



(11) **EP 2 947 169 A1**

(12) **EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 153(4) EPC

(43) Date of publication:  
**25.11.2015 Bulletin 2015/48**

(51) Int Cl.:  
**C22C 38/00** *(2006.01)* **C22C 38/58** *(2006.01)*

(21) Application number: **14741060.9**

(86) International application number:  
**PCT/JP2014/050363**

(22) Date of filing: **10.01.2014**

(87) International publication number:  
**WO 2014/112445 (24.07.2014 Gazette 2014/30)**

(84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB  
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO  
PL PT RO RS SE SI SK SM TR**  
Designated Extension States:  
**BA ME**

(30) Priority: **15.01.2013 JP 2013004891**  
**05.03.2013 JP 2013043250**  
**05.11.2013 JP 2013229754**

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(54) **DUPLEX STAINLESS STEEL MATERIAL AND DUPLEX STAINLESS STEEL PIPE**

(57) This duplex stainless steel material is composed of a ferrite phase and an austenite phase, and has a component composition that contains 0.100% by mass or less of C, 0.10-2.00% by mass of Si, 0.10-2.00% by mass of Mn, 0.050% by mass or less of P, 0.0100% by mass or less of S, 0.001-0.050% by mass of Al,

1.0-10.0% by mass of Ni, 22.0-28.0% by mass of Cr, 2.0-6.0% by mass of Mo and 0.20-0.50% by mass of N, while containing 0.01-0.50% by mass of Ta and/or 0.1-1.0% by mass of Ge, with the balance made up of Fe and unavoidable impurities.

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**Description**

## Technical Field

5 **[0001]** The present invention relates to a duplex stainless steel material and a duplex stainless steel pipe used in circumstances containing corrosive materials such as chlorides, hydrogen sulfide, and gaseous carbon dioxide (hereinafter sometimes referred to as corrosive circumstance).

## Background Art

10 **[0002]** A stainless steel material is a material spontaneously forming a stable surface layer mainly including Cr oxides referred to as a passive layer in a corrosive circumstance to develop corrosion resistance. Particularly, a duplex stainless steel material consisting of a ferrite phase and an austenite phase has excellent strength characteristics compared with austenitic stainless steel or ferritic stainless steel and has good pitting corrosion resistance and stress corrosion cracking resistance. Due to such features, duplex stainless steel materials are used as structural materials in seawater circumstances such as umbilicals, seawater desalination plants, and LNG vaporizers, as well as structural materials in severe corrosive circumstances such as oil well pipe and various chemical plants.

15 **[0003]** However, in a case where a working circumstance contains a great amount of corrosive materials such as chlorides (chloride ions), local corrosion, so-called pitting corrosion sometimes occurs in the duplex stainless steel materials starting from inclusions and defects in the passive layer of the duplex stainless steel materials. Further, in crevice portions of the duplex stainless steel material, corrosive materials such as chloride ions are concentrated inside the crevice portions to result in severer corrosive circumstance and, further, oxygen concentration cells are formed between the outside and the inside of the crevices, which sometimes further progresses local corrosion inside the crevices to generate so-called crevice corrosion. Further, since local corrosion such as pitting corrosion and crevice corrosion often forms origins of stress corrosion cracking (SCC), improvement of corrosion resistance, particularly, local corrosion resistant characteristics is further demanded from a viewpoint of safety.

20 **[0004]** Particularly, in oil well pipe materials used for excavation of oils and natural gases, oil wells or gas wells in deeper layers have been developed in recent years and since the materials are often exposed to circumstances at higher temperature containing a great amount of corrosive materials such as hydrogen sulfide, gaseous carbon dioxide and chlorides, better corrosion resistance than usual has been demanded.

25 **[0005]** The pitting corrosion resistance of stainless steels is represented by pitting resistance equivalent (PRE) calculated as  $[Cr] + 3.3 [Mo] + 16 [N]$ , or PREW in a case of containing W calculated as  $[C] + 3.3 [Mo] + 0.5 [W] + 16 [N]$ , assuming the amount of Cr (mass%) as  $[Cr]$ , the amount of Mo (mass%) as  $[Mo]$ , the amount of W (mass%) as  $[W]$ , and the amount of N (mass%) as  $[N]$ , and it is known that excellent pitting corrosion resistance is obtainable as the contents of Cr, Mo, and N are increased. An addition amount of Cr, Mo, N, and W is controlled such that PRE (or PREW) is 35 or more in usual duplex stainless steels and, further, PRE is 40 or more in super duplex stainless steels. Further, it is known that increase of the contents of Cr, Mo, and N also contributes to the improvement of crevice corrosion resistance.

30 **[0006]** For example, Patent Literature 1 discloses a duplex stainless steel excellent in the corrosion resistance having PREW of 40 or more by controlling the contents of Cr, Mo, N, and W. Further Patent Literature 2 discloses a duplex stainless steel excellent in corrosion resistance and hot workability by controlling the contents of B and Ta in addition to the control of the contents of Cr, Mo, W, and N. Patent Literature 3 discloses a duplex stainless steel excellent in corrosion resistance and hot workability by controlling the contents of Ti, V, Nb, Ta, Zr, B, etc. in addition to the control of the contents of Cr, Mo, W, and N.

35 **[0007]** Patent Literature 4 states that Cr and N, in particular, have an effect of improving the crevice corrosion resistance and discloses a duplex stainless steel excellent in crevice corrosion resistance and stretch-expand formability while saving Ni that increases the cost. Patent Literature 5 discloses a duplex stainless steel of improved crevice corrosion resistance by adding Cu and Al and controlling the amount of O, S, and Ca.

40 **[0008]** In Patent Literature 6, an amount of S is decreased to 3 ppm or less by using a CaO crucible and CaO-CaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-based slags in a vacuum melting furnace in order to decrease sulfide-based inclusions in the steel that give an adverse effect on the hot workability and the corrosion resistance.

45 **[0009]** Patent Literature 7 discloses a duplex stainless steel in which contents of Ca and Mg in total and the content of S in oxide-based inclusions are controlled and, further, the form and the density of inclusions are controlled as a technique of controlling oxide-based inclusions which form origins of the pitting corrosion. Further, since insoluble Al oxides containing Ca, Mg, and S by a predetermined amount or more form local corrosion origins, Patent Literature 7 discloses a duplex stainless steel of controlling the size and the number of the inclusions by optimal combination of slag basicity during reduction treatment, killing temperature and time in a cradle, and total working ratio after casting, thereby suppressing generation of local corrosion.

## Citation List

## Patent Literature

5 **[0010]**

[Patent Literature 1]: Japanese Unexamined Patent Application Publication No. H05(1993)-132741  
 [Patent Literature 2]: Japanese Unexamined Patent Application Publication No. H08(1996)-170153  
 [Patent Literature 3]: Japanese Unexamined Patent Application Publication No. S61(1986)-157626  
 10 [Patent Literature 4]: Japanese Unexamined Patent Application Publication No. 2006-200035  
 [Patent Literature 5]: Japanese Unexamined Patent Application Publication No. S63(1988)-157838  
 [Patent Literature 6]: Japanese Unexamined Patent Application Publication No. H03(1991)-291358  
 [Patent Literature 7]: International Laid-Open WO 2005/014872

15 Summary of Invention

## Technical Problem

20 **[0011]** When a duplex stainless steel material is used in a severe corrosive circumstance containing hydrogen sulfide, gaseous carbon dioxide, and chloride ions, it is necessary to improve the corrosion resistance. However, improvement of the corrosion resistance only by adjusting the contents of Cr, Mo, N, and W is sometimes insufficient.

**[0012]** Then, in Patent Literature 1, while the corrosion resistance (pitting corrosion resistance) of the steel material is evaluated by a pitting potential in 20%-NaCl at 80°C, the potential is about 300 mV at PREW = about 42, and it cannot always be said that sufficient corrosion resistance can be ensured in a severe corrosive circumstance demanded recently.

25 **[0013]** Further, in Patent Literature 2, B is added in the steel, but there may be a possibility that B is bonded with N in the steel to form BN, thereby lowering the concentration of N that contributes to the corrosion resistance. Further, in Patent Literature 2, the addition amount of W is as high as 5 to 10 mass%, and this increases the cost and is not economically advantageous.

30 **[0014]** Further, in Patent Literature 3, the Nb, Ti, and Zr are added in the steel, but such elements are bonded with N in the steel to form nitrides, and may lower the concentration of N that contributes to the corrosion resistance. Further, when the formed nitrides are coarse, toughness is deteriorated.

35 **[0015]** The duplex stainless steel disclosed in Patent Literature 4 is intended to be used as automobile materials but has no sufficient crevice corrosion resistance in severe corrosive circumstances such as oil wells. Further, in the duplex stainless steel disclosed in Patent Literature 5, the crevice corrosion resistance is evaluated in artificial seawater at 30°C and the crevice corrosion resistance is insufficient in severe corrosive circumstances such as oil wells.

**[0016]** Further, Patent Literature 6 describes that decrease of the concentration of S to 3 ppm or less gives a large industrial burden to increase the cost, and evaluates that those having a critical pitting corrosion generation temperature of 35°C or higher are excellent in the corrosion resistance, and it is considered that they are insufficient to be used in recent severe corrosive circumstances.

40 **[0017]** In Patent Literature 7 even when inclusions are controlled by adding Ca and Mg, there may be a possibility that they are agglomerated to cause local corrosion or form cracking start points. Further, the present invention is basically directed to decrease existent inclusions to form origins for pitting corrosion and excess decrease of O and S as the source thereof gives a large industrial burden to increase the cost.

45 **[0018]** In contrast, while the duplex stainless steel material is excellent in strength characteristics, working such as rolling and drawing therefor is often more difficult than that for usual stainless steel materials. Further, since  $\sigma$ -phase precipitation is promoted due to increase of Cr and Mo which are added with an aim of improving the corrosion resistance, there may be a possibility that hot workability becomes insufficient depending on the application use.

50 **[0019]** The present invention has been accomplished in view of the situations described above, and the subjects thereof are to provide a duplex stainless steel material that develops good corrosion resistance in a circumstance containing corrosive materials such as chlorides, hydrogen sulfide, and gaseous carbon dioxide, further provide a duplex stainless steel material that develops better hot workability, and provide a duplex stainless steel pipe that develops good corrosion resistance by using such duplex stainless steel material.

## Solution to Problem

55 **[0020]** As described above, the stainless steel material is a material developing the corrosion resistance by a passive layer mainly including Cr oxides. Since the duplex stainless steel material generally includes a ferrite phase and an austenite phase, discontinuity is present at the boundary between the different phases, and the passive layer tends to

be highly instable at the boundary between the ferrite phase and the austenite phase, the stainless steel material is liable to undergo the effect of chloride ions that damage the passive layer tending to induce the local corrosion. For solving the subjects, the present inventors have noted on enhancing the stability and the protective performance for the passive layer of the duplex stainless steel within a range not deteriorating the production situations and various characteristics and have made technical investigation for improving the corrosion resistance.

**[0021]** As described above, since the stainless steel material is a material developing the corrosion resistance by the passive layer mainly including Cr oxides, the present inventors have made a study from a viewpoint of improving the effective Cr concentration in the steel. As a result, it has been found that since the effective Cr concentration in the steel is lowered by the formation of unnecessary Cr-based inclusions in the steel, a method suppressing precipitation of the unnecessary Cr-base inclusions is effective.

**[0022]** Since inclusions in the stainless steel material generally include carbides and oxides, it is important to fix C and O in the steel that cause formation of the inclusions with other elements. Since O can be fixed with Si and Al that are added for deoxidization or with Ca and Mg, investigation has been made from a viewpoint of fixing, particularly, unnecessary C in the steel. Further, since the pitting corrosion resistance of the stainless steel material is represented by the pitting corrosion resistance equivalent PRE (W) containing the amount of N ("N") as described above, and the effective N concentration in the steel also gives an effect on the improvement of the corrosion resistance, investigation has been made also from a viewpoint of suppressing precipitation of unnecessary N-based inclusions.

**[0023]** Then, it has been found that the effective concentrations of Cr and N in the steel can be increased and, as a result, the stability of the passive layer is enhanced and the corrosion resistance is improved by properly adding Ta as an element having high fixing function of the unnecessary C in the steel and less fixing N necessary for ensuring the corrosion resistance in the steel.

**[0024]** Further, other than Cr, Mo has been known as an additive element for improving the corrosion resistance. When local corrosion occurs to form an acidic circumstance in the pittings, Mo is dissolved as ions to provide an effect of promoting repair of the passive layer (re-passivation). Then, the present inventors have noted on the effect and selected elements that dissolve ions in the acidic circumstance in the same manner as Mo. As a result, it has been found that Ge has electrochemical characteristics similar to those of Mo in the acidic region, and has a function of strengthening the re-passivation ability of the stainless steel and improving the local corrosion resistance by appropriate addition.

**[0025]** The duplex stainless steel material according to the present invention is a duplex stainless steel material consisting of a ferrite phase and an austenite phase in which the component composition of the duplex steel material contains one or more elements selected from C: 0.100 mass% or less, Si: 0.10 to 2.00 mass%, Mn: 0.10 to 2.00 mass%, P: 0.050 mass% or less, S: 0.0100 mass% or less, Al: 0.001 to 0.050 mass%, Ni: 1.0 to 10.0 mass%, Cr: 22.0 to 28.0 mass%, Mo: 2.0 to 6.0 mass%, N: 0.20 to 0.50 mass%, and further contains one or more elements selected from Ta: 0.01 to 0.50 mass% and Ge: 0.1 to 1.0 mass%, with the remainder of Fe and unavoidable impurities.

**[0026]** As described above, corrosion resistance of the duplex stainless steel material is improved when predetermined amounts of C, Si, Mn, P, S, Al, Ni, Cr, Mo, N and Ta and/or Ge are contained. Further, when Ta is selected as the element to be contained, deterioration of the hot workability is also suppressed.

**[0027]** Further, in the duplex stainless steel material according to the present invention, the PRE value represented by the following formula is preferably 40 or more assuming the Cr content (mass%) as [Cr], the Mo content (mass%) as [Mo], and the N content (mass%) as [N] since the corrosion resistance and the strength of the steel material are improved:

$$PRE = [Cr] + 3.3 [Mo] + 16 [N]$$

**[0028]** Further, in the duplex stainless steel material according to the present invention, it is preferred that Ta is contained, O as the impurity is restricted to 0.01 mass% or less, and Ta-containing sulfide-oxide-based composite inclusions having a major diameter of 1  $\mu$ m or more are present by the number of 500 or less per 1 mm<sup>2</sup> of a cross section perpendicular to a working direction, and the Ta content of the sulfide-oxide-based composite inclusions is 5 at% or more in the inclusions of the duplex stainless steel material. The corrosion resistance is improved further by such definition.

**[0029]** In the duplex stainless steel material according to the present invention, the component composition preferably contains one or more elements selected from the group consisting of Co: 0.10 to 2.00 mass%, Cu: 0.10 to 2.00 mass%, V: 0.01 to 0.50 mass%, Ti: 0.01 to 0.50 mass%, and Nb: 0.01 to 0.50 mass%.

**[0030]** As described above, the corrosion resistance of the duplex stainless steel material is improved further by further containing predetermined amounts of one or more elements selected from the group consisting of Co, Cu, V, Ti, and Nb. Further, Co and Cu also contribute to the stabilization of the austenite phase, and V, Ti, and Nb also contribute to the improvement of the strength characteristics and the hot workability.

**[0031]** Further, in the duplex stainless steel material according to the present invention, it is preferred that the component composition further contains one or two of Mg: 0.0005 to 0.0200 mass%, and Ca: 0.0005 to 0.0200 mass%.

**[0032]** As described above, in the duplex stainless steel material, formation of coarse inclusions such as MnS forming passive layer defect portions that tend to form origins of local corrosion is suppressed by further containing predetermined amounts of one or two of Mg and Ca, to improve the local corrosion resistance. Further, the hot workability is improved by suppressing the formation, for example, of coarse MnS inclusions.

**[0033]** Further, a duplex stainless steel pipe according to the present invention includes the duplex stainless steel material described above.

**[0034]** As described above, in the duplex stainless steel pipe, since the stability of the passive layer formed on the surface of the steel pipe is enhanced by constituting the steel pipe with the duplex stainless steel material, the local corrosion can be suppressed remarkably to improve the corrosion resistance.

#### Advantageous Effects of Invention

**[0035]** The duplex stainless material according to the present invention develops good corrosion resistance in the circumstance containing corrosive materials such as chlorides, hydrogen sulfide, and gaseous carbon dioxide. Further, when Ta is contained, good hot workability is also developed. Further, the duplex stainless steel pipe according to the present invention develops good corrosion resistance in a circumstance containing corrosive materials such as chlorides, hydrogen sulfide, and gaseous carbon dioxide. As a result, the duplex stainless steel pipe can be used in structural materials in seawater circumstances such as umbilicals, seawater desalination plants, and LNG vaporizers, as well as structural materials in the severe corrosive circumstance such as oil well pipes and various chemical plants.

#### Description of Embodiments

##### < Duplex Stainless Steel Material >

**[0036]** Embodiments of the duplex stainless steel material according to the present invention are to be described specifically.

**[0037]** The duplex stainless steel material according to the present invention is a duplex stainless steel material consisting of a ferrite phase and an austenite phase in which the component composition of the duplex stainless steel material contains predetermined amounts of C, Si, Mn, P, S, Al, Ni, Cr, Mo, and N and contains predetermined amounts of Ta and/or Ga, with the remainder of Fe and unavoidable impurities. Each of the constituents is to be described below.

##### (Steel Material Microstructure)

**[0038]** The duplex stainless steel material of the present invention consists of two phases of a ferrite phase and an austenite phase. In the duplex stainless steel material consisting of 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 the austenite phase stabilizing elements such as Ni and N tend to be concentrated in the austenite phase. When the area ratio of the ferrite phase to the austenite phase is less than 30% or more than 70%, the difference of concentration of elements contributing to the corrosion resistance such as Cr, Mo, Ni, and N between the ferrite phase and the austenite phase is excessively large, so that 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, it is also recommended to optimize the area ratio between the ferrite phase and the austenite phase. The area ratio of the ferrite phase is preferably 30 to 70% and more preferably 40 to 60% from a viewpoint of the corrosion resistance. The area ratio between the ferrite phase and the austenite phase can be optimized by adjusting the contents of the ferrite phase stabilizing elements and the austenite phase stabilizing elements.

**[0039]** Further, in the duplex stainless steel material of the present invention,  $\sigma$ -phase or different phases such as a phase containing Cr carbonitrides are also allowable in addition to the ferrite phase and the austenite phase to such an extent as not impairing various characteristics like corrosion resistance and mechanical characteristics. The area of the ferrite phase and the austenite phase in total is preferably 95% or more and, more preferably, 97% or more.

**[0040]** The reason for defining the range of numerical values of the component composition of the duplex stainless steel material is to be described.

(C: 0.100 mass% or less)

**[0041]** Carbon forms carbides with Cr in the steel material to deteriorate the corrosion resistance and the hot workability and, accordingly, is a harmful element. Accordingly, the C content is defined as 0.100 mass% or less. Since as small C

content as possible is preferred, it is preferably 0.080 mass% or less and, more preferably, 0.060 mass% or less. Also, C may not be contained in the steel material, that is, may be 0 mass%.

(Si: 0.10 to 2.00 mass%)

**[0042]** Si is an essential element for deoxidization and stabilization of the ferrite phase. In order to obtain such effects, Si content is defined as 0.10 mass% or more. However, since excess Si content deteriorates the hot workability, the Si content is defined as 2.00 mass% or less. A lower limit of the Si content is preferably 0.15 mass% and, more preferably, 0.20 mass%. Further, a preferred upper limit of the Si content is 1.50 mass% and a more preferred upper limit is 1.00 mass%.

(Mn: 0.10 to 2.00 mass%)

**[0043]** Mn, like Si, has a deoxidization effect and further Mn is an essential element for ensuring strength. In order to obtain such effects, Mn content is defined as 0.10 mass% or more. However, since excess Mn content forms coarse MnS to deteriorate the corrosion resistance and the hot workability, the Mn content is defined as 2.00 mass% or less. A lower limit of the Mn content is preferably 0.15 mass% and, more preferably, 0.20 mass%. Further, an upper limit of the Mn content is preferably 1.50 mass% and, more preferably, 1.00 mass%.

(P: 0.050 mass% or less)

**[0044]** P is an impurity intruded during melting and is an element harmful to the corrosion resistance. Further, P is an element deteriorating also the weldability and the workability. Accordingly, the P content is defined as 0.050 mass% or less. Further, since as small P content as possible is preferred, it is preferably 0.040 mass% or less and, more preferably, 0.030 mass%. Also, P may not be contained in the steel material, that is, may be 0 mass%. However, since excess decrease of the P content increases the production cost, a lower limit of the P content in view of practical operation is 0.010 mass%.

(S: 0.0100 mass% or less)

**[0045]** S, like P, is an impurity intruded during melting and sulfur is an element that is bonded with Mn or the like to form sulfide-based impurities and deteriorates the corrosion resistance and the hot workability. Accordingly, S content is defined as 0.0100 mass% or less. Since as small S content as possible is preferred, it is preferably 0.0030 mass% or less. Also, sulfur may not be contained in the steel material, that is, may be 0 mass%. However, since excess decrease of S content increases the production cost, a lower limit of the S content in view of practical operation is 0.0001 mass%.

(Al: 0.001 to 0.050 mass%)

**[0046]** Al, like Si and Mn, has an effect of deoxidization and is an essential element for decreasing the amount of oxygen during melting. In order to obtain such effects, Al content is defined as 0.001 mass% or more. However, since excess Al content forms oxide-based inclusions to give an adverse effect on the pitting corrosion resistance, the Al content is defined as 0.050 mass%. A preferred range of the Al content is 0.010 to 0.020 mass%.

(Ni: 1.0 to 10.0 mass%)

**[0047]** Ni is an essential element for improving the corrosion resistance and has a marked effect of suppressing the local corrosion particularly in chloride circumstances. Further, nickel is effective also for improving low temperature toughness and, further, is an essential element also for stabilizing the austenite phase. In order to obtain such effects, the Ni content is defined as 1.0 mass% or more. However, since excess Ni content increases the austenite phase excessively to deteriorate the strength and tends to form intermetallic compounds ( $\sigma$ -phase) thereby deteriorating the hot workability, the Ni content is defined as 10.0 mass% or less. A lower limit of the Ni content is preferably 2.0 mass% and, more preferably, 3.0 mass%. Further, an upper limit of the Ni content is preferably 9.5 mass% and, more preferably, 9.0 mass%.

(Cr: 22.0 to 28.0 mass%)

**[0048]** Cr is a main component of the passive layer and is a fundamental element of developing the corrosion resistance of the stainless steel material. Further, Cr is also an element of stabilizing the ferrite phase. In order to maintain the dual

phase microstructure of the ferrite phase and the austenite phase to compatibilize the corrosion resistance and the strength, Cr content is defined as 22.0 mass% or more. However, since excess Cr content tends to form intermetallic compounds ( $\sigma$ -phase) thereby deteriorating the hot workability, the Cr content is defined as 28.0 mass% or less. A lower limit of the Cr content is preferably 23.0 mass% and, more preferably, 24.0 mass%. Further, an upper limit of the Cr content is preferably 27.5 mass% and, more preferably, 27.0 mass%.

(Mo: 2.0 to 6.0 mass%)

**[0049]** Mo is an element that has an effect of forming molybdic acid during melting to improve the local corrosion resistance due to an inhibitor effect, to improve the corrosion resistance. Further Mo is also an element of stabilizing the ferrite phase and also an element of improving the pitting corrosion resistance and the cracking resistance of the steel material. In order to obtain such effects, Mo content is defined as 2.0 mass% or more. However, since excess Mo content progresses formation of intermetallic compounds such as the  $\sigma$ -phase to deteriorate the corrosion resistance and the hot workability, Mo content is defined as 6.0 mass% or less. A lower limit of Mo content is preferably 2.2 mass% and, more preferably, 2.5 mass%. Further, an upper limit of Mo content is preferably 5.5 mass% and, more preferably, 5.0 mass%.

(N: 0.20 to 0.50 mass%)

**[0050]** N is an element of intensely stabilizing the austenite phase and has an effect of improving the corrosion resistance without increasing the sensitivity to  $\sigma$ -phase formation and is also an element effective to strengthen the steel material. In order to obtain such effects, N content is defined as 0.20 mass% or more. However, since excess N content forms nitrides to deteriorate the toughness and the corrosion resistance, as well as deteriorate the hot workability to induce broken edges and surface defects during forging and rolling, the N content is defined as 0.50 mass% or less. A lower limit of the N content is preferably 0.22 mass% and, more preferably, 0.25 mass%. Further, an upper limit of the N content is preferably 0.45 mass% and, more preferably, 0.40 mass%.

(Ta: 0.01 to 0.50 mass%)

**[0051]** Ta is an element bonding with carbon and having an effect of suppressing formation of Cr-based carbides and suppressing precipitation of  $\sigma$ -phase that gives an effect on the deterioration of the toughness and the corrosion resistance and tantalum has an effect of contributing to the improvement of substantial Cr concentration in the steel material. In order to obtain such effects, Ta content is defined as 0.01 mass% or more. However, Ta added excessively is bonded with N in the steel and precipitates as nitrides to deteriorate the toughness and the hot workability. Further, effective N concentration is decreased by the precipitation of the nitrides and the corrosion resistance is deteriorated by precipitation of the  $\sigma$ -phase. Accordingly, Ta content is defined as 0.50 mass% or less. A lower limit of the Ta content is preferably 0.02 mass% and, more preferably, 0.03 mass%. An upper limit of the Ta content is preferably 0.30 mass% and, more preferably, 0.25 mass%.

(Ge: 0.1 to 1.0 mass%)

**[0052]** Ge has an effect of increasing and stabilizing a Cr concentration in the passive layer thereby improving the local corrosion resistance. In order to obtain such effects, Ge is added by 0.1 mass% or more and, preferably, 0.2 mass% or more. On the other hand, since excess addition deteriorates the hot workability and increases the cost, the upper limit is defined as 1.0% mass% or less and more preferably, 0.9 mass% or less.

**[0053]** For improving the corrosion resistance, one of Ta and Ge may be contained and, when the hot workability is also intended to be improved, Ta is selected preferably.

(Unavoidable Impurity)

**[0054]** Unavoidable impurities can be contained to such an extent as not deteriorating various characteristics of the duplex stainless steel material. The content, for example, of O is 0.1 mass% or less and, preferably, 0.05 mass% or less. When tantalum is contained, the amount of O is more preferably 0.01 mass% or less while details are to be described later. This can maximize the effect of developing the corrosion resistance of the present invention.

**[0055]** Further, in the duplex stainless steel of the present invention, other elements may also be contained further within a range not giving adverse influence on the effect of the present invention. For example, in the duplex stainless steel material of the present invention, the component composition described above preferably contains further one or more predetermined amounts of elements from the group consisting of Co, Cu, V, Ti, and Nb.

(One or more elements from the group consisting of Co: 0.10 to 2.00 mass%, Cu: 0.10 to 2.00 mass%, V: 0.01 to 0.50 mass%, Ti: 0.01 to 0.50 mass%, and Nb: 0.01 to 0.50 mass%)

**[0056]** Co and Cu are elements of improving the corrosion resistance and stabilizing the austenite phase. In order to obtain such effects, the content of each of the elements is defined as 0.10 mass% or more. However, since excess content of Co and Cu deteriorates the hot workability, the content of each of the elements is defined as 2.00 mass% or less. A preferred lower limit of the elements is 0.20 mass%. Further, a preferred upper limit of the elements is 1.50 mass%.

**[0057]** V, Ti and Nb are elements for improving the corrosion resistance and improving strength characteristics and the hot workability. In order to obtain such effects, the content of each of the elements is defined as 0.01 mass% or more. However, since excess content of V, Ti and Nb forms coarse carbides or nitrides to deteriorate the toughness, the content of each of the elements is defined as 0.50 mass% or less. A preferred lower limit of the content of each of the elements is 0.05 mass%. Further, a preferred upper limit of the content of each of the elements is 0.40 mass%.

**[0058]** Further, in the duplex stainless steel material of the present invention, the component composition preferably contains a predetermined amount of one or more of Mg and Ca.

(One or more of Mg: 0.0005 to 0.020 mass%, Ca: 0.0005 to 0.020 mass%)

**[0059]** Mg and Ca have an effect of being bonded with S or O contained as impurities in the steel and suppressing formation of inclusions such as MnS or  $Al_2O_3$  thereby improving the hot workability. In order to obtain such effects, the content of each of the elements is defined as 0.0005 mass% or more. However, since excess content of Mg and Ca increases the oxide-based inclusions and such inclusions form pit corrosion and origins of cracking to deteriorate the corrosion resistance and the hot workability, the content of each of the elements is defined as 0.020 mass% or less. A preferred content of each of the element is 0.002 to 0.020 mass%.

**[0060]** Further, in the duplex stainless steel material according to the present invention, the component composition preferably satisfies a relation:  $[Cr] + 3.3 [Mo] + 16 [N] \geq 40$  assuming the Cr amount as [Cr], the Mo amount as [Mo], and the N amount as [N].

**[0061]**  $[Cr] + 3.3 [Mo] + 16 [N]$  is a pitting resistance equivalent (PRE) known so far as an index expressing the corrosion resistance of steel materials. At  $PRE \geq 40$ , the balance among the Cr amount, the Mo amount, and the N amount in the microstructure is optimized to improve the corrosion resistance and the strength of the steel material.

(Sulfide-Oxide-based Composite Inclusions)

**[0062]** In the duplex stainless steel material according to the present invention, when Ta is contained and the amount of oxygen is controlled to a predetermined amount (0.01 mass% or less), sulfide-oxide-based composite inclusions in the steel can be modified to further improve the corrosion resistance.

**[0063]** Specifically, when the steel material is refined with addition of Ta, sulfide-based inclusions (MnS) contained in usual stainless steel are modified to the Ta-containing sulfide-oxide-based composite inclusions. The Ta-containing sulfide-oxide-based composite inclusions improve the local corrosion resistance.

**[0064]** For this purpose, Ta content in the Ta-containing sulfide-oxide-based composite inclusions is defined as 5 at% or more, preferably, 7 at% or more and, more preferably, 10 at% or more. While the upper limit of the Ta content is not particularly restricted, it is about 50 at%.

**[0065]** Even when the inclusions are modified by Ta addition, if many coarse inclusions are present in the steel, they deteriorate the hot workability. Accordingly, the number of the Ta-containing sulfide-oxide-based composite oxides having a major diameter of 1  $\mu m$  or more is defined as 500 N or less, preferably, 450 N or less and, more preferably, 400 N or less per 1 mm<sup>2</sup> cross section perpendicular to the working direction. While the lower limit of the number density of the Ta-containing sulfide-oxide-based composite inclusions is not particularly defined, it is about 20 N per 1 mm<sup>2</sup>. Fine inclusions having a major diameter of less than 1  $\mu m$  are excluded from the object since they give a less adverse effect on the local corrosion resistance.

**[0066]** Further, the Ta content and the number density of such sulfide-oxide-based composite inclusions are obtained by controlling the Ta content and the O content in the duplex stainless steel material and controlling the hot working conditions in production of the steel materials.

(Method of Producing Duplex Stainless Steel Material)

**[0067]** In a case of producing the duplex stainless steel material according to the present invention, when the sulfide-oxide-based composite inclusions are not controlled, the steel material can be produced by production equipment and production method used usually for mass production of the stainless steel material. For example, after adjusting the components of a molten steel melted by a converter or an electric furnace by refining using an AOD method, a VOD



method, etc. they are cast into steel ingots by a casting method such as a continuous casting method or an ingot making method. The obtained steel ingots are hot worked in a temperature region of about 1000°C to 1200°C and then can be subjected to cold working into desired size and shape.

[0068] In the present invention, it is preferred that solution heat treatment is applied optionally followed by rapid cooling in order to eliminate precipitates harmful to mechanical characteristics. The temperature for the solution heat treatment is preferably 1000 to 1100°C, the holding time is preferably from 10 minutes to 30 minutes, and rapid cooling is applied preferably at a cooling rate of 10°C/sec or more. Further, pickling can be applied optionally for surface conditioning such as scale removal.

[0069] Further, in a case of producing the duplex stainless steel material according to the present invention, when the sulfide-oxide-based composite inclusions are controlled, the steel material is produced as described below.

[0070] First, for decreasing O as an impurity in the steel, deoxidization is conducted by adding elements such as Si and Al having high affinity with oxygen in larger amounts and, further, oxide-based inclusions are removed by applying secondary refining such as degassing in vacuum or stirring under an argon gas for a longer time or in plurality of times.

[0071] Subsequently, components of molten steel melted in a converter or an electric furnace are adjusted in refining by using an AOD method, a VOD method or the like and then formed into steel ingots by a casting method such as a continuous casting method or an ingot making method in the same manner as described above. The obtained steel ingot is hot worked in a temperature region of about 1000 to 1200°C and then cold worked into desired size and shape. The total working ratio during hot working (cross section of original steel ingot/cross section after working) is about 10 to 50 as usual. For attaining a state where desired Ta-containing sulfide-oxide-based composite inclusions are present, hot working is applied preferably such that the working ratio (total area before working/total area after working) in a temperature region of 1100 to 1200°C exceeds 50% of the total working ratio.

[0072] As described above, while the steel ingot is subjected to hot working in a temperature region of about 1000 to 1200°C also in the production of usual duplex stainless steel materials, the working ratio in the temperature region of 1000 to 1100°C is higher than the working ratio in the temperature region of 1100 to 1200°C due to the effect of temperature lowering during working if intentional control is not conducted particularly. As a result, in the existent production, the working ratio in the temperature region of 1100 to 1200°C is 50% or less of the total working ratio. When the sulfide-oxide-based composite inclusions are also controlled as described above in the present invention, a state where desired Ta-containing sulfide-oxide-based composite inclusions are present is obtained by intentionally increasing the working ratio in the temperature region of 1100 to 1200°C.

#### < Duplex Stainless Steel Pipe >

[0073] A preferred embodiment of the duplex stainless steel pipe according to the present invention is to be described below.

[0074] A duplex stainless steel pipe according to the present invention includes the duplex stainless steel material described above and can be manufactured by using usual production equipment and production method used for usual mass production of stainless steel pipes. For example, the steel pipe can be formed into a desired size by extrusion pipe production or a Mannesmann pipe production method using a round bar as a material, or welding pipe production starting from a sheet material and welding the seam after fabrication. Further, the size of the dual phase stainless steel pipe can be determined appropriately in accordance with umbilicals, seawater desalination plants, LNG vaporizers, oil well pipes, and various kinds of chemical plants for which the steel pipes are used.

[Example]

[0075] Examples of duplex steel stainless materials according to the present invention are to be described below.

[Example 1: Example of Ta-containing Steel]

(Preparation of Specimen)

[0076] Steels of component compositions shown in Table 1 (steel symbols A to Z) were melted respectively by a steel melting facility having an electrode arc heating function and cast by using a 50 kg round billet mold (main body: about  $\phi 140 \times 320$  mm). Solidified steel ingots were heated up to 1200°C, applied with hot forging at an identical temperature and then cut, applied with solution heat treatment by maintaining at 1100°C for 30 minutes, and finished by water cooling into forged steel products of  $600 \times 120 \times 60$  mm (specimen Nos. 1 to 26).

[0077] Further, for each of steels,  $PRE = [Cr] + 3.3 [Mo] + 16 [N]$  was calculated and the result is also shown in Table 1. Further, the finished forged steel product was buried at a cross section parallel with the working direction, mirror polished, subjected to electrolytic etching in an aqueous oxalic acid solution, then observed under an optical microscope

at 100x magnification ratio, and the microstructure of each of the forged steel products was confirmed. As a result, each of the forged steel products consisted of two phases of the ferrite phase and the austenite phase.

(Sampling of Specimen)

**[0078]** Then, pitting corrosion resistance and hot workability were evaluated by the following procedures using specimens sampled from the forged steel products in the direction parallel with the working direction (20 mm × 30 mm × 2 mm).

(Evaluation of pitting corrosion resistance)

**[0079]** After wet polishing the surfaces of specimens by SiC #600 polishing paper and supersonically cleaning the surface, the specimens were passivated by being immersed in 30% nitric acid at 50°C for one hour. Then, conduction leads were attached by spot welding to each specimen and they were covered with an epoxy resin while leaving a test portion (test area: 10 mm × 10 mm). After immersing the specimens in an aqueous 20% NaCl solution kept at 80°C, they were held at +600 mV (vs. SCE: saturated calomel electrode) for one minute and the maximum pitting corrosion depth in the test portion was measured under a laser microscope. Then, the specimens were evaluated such that pitting corrosion resistance was poor (×) for those having a maximum pitting corrosion depth of 40 μm or more, pitting corrosion resistance was good (○) for those having a maximum pitting corrosion depth of 40 μm or less and more than 20 μm, and pitting corrosion resistance was excellent (◎) for those having a maximum pitting corrosion depth of 20 μm or less. The result is shown in Table 2.

(Evaluation for hot workability)

**[0080]** The surfaces of forged steel products were observed by naked eyes and presence or absence of surface defects was observed. Then, they were evaluated such that hot workability was poor (x) for those causing crackings, hot workability was somewhat poor (Δ) for those frequently causing surface defects, hot workability was good (○) for those causing slight surface defects, and hot workability was excellent (◎) for those with no surface defects. The result is shown in Table 2.

[Table 1]

| Steel symbol | Component composition (mass%) |      |      |       |        |       |     |      |     |      |      |                  | PRE  |
|--------------|-------------------------------|------|------|-------|--------|-------|-----|------|-----|------|------|------------------|------|
|              | C                             | Si   | Mn   | P     | S      | Al    | Ni  | Cr   | Mo  | N    | Ta   | Others           |      |
| A            | 0.021                         | 0.31 | 0.50 | 0.018 | 0.0019 | 0.011 | 6.9 | 25.1 | 3.7 | 0.26 | 0.05 |                  | 41.5 |
| B            | 0.019                         | 0.33 | 0.48 | 0.019 | 0.0022 | 0.010 | 6.5 | 24.7 | 4.1 | 0.30 | 0.07 | CtjcQ33          | 43.0 |
| C            | 0.022                         | 0.29 | 0.51 | 0.020 | 0.0020 | 0.012 | 7.0 | 25.4 | 3.8 | 0.27 | 0.03 | V:0.12           | 42.3 |
| D            | 0.018                         | 0.35 | 0.67 | 0.023 | 0.0021 | 0.016 | 5.5 | 24.1 | 4.3 | 0.26 | 0.10 | Ti:0.15          | 42.5 |
| E            | 0.019                         | 0.32 | 0.55 | 0.022 | 0.0023 | 0.017 | 6.0 | 25.0 | 3.7 | 0.32 | 0.07 | Co:0.21          | 42.3 |
| F            | 0.020                         | 0.30 | 0.61 | 0.018 | 0.0019 | 0.016 | 7.1 | 25.1 | 3.6 | 0.30 | 0.08 | Ca:0.003         | 41.8 |
| G            | 0.018                         | 0.33 | 0.52 | 0.021 | 0.0008 | 0.013 | 7.0 | 24.6 | 3.9 | 0.31 | 0.12 |                  | 42.4 |
| H            | 0.017                         | 0.31 | 0.55 | 0.019 | 0.0009 | 0.015 | 6.5 | 24.5 | 4.1 | 0.28 | 0.10 | Cr:0.52          | 42.5 |
| I            | 0.020                         | 0.32 | 0.72 | 0.016 | 0.0007 | 0.018 | 7.1 | 25.2 | 3.8 | 0.28 | 0.08 | Ca:0.003         | 42.2 |
| J            | 0.019                         | 0.29 | 0.54 | 0.020 | 0.0008 | 0.019 | 6.6 | 24.7 | 3.5 | 0.31 | 0.05 | V:0.22           | 41.2 |
| K            | 0.018                         | 0.30 | 0.48 | 0.021 | 0.0009 | 0.017 | 6.0 | 25.1 | 4.1 | 0.25 | 0.10 | Ti:0.23          | 42.6 |
| L            | 0.022                         | 0.34 | 0.50 | 0.018 | 0.0007 | 0.016 | 7.2 | 25.3 | 3.8 | 0.32 | 0.11 | Co:0.40          | 43.0 |
| M            | 0.019                         | 0.31 | 0.53 | 0.020 | 0.0008 | 0.018 | 7.0 | 24.6 | 3.9 | 0.28 | 0.07 | Cr:0.51, Ti:0.20 | 42.0 |
| N            | 0.018                         | 0.33 | 0.55 | 0.017 | 0.0009 | 0.019 | 6.7 | 25.2 | 3.7 | 0.31 | 0.12 | Mg:0.002, V:0.21 | 42.4 |
| O            | 0.017                         | 0.30 | 0.50 | 0.019 | 0.0010 | 0.017 | 7.1 | 25.0 | 3.8 | 0.29 | 0.08 | Nb:0.15          | 42.2 |
| P            | 0.019                         | 0.31 | 0.51 | 0.018 | 0.0020 | 0.018 | 7.0 | 25.0 | 3.6 | 0.20 | 0.07 |                  | 39.8 |
| Q            | 0.020                         | 0.35 | 0.47 | 0.020 | 0.0008 | 0.017 | 5.2 | 25.4 | 4.0 | 0.28 | 0.08 |                  | 43.1 |
| R            | 0.017                         | 0.30 | 0.51 | 0.018 | 0.0009 | 0.018 | 6.0 | 23.2 | 3.7 | 0.31 | 0.05 |                  | 40.4 |
| S            | 0.020                         | 0.31 | 0.48 | 0.017 | 0.0023 | 0.019 | 7.0 | 24.7 | 3.9 | 0.27 | 0.60 |                  | 41.9 |
| T            | 0.022                         | 0.33 | 0.69 | 0.016 | 0.0008 | 0.017 | 5.1 | 24.5 | 4.1 | 0.26 |      | Ti:0.30          | 42.2 |
| U            | 0.025                         | 0.35 | 2.20 | 0.019 | 0.0050 | 0.020 | 7.3 | 26.5 | 3.3 | 0.26 | 0.02 |                  | 41.6 |
| V            | 0.018                         | 0.32 | 0.79 | 0.021 | 0.0200 | 0.018 | 6.5 | 25.1 | 3.4 | 0.29 | 0.05 |                  | 41.0 |
| W            | 0.020                         | 0.29 | 0.80 | 0.017 | 0.0030 | 0.017 | 7.0 | 20.7 | 4.0 | 0.29 | 0.08 |                  | 38.5 |
| X            | 0.017                         | 0.30 | 0.60 | 0.018 | 0.0022 | 0.019 | 0.5 | 25.6 | 3.8 | 0.26 | 0.04 |                  | 42.3 |

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(continued)

| Steel symbol                                                                                | Component composition (mass%) |      |      |       |        |       |     |      |     |      |      |        | PRE  |
|---------------------------------------------------------------------------------------------|-------------------------------|------|------|-------|--------|-------|-----|------|-----|------|------|--------|------|
|                                                                                             | C                             | Si   | Mn   | P     | S      | Al    | Ni  | Cr   | Mo  | N    | Ta   | Others |      |
| Y                                                                                           | 0.202                         | 0.34 | 0.48 | 0.020 | 0.0021 | 0.020 | 6.7 | 24.8 | 4.0 | 0.28 | 0.06 |        | 42.5 |
| Z                                                                                           | 0.018                         | 0.31 | 0.51 | 0.017 | 0.0020 | 0.018 | 7.0 | 25.4 | 7.0 | 0.26 | 0.04 |        | 52.7 |
| (Note) Remainder of the component composition is Fe and unavoidable impurities.             |                               |      |      |       |        |       |     |      |     |      |      |        |      |
| (Note) Blanks in the component composition show that relevant components are not contained. |                               |      |      |       |        |       |     |      |     |      |      |        |      |

[Table 2]

| Specimen No.  |    | Steel symbol | Pitting corrosion resistance         |            | Evaluation for hot workability |
|---------------|----|--------------|--------------------------------------|------------|--------------------------------|
|               |    |              | Maximum pitting corrosion depth (μm) | Evaluation |                                |
| Example       | 1  | A            | 29                                   | ○          | ○                              |
|               | 2  | B            | 22                                   | ○          | ○                              |
|               | 3  | C            | 24                                   | ○          | ◎                              |
|               | 4  | D            | 25                                   | ○          | ○                              |
|               | 5  | E            | 21                                   | ○          | ○                              |
|               | 6  | F            | 31                                   | ○          | ○                              |
|               | 7  | G            | 25                                   | ○          | ◎                              |
|               | 8  | H            | 0                                    | ◎          | ◎                              |
|               | 9  | I            | 8                                    | ◎          | ◎                              |
|               | 10 | J            | 0                                    | ◎          | ◎                              |
|               | 11 | K            | 5                                    | ◎          | ◎                              |
|               | 12 | L            | 0                                    | ◎          | ◎                              |
|               | 13 | M            | 0                                    | ◎          | ◎                              |
|               | 14 | N            | 0                                    | ◎          | ◎                              |
|               | 15 | O            | 4                                    | ◎          | ◎                              |
|               | 16 | P            | 39                                   | ○          | ◎                              |
|               | 17 | Q            | 22                                   | ○          | ◎                              |
|               | 18 | R            | 38                                   | ○          | ◎                              |
| Comp. Example | 19 | S            | 73                                   | ×          | ×                              |
|               | 20 | T            | 46                                   | ×          | Δ                              |
|               | 21 | U            | 84                                   | ×          | ×                              |
|               | 22 | V            | 127                                  | ×          | ×                              |
|               | 23 | W            | 223                                  | ×          | Δ                              |
|               | 24 | X            | 68                                   | ×          | Δ                              |
|               | 25 | Y            | 278                                  | ×          | ×                              |
|               | 26 | Z            | 243                                  | ×          | ×                              |

**[0081]** From the result of Table 2, it was confirmed that specimens Nos. 1 to 18 (examples) produced by using steels (steel symbols A to R) satisfying the conditions of the present invention had good or excellent pitting corrosion resistance and had good or excellent hot workability.

**[0082]** On the contrary, it was confirmed that specimens No. 19 to 26 (comparative examples) produced by using steels not satisfying the conditions of the present invention (steel symbols S to Z) had the following disadvantages.

**[0083]** In Specimen No. 19, since Ta was excessive, coarse nitrides were formed in a great amount and the hot workability was poor. Further, the  $\sigma$ -phase was also formed and the pitting corrosion resistance was also poor. In Specimen No. 20, since Ta was not added,  $\sigma$ -phase was formed in a great amount and the pitting corrosion resistance and the hot workability were poor. In Specimen No. 21, since Mn was excessive, a great amount of inclusions (MnS) was precipitated and the pitting corrosion resistance and the hot workability were poor. In Specimen No. 22, since S was excessive, coarse sulfides were formed in a great amount and the pitting corrosion resistance and the hot workability were poor. In Specimen No. 23, since Cr was insufficient, the pitting corrosion resistance and the hot workability were poor. In Specimen No. 24, since Ni was insufficient, the pitting corrosion resistance and the hot workability were poor.

In specimen No. 25, since C was excessive, carbides were formed in a great amount and the pitting corrosion resistance and the hot workability were poor. In Specimen No. 26, since Mo was excessive, the  $\sigma$ -phase was formed in a great amount and the pitting corrosion resistance and the hot workability were poor.

5 [Example 2: Example of Ge-containing steel]

(Preparation of Specimens Nos. 1 to 17)

10 **[0084]** Stainless steels of component compositions shown in Table 3 (remainder including Fe and unavoidable impurities) were melted respectively by a molten steel processing facility having an electrode arc heating function and cast by using a 50-kg square mold (main body: about  $\square 120 \times 450$  mm). Further, Table 3 also shows a result of calculation for PRE values of the microstructure of each steel. In Table 3, blanks show that the relevant components are not contained. Solidified steel ingots were heated to 1200°C, hot forged at that temperature and finished into forged steel products of  $600 \times 120 \times 60$  mm. Then, they were cut and held at 1100°C for 30 minutes as heat treatment and then  
15 water cooled.

(Sampling of Specimens Nos. 1 to 17)

20 **[0085]** Then, for specimens ( $20 \text{ mm} \times 30 \text{ mm} \times 2 \text{ mm}$ ) sampled from the forged steel products in a direction parallel with the working direction, crevice corrosion resistance was evaluated by the procedures shown below.

(Evaluation of Crevice Corrosion Resistance)

25 **[0086]** The crevice corrosion resistance was evaluated according to the Method F of ASTM-G48 by immersing specimens formed with crevice in 6%  $\text{FeCl}_3 + 0.05\text{N HCl}$  for 24 hours and measuring the maximum crevice corrosion depth after the test. The test temperature was 60°C. The crevice corrosion resistance was judged as excellent when the maximum crevice corrosion depth was less than 200  $\mu\text{m}$ , as good when it was 200  $\mu\text{m}$  or more and less than 400  $\mu\text{m}$ , and as poor when it was 400  $\mu\text{m}$  or more. The result is shown in Table 3.

30 (Component Composition)

**[0087]** The component composition was measured by the following method. C and S: infrared absorption, Si, Mn, P, Ni, and Cr: X-ray fluorescence spectroscopy, Mo, Sn, Ge, and Ta: ICP spectroscopy, S and N: inert gas fusion method. The portion for measurement of the specimen is not particularly restricted so long as measurement is possible. In Table  
35 3, compositions not satisfying the definition of the present invention are shown by attaching underlines below numerical values.

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[Table 3]

| Specimen No. | Composition symbol | Component composition (mass%), remainder: Fe and unavoidable impurities |             |       |      |     |     |      |             |       |       |               |      |                          | Max crevice corrosion depth (μm) |
|--------------|--------------------|-------------------------------------------------------------------------|-------------|-------|------|-----|-----|------|-------------|-------|-------|---------------|------|--------------------------|----------------------------------|
|              |                    | Si                                                                      | Mn          | Al    | Cr   | Ni  | Mo  | N    | Ge          | C     | P     | S             | PRE  | Others                   |                                  |
| 1            | A1                 | 0.31                                                                    | 0.1         | 0.015 | 25.0 | 7.2 | 4.0 | 0.31 | 0.79        | 0.018 | 0.020 | 0.0019        | 43.2 |                          | 151                              |
| 2            | A2                 | 0.34                                                                    | 0.49        | 0.019 | 25.0 | 6.7 | 4.0 | 0.30 | 0.51        | 0.016 | 0.020 | 0.0012        | 43.0 |                          | 283                              |
| 3            | A3                 | 0.34                                                                    | 0.48        | 0.011 | 24.0 | 6.7 | 3.8 | 0.28 | 0.68        | 0.015 | 0.017 | 0.0009        | 41.0 | Cu:0.51                  | 190                              |
| 4            | A4                 | 0.35                                                                    | 0.59        | 0.014 | 25.3 | 7.4 | 3.9 | 0.29 | 0.61        | 0.017 | 0.019 | 0.0013        | 42.8 | V:0.19                   | 276                              |
| 5            | A5                 | 0.28                                                                    | 0.62        | 0.018 | 24.9 | 7.0 | 3.8 | 0.32 | 0.72        | 0.022 | 0.017 | 0.0015        | 42.6 | Ta:0.08                  | 258                              |
| 6            | A6                 | 0.30                                                                    | 0.43        | 0.012 | 24.8 | 7.1 | 3.9 | 0.30 | 0.81        | 0.019 | 0.018 | 0.0006        | 42.3 | Cu:1.0, V:0.15           | 219                              |
| 7            | A7                 | 0.32                                                                    | 0.53        | 0.016 | 25.2 | 6.9 | 4.1 | 0.27 | 0.75        | 0.021 | 0.021 | 0.0005_       | 43.1 | Cu:0.62, Ta:0.07         | 253                              |
| 8            | A8                 | 0.32                                                                    | 0.50        | 0.013 | 25.5 | 7.1 | 4.1 | 0.29 | 0.71        | 0.026 | 0.017 | 0.0012        | 43.7 | Cu:0.42, Ta:0.09         | 184                              |
| 9            | A9                 | 0.31                                                                    | 0.55        | 0.015 | 25.6 | 7.3 | 4.3 | 0.26 | 0.65        | 0.019 | 0.020 | 0.0017        | 44.0 | V:0.21, Ta:0.09          | 179                              |
| 10           | A10                | 0.33                                                                    | 0.68        | 0.010 | 25.1 | 7.0 | 3.8 | 0.31 | 0.77        | 0.020 | 0.019 | 0.0023        | 42.6 | Cu:0.55, V:0.20, Ta:0.08 | 199                              |
| 11           | A11                | 0.30                                                                    | 0.59        | 0.022 | 24.6 | 6.8 | 4.0 | 0.28 | 0.88        | 0.018 | 0.020 | 0.0008        | 42.3 | V:0.25, Ca:0.003         | 175                              |
| 12           | A12                | 0.34                                                                    | 0.53        | 0.017 | 25.2 | 7.2 | 3.7 | 0.30 | 0.78        | 0.023 | 0.024 | 0.0011        | 42.2 | Ta:0.06 Mg:0.003         | 234                              |
| 13           | B1                 | 0.30                                                                    | 0.57        | 0.018 | 25.6 | 7.0 | 3.8 | 0.31 | <u>2.00</u> | 0.024 | 0.018 | 0.0021        | 43.1 |                          | 402                              |
| 14           | B2                 | 0.31                                                                    | 0.47        | 0.015 | 25.3 | 7.4 | 4.0 | 0.27 | -           | 0.025 | 0.019 | 0.0017        | 42.8 |                          | 637                              |
| 15           | B3                 | 0.                                                                      | 0.56        | 0.016 | 24.8 | 6.9 | 4.2 | 0.26 | 0.75        | 0.013 | 0.022 | <u>0.0508</u> | 42.8 |                          | 715                              |
| 16           | B4                 | 0.29                                                                    | <u>2.52</u> | 0.021 | 25.6 | 6.8 | 3.9 | 0.28 | 0.82        | 0.017 | 0.021 | 0.0021        | 43.1 |                          | 566                              |
| 17           | B5                 | 0.30                                                                    | 0.52        | 0.019 | 25.5 | 7.1 | 3.8 | 0.13 | 0.79        | 0.019 | 0.020 | 0.0018        | 40.1 |                          | 682                              |

**[0088]** It can be seen that all stainless steel materials having composition symbols A1 to A12 that satisfy the component composition as the conditions of the present invention (Specimens Nos. 1 to 12) have good crevice corrosion resistance.

**[0089]** On the contrary, composition symbols B1 to B5 (Specimens Nos. 13 to 17) have the following disadvantages.

**[0090]** In B1, since Ge was added in a great amount and the  $\sigma$ -phase was increased, and the crevice corrosion resistance was deteriorated. In B2, since Ge was not added, the passive layer was instable and the crevice corrosion resistance was deteriorated. In B3 and B4, since S and Mn were contained in a great amount respectively, a great amount of Mn sulfides was precipitated and the crevice corrosion resistance was deteriorated. In B5, the N amount was small and the crevice corrosion resistance was deteriorated.

[Example 3: Example of Ta-containing steel in which sulfide-oxide-based composite inclusions were also controlled]

(Production of Steel Material)

**[0091]** Steels of component compositions shown in Table 4 (steel symbols: A1 to A16, B1 to B9) were melted respectively by a steel melting facility having an electrode arc heating function and cast by using a 50 kg round billet mold (main body: about  $\phi 140 \times 320$  mm). Further, for each of steels, result of calculation for  $PRE = [Cr] + 3.3 [Mo] + 16 [N]$  is also shown in Table 4. For the columns of component composition in Table 4, blank columns show that relevant components are not contained, and the remainder includes Fe and unavoidable impurities.

**[0092]** Solidified steel ingots were heated to 1200°C, hot forged at that temperature (forging temperature: 1000 to 1200°C) and then cut. Then, they were applied with cold rolling and solution heat treatment at 1100°C for holding time of 30 minutes, water cooled at a cooling rate of 12°C/sec, and then cut and finished into steel materials each of  $300 \times 120 \times 10$  mm (Nos. 1 to 25).

**[0093]** For the steels (steel symbols: A11 to A16), a deoxidization step was applied a little harder than usual during melting in order to decrease the O amount. Further, for steel materials (Nos. 1 to 16 and 18 to 25), hot forging at 1100 to 1200°C was applied at a working ratio exceeding 50% of the total working ratio during hot forging. For the steel material (No. 17), hot forging at 1100 to 1200°C was applied at a working ratio of 50% or less of the total working ratio during hot forging.

(Sampling of Specimen)

**[0094]** Then, the number density and the Ta-content of the sulfide-oxide-based composite inclusions were measured by the following procedures using specimens ( $20 \text{ mm} \times 30 \text{ mm} \times 2 \text{ mm}$ ) sampled from the steel materials in parallel with the working direction, and pitting corrosion resistance and hot workability were evaluated. The result is shown in Table 5.

**[0095]** Further, the cross section of the specimens perpendicular to the working direction was buried, mirror polished, and subjected to electrolytic etching in an aqueous oxalic acid solution. Then, the microstructure of each of the specimens was observed under an optical microscope at 100x magnification ratio. As a result, any of the specimens consisted of two phases of a ferrite phase and an austenite phase.

(Measurement of Number Density and Ta content of Sulfide-oxide-based Composite Inclusions)

**[0096]** The major diameter (circle equivalent diameter), the number density, and the Ta content of the inclusions can be measured by the following procedures. That is, for the specimens used in the observation of microstructure, image analysis is performed to the surface of the specimen by SEM-EPMA (scanning electron microscope-electron beam probe microanalyzer, "JXA-8900RL", "XM-Z0043T", "XM-87562" manufactured by JEOL), and the component compositions of observed inclusions are analyzed by EDX (energy dispersive X-ray spectroscopy). Analysis of the component composition by EDX is performed for inclusions having a major diameter of 1  $\mu\text{m}$  or more as an object and may be analyzed automatically for about 10 seconds on every one point for the gravitational center of the inclusions. Inclusions having the major diameter of less than 1  $\mu\text{m}$  give less adverse effects on the local corrosion resistance. Accordingly, in the present invention, inclusions having the major diameter of less than 1  $\mu\text{m}$  are excluded from the object of measurement in order to improve the efficiency of measurement.

**[0097]** In the measurement for the number density and the Ta content of the sulfide-oxide-based composite inclusions, the inclusions were observed by the procedures described above by automatic EPMA, and the number density and the Ta content for each of the inclusions were measured for the sulfide-based inclusions and the oxide-based inclusions having the major diameter of 1  $\mu\text{m}$  or more observed in a measuring area of 3  $\text{mm}^2$  and they were determined as a mean value thereof.



(Evaluation for Pitting Corrosion Resistance)

**[0098]** Pitting corrosion resistance was evaluated with reference to the method according to JIS G0577. After wet polishing the surfaces of specimens with SiC #600 polishing paper and supersonically cleaning the surfaces, conduction leads were attached to the specimen by spot welding, and a portion other than the test surface of the specimen surface (10 mm × 10 mm) was covered with an epoxy resin. After immersing the specimen 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<sup>2</sup> was taken as pitting corrosion potential ( $V_{c'100}$ ). The pitting corrosion resistance was evaluated as good (○) for those showing the pitting potential exceeding 500 mV (vs. SCE) (saturated calomel electrode)), as somewhat poor (Δ) for those showing 100 to 500 mV (vs. SCE), and as poor (×) for those showing lower than 100 mV (vs. SCE).

(Evaluation of Hot Workability)

**[0099]** The surfaces of the specimens were observed with naked eyes and presence or absence of surface defects was observed (◎: no defects, ○: slight defects, Δ: marked defects, ×: cracking generated). The result is shown in Table 5.

[Table 4]

| Steel symbol | Component composition (mass%) |      |      |       |        |       |     |      |     |      |      |        |                |      |
|--------------|-------------------------------|------|------|-------|--------|-------|-----|------|-----|------|------|--------|----------------|------|
|              | C                             | Si   | Mn   | P     | S      | Al    | Ni  | Cr   | Mo  | N    | Ta   | O      | Others         | PRE  |
| A1           | 0.022                         | 0.31 | 0.50 | 0.020 | 0.0016 | 0.018 | 7.0 | 25.1 | 3.9 | 0.31 | 0.07 | 0.0054 |                | 42.9 |
| A2           | 0.012                         | 0.22 | 0.59 | 0.020 | 0.0020 | 0.015 | 74  | 25.6 | 4.0 | 0.28 | 0.11 | 0.0061 |                | 43.3 |
| A3           | 0.023                         | 0.34 | 0.63 | 0.019 | 0.0018 | 0.011 | 6.8 | 24.8 | 4.1 | 0.30 | 0.05 | 0.0047 |                | 43.1 |
| A4           | 0.029                         | 0.30 | 0.43 | 0.021 | 0.0020 | 0.019 | 6.5 | 24.1 | 3.8 | 0.35 | 0.10 | 0.0052 | Cu:0.23        | 42.2 |
| A5           | 0.030                         | 0.28 | 0.53 | 0.023 | 0.0021 | 0.019 | 6.9 | 250  | 4.0 | 0.32 | 0.09 | 0.0035 | V:0.19         | 43.3 |
| A6           | 0.019                         | 0.33 | 0.49 | 0.018 | 0.0024 | 0.014 | 7.1 | 25.6 | 4.2 | 0.27 | 0.08 | 0.0056 | Co:0.4         | 43.8 |
| A7           | 0.027                         | 0.35 | 0.45 | 0.019 | 0.0021 | 0.018 | 7.3 | 25.8 | 4.3 | 0.29 | 0.09 | 0.0038 | Cu:0.49 V:0.22 | 44.6 |
| A8           | 0.024                         | 0.29 | 0.38 | 0.018 | 0.0019 | 0.017 | 7.0 | 24.9 | 3.7 | 0.28 | 0.11 | 0.0064 | V:0.20 Nb:0.10 | 41.6 |
| A9           | 0.011                         | 0.30 | 0.55 | 0.020 | 0.0023 | 0.013 | 7.7 | 25.6 | 3.9 | 0.30 | 0.10 | 0.0055 | Cu:0.20 V:0.15 | 43.3 |
| A10          | 0.030                         | 0.32 | 0.52 | 0.021 | 0.0021 | 0.016 | 6.4 | 24.3 | 4.1 | 0.29 | 0.07 | 0.0073 | Ti:0.08        | 42.5 |
| A11          | 0.014                         | 0.29 | 0.47 | 0.018 | 0.0020 | 0.020 | 6.8 | 24.8 | 4.0 | 0.25 | 0.08 | 0.0009 |                | 42.0 |
| A12          | 0.020                         | 0.25 | 0.58 | 0.022 | 0.0018 | 0.017 | 6.7 | 24.9 | 4.1 | 0.24 | 0.13 | 0.0012 | Cu:0.18        | 42.3 |
| A13          | 0.026                         | 0.32 | 0.54 | 0.021 | 0.0019 | 0.016 | 6.9 | 25.3 | 4.2 | 0.30 | 0.08 | 0.0018 | V:0.15         | 44.0 |
| A14          | 0.033                         | 0.33 | 0.44 | 0.025 | 0.0016 | 0.019 | 7.2 | 25.5 | 3.6 | 0.33 | 0.08 | 0.0015 | Nb:0.08        | 42.7 |
| A15          | 0.026                         | 0.30 | 0.49 | 0.022 | 0.0020 | 0.014 | 7.3 | 25.1 | 3.8 | 0.28 | 0.12 | 0.0022 |                | 42.1 |
| A16          | 0.014                         | 0.35 | 0.51 | 0.020 | 0.0013 | 0.020 | 7.1 | 25.1 | 3.9 | 0.29 | 0.10 | 0.0025 | Ca:0.0015      | 42.6 |
| B1           | 0.022                         | 0.29 | 0.61 | 0.018 | 0.0019 | 0.016 | 7.0 | 25.0 | 3.7 | 0.27 | 0.06 | 0.0054 |                | 41.5 |
| B2           | 0.017                         | 0.27 | 0.51 | 0.019 | 0.0021 | 0.023 | 6.8 | 24.6 | 3.8 | 0.28 |      | 0.0064 |                | 41.6 |
| B3           | 0.036                         | 0.31 | 0.57 | 0.017 | 0.0020 | 0.016 | 6.9 | 24.8 | 4.2 | 0.30 | 2.00 | 0.0070 |                | 43.5 |
| B4           | 0.024                         | 0.39 | 0.53 | 0.022 | 0.0022 | 0.018 | 7.0 | 24.9 | 4.1 | 0.27 | 0.07 | 0.0152 |                | 42.8 |
| B5           | 0.016                         | 0.24 | 0.48 | 0.021 | 0.0018 | 0.019 | 7.1 | 21.6 | 3.5 | 0.22 | 0.09 | 0.0053 |                | 36.7 |
| B6           | 0.021                         | 0.28 | 0.50 | 0.023 | 0.0600 | 0.015 | 7.0 | 25.7 | 3.5 | 0.30 | 0.10 | 0.0066 | Cu:0.15        | 42.1 |
| B7           | 0.016                         | 0.29 | 2.80 | 0.020 | 0.0058 | 0.017 | 7.5 | 25.9 | 3.9 | 0.32 | 0.11 | 0.0050 |                | 43.9 |
| B8           | 0.020                         | 0.29 | 0.48 | 0.020 | 0.0025 | 0.018 | 7.2 | 24.8 | 1.5 | 0.30 | 0.10 | 0.0580 |                | 34.6 |

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(continued)

| Steel symbol | Component composition (mass%) |      |      |       |        |       |     |      |     |      |      |        |        |      |
|--------------|-------------------------------|------|------|-------|--------|-------|-----|------|-----|------|------|--------|--------|------|
|              | C                             | Si   | Mn   | P     | S      | Al    | Ni  | Cr   | Mo  | N    | Ta   | O      | Others | PRE  |
| B9           | 0.017                         | 0.28 | 0.49 | 0.017 | 0.0024 | 0.017 | 7.1 | 24.7 | 3.7 | 0.14 | 0.09 | 0.0052 |        | 39.2 |

[Table 5]

| Steel material No. | Steel symbol | Sulfide-oxide-based composite inclusions |                  | Pitting corrosion resistance  |            | Hot workability                                |
|--------------------|--------------|------------------------------------------|------------------|-------------------------------|------------|------------------------------------------------|
|                    |              | Number density (N/mm <sup>2</sup> )      | Ta content (at%) | Pitting potential (mV vs.SCE) | Evaluation | Surface defect during hot working (naked eyes) |
| 1                  | A1           | 262                                      | 9                | 649                           | ○          | ◎                                              |
| 2                  | A2           | 298                                      | 14               | 750                           | ○          | ◎                                              |
| 3                  | A3           | 232                                      | 7                | 579                           | ○          | ◎                                              |
| 4                  | A4           | 279                                      | 8                | 613                           | ○          | ◎                                              |
| 5                  | A5           | 282                                      | 11               | 681                           | ○          | ◎                                              |
| 6                  | A6           | 281                                      | 10               | 675                           | ○          | ◎                                              |
| 7                  | A7           | 290                                      | 13               | 723                           | ○          | ◎                                              |
| 8                  | A8           | 308                                      | 11               | 689                           | ○          | ○                                              |
| 9                  | A9           | 286                                      | 12               | 708                           | ○          | ◎                                              |
| 10                 | A10          | 253                                      | 8                | 604                           | ○          | ◎                                              |
| 11                 | A11          | 264                                      | 9                | 593                           | ○          | ◎                                              |
| 12                 | A12          | 324                                      | 14               | 766                           | ○          | ◎                                              |
| 13                 | A13          | 267                                      | 11               | 652                           | ○          | ◎                                              |
| 14                 | A14          | 249                                      | 8                | 600                           | ○          | ◎                                              |
| 15                 | A15          | 311                                      | 14               | 783                           | ○          | ○                                              |
| 16                 | A16          | 272                                      | 12               | 773                           | ○          | ◎                                              |
| 17                 | B1           | 225                                      | 4                | 323                           | △          | ○                                              |
| 18                 | B2           | 255                                      | 0                | 86                            | ×          | ○                                              |
| 19                 | B3           | 725                                      | 13               | 93                            | ×          | ×                                              |
| 20                 | B4           | 646                                      | 3                | 178                           | △          | ×                                              |
| 21                 | B5           | 268                                      | 11               | 84                            | ×          | ○                                              |
| 22                 | B6           | 288                                      | 1                | 92                            | ×          | ×                                              |
| 23                 | B7           | 300                                      | 7                | 75                            | ×          | ×                                              |
| 24                 | B8           | 186                                      | 7                | 81                            | ×          | ○                                              |
| 25                 | B9           | 153                                      | 8                | 90                            | ×          | ○                                              |

**[0100]** In view of the results of Table 4 and Table 5, it can be seen that all examples satisfying the conditions of the present invention (steel materials Nos. 1 to 16) have excellent pitting corrosion resistance and hot workability.

**[0101]** On the contrary, steel materials Nos. 17 to 25 were in the following situations.

**[0102]** In a reference example (steel material No. 17), while the component composition satisfies the conditions of the present invention, since the working ratio in the hot forging at 1100 to 1200°C was 50% or less of the total working ratio, the Ta content in the sulfide-oxide-based composite inclusions was less than the lower limit. While the pitting corrosion resistance was excellent when compared with existent steels not containing Ta, characteristics were somewhat poor compared with the steel materials Nos. 1 to 16 by so much as the sulfide-oxide-based composite inclusions were not formed.

**[0103]** In a comparative example (steel material No. 18), since Ta was not contained, sulfide-oxide-based composite inclusions were not modified and the pitting corrosion resistance was poor. In a comparative example (steel No. 19), while the sulfide-oxide-based composite inclusions were modified since the Ta content exceeded the upper limit, the

pitting corrosion resistance and the hot workability were poor since the number density exceeded the upper limit and since coarse nitrides were also precipitated.

[0104] In a reference example (steel material No. 20), since O content exceeded 0.01 mass%, Ta content of the sulfide-oxide-based composite inclusions was less than the lower limit and also the number density exceeded the upper limit. At the same time, since Cr-based oxides were also precipitated in a great amount, while the pitting corrosion resistance was excellent compared with the existent steels, etc. not containing Ta, the characteristics were somewhat poor compared with steel materials Nos. 1 to 16 by so much as the sulfide-oxide-based composite inclusions were not formed.

[0105] In a comparative example (steel No. 21), since the Cr content was less than the lower limit, the pitting corrosion resistance was poor.

[0106] In a comparative example (steel material No. 22), since S content exceeded the upper limit, Ta content of the sulfide-oxide-based composite inclusions was less than the lower limit and, since also the sulfide-based inclusions (MnS) were precipitated in a great amount, the pitting corrosion resistance and the hot workability were poor. In a comparative example (steel material No. 23), since Mn content exceeded the upper limit, suppression of MnS precipitation was insufficient and the pitting corrosion resistance and the hot workability were poor.

[0107] In a comparative example (steel material No. 24), since Mo content was less than the lower limit, the pitting corrosion resistance was poor. In a comparative example (steel material No. 25), since N content was less than the lower limit, the pitting corrosion resistance was poor.

[0108] As has been described above, while the present invention has been explained with reference to the duplex stainless steel material and the duplex stainless steel pipe, the present invention is not restricted by the embodiments and the examples but can be practiced with appropriate modifications within a scope conforming to the gist of the present invention and any of such modifications is encompassed within the technical range of the present invention.

[0109] While the present invention has been described specifically with reference to the specific embodiments, it will be apparent to a person skilled in the art that various changes and modifications are applicable without departing the spirit and the range of the present invention.

[0110] The present application is based on Japanese Patent Application filed on January 15, 2013 (Japanese patent application No. 2013-004891), Japanese patent application filed on March 5, 2013 (Japanese patent application No. 2013-043250), and Japanese patent application filed on November 5, 2013 (Japanese patent application No. 2013-229754), the contents of which are incorporated herein for reference.

#### Industrial Applicability

[0111] The duplex stainless steel material of the present invention is useful as structural materials in seawater circumstances such as umbilicals, seawater desalination plants, and LNG vaporizers, as well as structural materials in severe corrosive circumstances such as oil ceiling pipes and various chemical plants.

#### Claims

1. A duplex stainless steel material consisting of a ferrite phase and an austenite phase in which the component composition of the duplex stainless steel material contains:

C: 0.100 mass% or less,

Si: 0.10 to 2.00 mass%,

Mn: 0.10 to 2.00 mass%,

P: 0.050 mass% or less,

S: 0.0100 mass% or less,

Al: 0.001 to 0.050 mass%,

Ni: 1.0 to 10.0 mass%,

Cr: 22.0 to 28.0 mass%,

Mo: 2.0 to 6.0 mass%,

N: 0.20 to 0.50 mass% and, further contains one or more elements selected from

Ta: 0.01 to 0.50 mass% and Ge: 0.1 to 1.0 mass%, with the remainder being Fe and unavoidable impurities.

2. The duplex stainless steel material according to claim 1, wherein a PRE value represented by the following formula is 40 or more assuming a Cr content (mass%) as [Cr], an Mo content (mass%) as [Mo], and an N content (mass%) as [N]:

$$PRE = [Cr] + 3.3 [Mo] + 16 [N].$$

- 5        3. The duplex stainless steel material according to claim 1 wherein Ta described above is contained, oxygen as an impurity is restricted to 0.01 mass%, and Ta-containing sulfide-oxide-based composite inclusions having a major diameter of 1  $\mu\text{m}$  or more are present by the number of 500 or less per 1  $\text{mm}^2$  of a cross section perpendicular to a working direction in the inclusions of the duplex stainless steel material, and the Ta content of the sulfide-oxide-based composite inclusions is 5 at% or more.
- 10      4. The duplex stainless steel material according to any one of claims 1 to 3, wherein the component composition further contains one or more elements selected from the group consisting of Co: 0.10 to 2.00 mass%, Cu: 0.10 to 2.00 mass%, V: 0.01 to 0.50 mass%, Ti: 0.01 to 0.50 mass%, Nb: 0.01 to 0.50 mass%, Mg: 0.0005 to 0.020 mass%, and Ca: 0.0005 to 0.020 mass%.
- 15      5. A duplex stainless steel pipe comprising the duplex stainless steel material according to any one of claims 1 to 3.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/050363

## A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01) i, C22C38/58(2006.01) i

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C1/00-49/14

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 1996-2014

Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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 6-145903 A (Kubota Corp.),<br>27 May 1994 (27.05.1994),<br>(Family: none)                                                                                                                                                                     | 1-5                   |
| A         | JP 2005-520934 A (PARK, Yong-Soo),<br>14 July 2005 (14.07.2005),<br>& US 2005/0158201 A1 & EP 1495150 A<br>& EP 1803832 A1 & WO 2003/080886 A1<br>& DE 60313763 D & KR 10-2003-0077239 A<br>& CN 1643176 A & CN 101580917 A<br>& AU 2003221202 A | 1-5                   |
| P, A      | WO 2013/191208 A1 (Nippon Steel & Sumitomo<br>Metal Corp.),<br>27 December 2013 (27.12.2013),<br>(Family: none)                                                                                                                                  | 1-5                   |

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

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"&amp;" document member of the same patent family

Date of the actual completion of the international search

04 March, 2014 (04.03.14)

Date of mailing of the international search report

18 March, 2014 (18.03.14)

Name and mailing address of the ISA/  
Japanese Patent Office

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Form PCT/ISA/210 (second sheet) (July 2009)

**REFERENCES CITED IN THE DESCRIPTION**

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