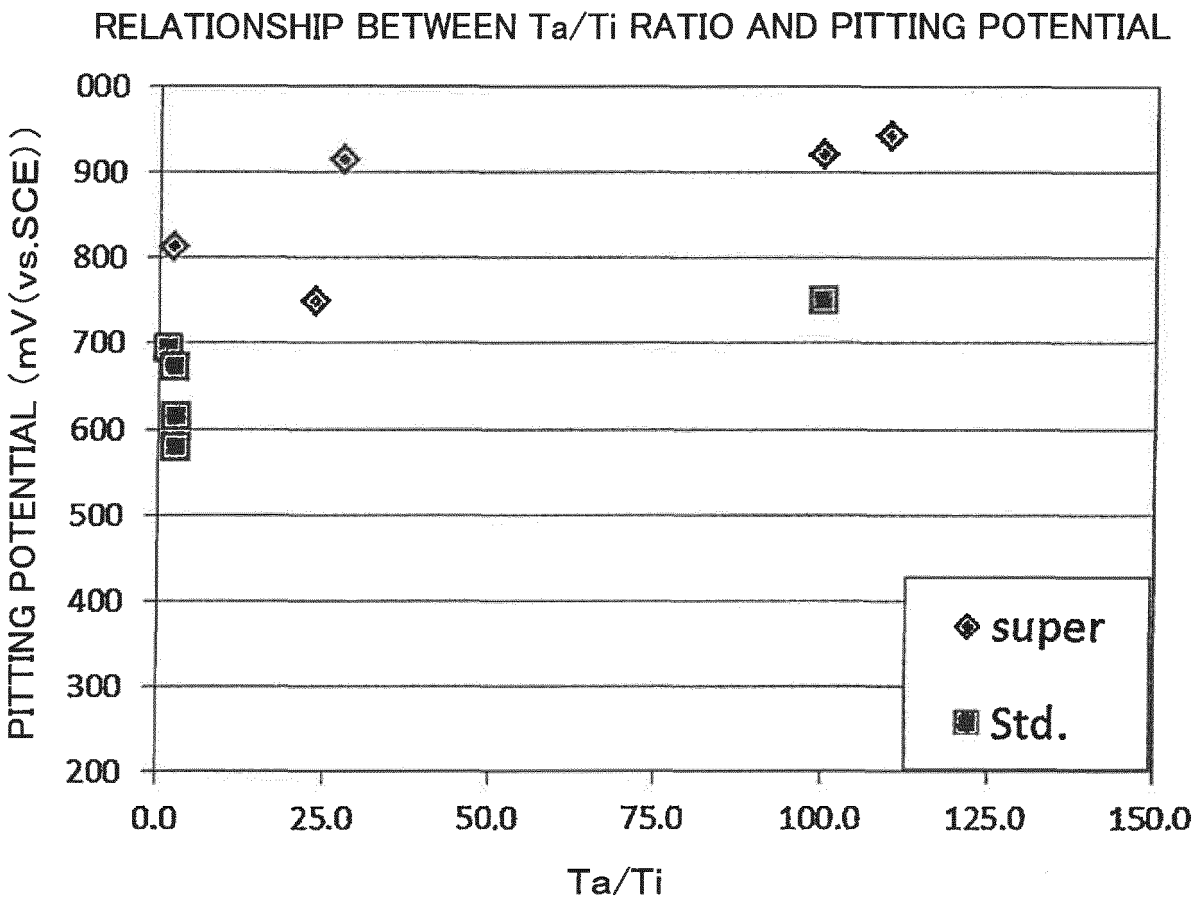

RELATIONSHIP BETWEEN Ta CONTENT IN COVERING INCLUSION AND PITTING POTENTIAL
PITTING POTENTIAL (mV(vs.SCE))
1000
900
800
700
600
500
0
2
4
6
8
Ta CONTENT (atom%) IN COVERING INCLUSION
super
standard

FIG.8


RELATIONSHIP BETWEEN Ta/Ti RATIO AND PITTING POTENTIAL
PITTING POTENTIAL (mV(vs.SCE))
000
900
800
700
600
500
400
300
200
0.0
25.0
50.0
75.0
100.0
125.0
150.0
Ta/Ti
super
Std.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/082652

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/58*(2006.01)i, *C21D8/00*(2006.01)n, *C21D8/10*(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00-C22C38/60, C21D8/00-C21D8/10

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 1996-2017
Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2015-78429 A (Kobe Steel, Ltd.), 23 April 2015 (23.04.2015), claims; 0001 to 0003, 0013 to 0017, 0049 to 0057; tables 1 to 2 (Family: none)	1-10
A	JP 2015-110828 A (Kobe Steel, Ltd.), 18 June 2015 (18.06.2015), claims; 0001 to 0004, 0045 to 0053; examples & US 2015/0354038 A1 claims; 0001 to 0004, 0069 to 0081; example 3 & WO 2014/112445 A1 & EP 2947169 A1 & KR 10-2015-0087430 A & CN 104919072 A	1-10
A	JP 2013-253315 A (Kobe Steel, Ltd.), 19 December 2013 (19.12.2013), (Family: none)	1-10

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 January 2017 (19.01.17)	31 January 2017 (31.01.17)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/082652

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	JP 2008-38214 A (Nippon Steel & Sumikin Stainless Steel Corp.), 21 February 2008 (21.02.2008), & US 2009/0098007 A1 & WO 2008/018242 A1 & EP 2050832 A1 & KR 10-2008-0038217 A & CN 101346486 A	1-10
A	JP 2005-105346 A (Nippon Steel Corp.), 21 April 2005 (21.04.2005), claims; 0023; tables 1 to 2 (Family: none)	1-10
A	JP 2002-241838 A (Sumitomo Metal Industries, Ltd.), 28 August 2002 (28.08.2002), claims; 0050, 0067 (Family: none)	1-10
A	JP 4-165019 A (Sumitomo Metal Industries, Ltd.), 10 June 1992 (10.06.1992), claims; page 2, lower right column, line 3 to page 3, lower left column, line 10; page 4, lower right column, line 9 to page 5, lower right column, line 13 (Family: none)	1-10
A	JP 2013-234344 A (Kobe Steel, Ltd.), 21 November 2013 (21.11.2013), (Family: none)	1-10

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2015110828 A **[0011]**
- JP 2015225214 A **[0136]**
- JP 2016170298 A **[0136]**

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- **IZUMI MUTO.** *FERRUM,* 2012, vol. 17 (12), 858-863 **[0012]**