

(11) EP 3 712 289 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication: 23.09.2020 Bulletin 2020/39

(21) Application number: 18879992.8

(22) Date of filing: 14.11.2018

(51) Int Cl.: C22C 38/00 (2006.01) C22C 38/54 (2006.01)

C21D 8/00 (2006.01)

(86) International application number: **PCT/JP2018/042114**

(87) International publication number: WO 2019/098233 (23.05.2019 Gazette 2019/21)

(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:

BAME

Designated Validation States:

KH MA MD TN

(30) Priority: 15.11.2017 JP 2017220172

(71) Applicant: Nippon Steel Corporation Tokyo 100-8071 (JP)

(72) Inventors:

- SAGARA, Masayuki Tokyo 100-8071 (JP)
- TOMIO, Yusaku Tokyo 100-8071 (JP)
- OSUKI, Takahiro Tokyo 100-8071 (JP)
- UGAWA, Yusuke Tokyo 100-8071 (JP)
- (74) Representative: Zimmermann & Partner Patentanwälte mbB
 Postfach 330 920
 80069 München (DE)

(54) TWO-PHASE STAINLESS STEEL AND METHOD FOR MANUFACTURING TWO-PHASE STAINLESS STEEL

(57) A duplex stainless steel with occurrence of pitting suppressed is provided. A duplex stainless steel according to the present disclosure has a chemical composition consisting of, in mass%, Cr: more than 27.00% to 29.00%, Mo: 2.50 to 3.50%, Ni: 5.00 to 8.00%, W: 4.00 to 6.00%, Cu: 0.01 to less than 0.10%, N: more than 0.400% to 0.600%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, sol.Al: 0.040% or less, V: 0.50% or less, O: 0.010% or less, P: 0.030% or less, and S: 0.020% or less with the balance being Fe and impurities and satisfying Formula (1), a microstructure consisting of 35 to 65 volume% of ferrite phase with the balance being the austenite phase, and the area fraction of Cu precipitated in the ferrite phase is 0.5% or less.

 $Cr+4.0\times Mo+2.0\times W+20\times N-5\times ln(Cu)\geq 65.2$ (1)

EP 3 712 289 A1

Description

10

15

30

35

40

TECHNICAL FIELD

5 [0001] The present invention relates to a duplex stainless steel and a method for producing the duplex stainless steel.

BACKGROUND ART

[0002] A duplex stainless steel having a dual phase structure consisting of the ferrite phase and the austenite phase is known to have excellent corrosion resistance. A duplex stainless steel is particularly superior in corrosion resistance against pitting and/or crevice corrosion (hereinafter referred to as "pitting resistance"), which is taken as a problem in an aqueous solution containing chlorides. A duplex stainless steel is therefore widely used in a wet environment containing chlorides, such as seawater. In a wet environment containing chlorides, a duplex stainless steel is used, for example, in a flow line pipe, an umbilical tube, and a heat exchanger.

[0003] In recent years, the corrosion conditions in the environment in which a duplex stainless steel is used have been increasingly severe. A duplex stainless steel is therefore required to have more excellent pitting resistance. To further enhance the pitting resistance of a duplex stainless steel, a variety of technologies have been proposed.

[0004] International Application Publication No. 2013/191208 (Patent Literature 1) discloses a duplex stainless steel containing, in mass%, Ni: 3 to 8%, Cr: 20 to 35%, Mo: 0.01 to 4.0%, and N: 0.05 to 0.60% and further containing one or more types of element selected from Re: 2.0% or less, Ga: 2.0% or less, and Ge: 2.0% or less. In Patent Literature 1, the fact that the duplex stainless steel contains Re, Ga, or Ge increases the critical potential at which pitting occurs (pitting potential) to enhance the pitting resistance and crevice corrosion resistance.

[0005] International Application Publication No. 2010/082395 (Patent Literature 2) discloses a method for producing a duplex stainless steel pipe by performing hot working or hot working and further solid solution heat treatment on a duplex stainless steel material containing, in mass%, Cr: 20 to 35%, Ni: 3 to 10%, Mo: 0 to 6%, W: 0 to 6%, Cu: 0 to 3%, and N: 0.15 to 0.60% to produce a steel pipe for cold working and then performing cold rolling on the steel pipe. The method for producing a duplex stainless steel pipe in Patent Literature 2 is a method for producing a duplex stainless steel pipe having a minimum yield strength ranging from 758.3 to 965.2 MPa by performing cold rolling that allows the working ratio Rd (=exp[{ln(MYS)-ln(14.5×Cr+48.3×Mo+20.7×W+6.9×N)}/0.195]) at the area reduction ratio in the final cold rolling step to fall within a range from 10 to 80%. Patent Literature 2 describes that the method described above provides a duplex stainless steel pipe that can be used, for example, in an oil well and a gas well, shows excellent corrosion resistance also in a carbon dioxide gas corrosion environment or a stress corrosion environment, and has high strength.

[0006] Japanese Patent Application Publication No. 2007-84837 (Patent Literature 3) discloses a duplex stainless steel containing, in mass%, Cr: 20 to 30%, Ni: 1 to 11%, Cu: 0.05 to 3.0%, Nd: 0.005 to 0.5%, and N: 0.1 to 0.5% and/or Mo: 0.5 to 6% and W: 1 to 10%. In Patent Literature 3, the hot workability of the duplex stainless steel is enhanced because the duplex stainless steel contains Nd.

[0007] National Publication of International Patent Application No. 2005-520934 (Patent Literature 4) discloses a super duplex stainless steel containing, in weight%, Cr: 21.0% to 38.0%, Ni: 3.0% to 12.0%, Mo: 1.5% to 6.5%, W: 0 to 6.5%, N: 0.2% to 0.7%, and Ba: 0.0001 to 0.6% and having a pitting resistance equivalent index PREW that satisfies $40 \le PREW \le 67$. Patent Literature 4 describes that the thus configured super duplex stainless steel is superior in corrosion resistance, embrittlement resistance, castability, and hot workability with formation of intermetal phases, such as the brittle sigma (σ) phase and the chi (χ) phase, suppressed.

45 CITATION LIST

PATENT LITERATURE

[8000]

50

Patent Literature 1: International Application Publication No. 2013/191208

Patent Literature 2: International Application Publication No. 2010/082395
Patent Literature 3: Japanese Patent Application Publication No. 2007-84837

Patent Literature 4: National Publication of International Patent Application No. 2005-520934

55

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0009] As described above, a duplex stainless steel having more excellent pitting resistance has been required in recent years. Technical means other than the technologies described in Patent Literatures 1 to 4 may therefore provide a duplex stainless steel showing excellent pitting resistance.

[0010] An objective of the present disclosure is to provide a duplex stainless steel having excellent pitting resistance and a method for producing the duplex stainless steel.

SOLUTION TO PROBLEM

10

20

25

30

40

45

50

[0011] A duplex stainless steel according to the present disclosure has a chemical composition consisting of, in mass%, Cr: more than 27.00% to 29.00%, Mo: 2.50 to 3.50%, Ni: 5.00 to 8.00%, W: 4.00 to 6.00%, Cu: 0.01 to less than 0.10%, N: more than 0.400% to 0.600%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, sol.Al: 0.040% or less, V: 0.50% or less, O: 0.010% or less, P: 0.030% or less, S: 0.020% or less, Ca: 0 to 0.0040%, Mg: 0 to 0.0040%, and B: 0 to 0.0040% with the balance being Fe and impurities and satisfying Formula (1), and a microstructure consisting of 35 to 65 volume% of ferrite phase with the balance being an austenite phase. In the duplex stainless steel according to the present disclosure, an area fraction of Cu precipitated in the ferrite phase is 0.5% or less.

$Cr+4.0\times Mo+2.0\times W+20\times N-5\times ln(Cu)\geq 65.2$ (1)

where, a content in mass% of each of the elements is substituted into a corresponding symbol of the element in Formula (1).

[0012] A method for producing a duplex stainless steel according to the present disclosure includes a preparation step, a hot working step, a cooling step, and a solution heat treatment step. In the preparation step, a starting material having the chemical composition described above is prepared. In the hot working step, the starting material is subjected to hot working at 850°C or more. In the cooling step, the starting material subjected to the hot working is cooled at a rate of 5°C/sec or more. In the solution heat treatment step, the cooled starting material is subjected to a solution heat treatment at 1070°C or more.

ADVANTAGEOUS EFFECTS OF INVENTION

[0013] The duplex stainless steel according to the present disclosure has excellent pitting resistance. The method for producing the duplex stainless steel according to the present disclosure allows production of the duplex stainless steel described above.

DESCRIPTION OF EMBODIMENTS

[0014] The present inventors have investigated and studied an approach for enhancing the pitting resistance of a duplex stainless steel. As a result, the following findings have been achieved.

[0015] Cr, Mo, and Cu are known to be effective in improvement of the pitting resistance of a duplex stainless steel. Among Cr, Mo, and Cu, Cr and Mo are believed to have a mechanism that enhances the pitting resistance of a duplex stainless steel as follows: Cr serves as a primary component of a passive film as an oxide on the surface of a duplex stainless steel. The passive film prevents contact between corrosion factors and the surface of the duplex stainless steel. As a result, the duplex stainless steel on the surface of which the passive film has been formed has enhanced pitting resistance. Mo is contained in the passive film and further enhances the pitting resistance of the passive film.

[0016] On the other hand, among Cr, Mo, and Cu, Cu is believed to have a mechanism that enhances the pitting resistance of a duplex stainless steel as follows: It is believed that there are the following two steps that cause pitting to occur. The first step is occurrence of pitting (initial stage). The next step is propagation of the pitting (propagation stage). It has been believed that Cu is effective in suppressing the propagation of pitting. Particularly in an acidic solution, an active site where the duplex stainless steel melts at high speed is formed on the surface of the duplex stainless steel. Cu coats the active site to suppress the melting of the duplex stainless steel. It has been believed that the thus functioning Cu suppresses the propagation of the pitting that occurs on a duplex stainless steel.

[0017] It has been believed based on the mechanism described above that Cr, Mo, and Cu are elements effective in improvement in pitting resistance of a duplex stainless steel. Cr, Mo, and Cu have therefore been actively contained in

a duplex stainless steel to enhance the pitting resistance. However, the following findings that had not been known have been obtained as a result of the studies conducted by the present inventors. Specifically, the present inventors have found that among Cr, Mo, and Cu, Cu instead lowers the pitting resistance in some cases at the occurrence of pitting (initial stage).

[0018] Table 1 is a table showing the chemical compositions of test specimens labeled with test numbers 2 and 5 and the pitting potential, which is an index of the pitting resistance, of the test specimens in Examples described later. The chemical compositions listed in two rows in Table 1 are those of steels of B and E, correspond to the test numbers 2 and 5, and are extracted from Table 3, which will be described later. The chemical compositions in Table 1 are expressed in mass%, and the balance is Fe and impurities. The pitting potentials listed in Table 1 are those labeled with the corresponding test numbers and are extracted from Table 4, which will be described later.

[Table 1]

10

15

20

25

[0019]

TABLE 1

Test No.	Steel	Cr	Мо	Ni	W	Cu	N	С	Si	Mn
2	В	28.10	3.11	5.31	4.19	0.14	0.421	0.016	0.49	0.97
5	Е	27.53	2.61	6.97	4.31	0.04	0.419	0.016	0.48	0.92
Test No.	Steel	sol.Al	V	0	Р	S	Ca	Mg	В	
2	В	0.013	0.10	0.004	0.018	0.001	0.0025	0.0001	0.0019	
5	Е	0.017	0.10	0.005	0.016	0.001	0.0010	0.0025	0.0013	
Test No.	Steel	Pittin	g potenti	al (mVvs.	SCE)					
2	В		-	71						
5	Е		3	46						

30

35

[0020] Referring to Table 1, the test specimen labeled with the test number 2 has a higher Cu content than the Cu content in the test specimen labeled with the test number 5. Further, the test specimen labeled with the test number 2 has higher Cr and Mo contents than the Cr and Mo contents in the test specimen labeled with the test number 5. It can therefore be expected based on the findings in the related art that the test specimen labeled with the test number 2, which has higher Cr, Mo, and Cu contents, has more excellent pitting resistance than the test specimen labeled with the test number 5. The pitting potential, which is an index of the pitting resistance, of the test specimen labeled with the test number 2 is, however, 71 mVvs.SCE, which is smaller than the pitting potential of 346 mVvs.SCE of the test specimen labeled with the test number 5.

40

[0021] That is, the pitting resistance of the test specimen labeled with the test number 2, which is expected based on the findings in the related art to have more excellent pitting resistance than the test specimen labeled with the test number 5, is instead smaller than the pitting resistance of the test specimen labeled with the test number 5. In view of the fact described above, the present inventors have focused on the microstructures of the test specimens labeled with the test numbers 2 and 5 and have investigated the microstructures in more detail. As a result, the investigation clearly showed that the test specimen labeled with the test number 2 has a greater area fraction of Cu precipitated in the ferrite phase (called Cu area fraction in ferrite phase) than the test specimen labeled with the test number 5.

50

[0022] In view of the fact described above, the present inventors have investigated and studied the effect of Cu precipitated in the ferrite phase on the pitting resistance of the duplex stainless steel. Table 2 is a table showing the chemical compositions of test specimens labeled with the test numbers 3 and 6, the Cu area fractions thereof in the ferrite phase, and the pitting potential thereof, which is an index of the pitting resistance, in Examples described later. The chemical compositions listed in two rows in Table 2 are those of steel of C, correspond to the test numbers 3 and 6, and are extracted from Table 3, which will be described later. The chemical compositions in Table 2 are expressed in mass%, and the balance is Fe and impurities. The Cu area fractions thereof in the ferrite phase listed in Table 2 are those labeled with the corresponding test numbers and are extracted from Table 4, which will be described later. The pitting potentials listed in Table 2 are those labeled with the corresponding test numbers and are extracted from Table 4, which will be described later.

55

[Table 2]

[0023]

5

10

15

20

35

40

50

TABLE 2

Test No.	Steel	Cr	Мо	Ni	W	Cu	N	С	Si	Mn
3	С	28.24	2.96	5.76	4.25	0.08	0.416	0.014	0.51	0.91
6	С	28.24	2.96	5.76	4.25	0.08	0.416	0.014	0.51	0.91
Test No.	Steel	sol.Al	V	0	Р	S	Ca	Mg	В	
3	С	0.012	0.10	0.004	0.019	0.001	0.0015	0.0002	0.0012	
6	С	0.012	0.10	0.004	0.019	0.001	0.0015	0.0002	0.0012	
Test No.	Steel	Cu area	fraction i	n ferrite pl	nase (%)	Pitting p	otential (m			
3	С		C).7			-12			
6	С			0			204			

[0024] Referring to Table 2, the test specimen labeled with the test number 3 and the test specimen labeled with the test number 6 had the same chemical composition. On the other hand, the test specimen labeled with the test number 6 had a smaller Cu area fraction in the ferrite phase than the Cu area fraction in the ferrite phase of the test specimen labeled with the test number 3. As a result, the pitting potential of the test specimen labeled with the test number 6 was 204 mVvs.SCE, which was greater than the pitting potential of -12 mVvs.SCE of the test specimen labeled with the test number 3. That is, the test specimen labeled with the test number 6 had more excellent pitting resistance than the test specimen labeled with the test number 3 as a result of a decrease in the amount of precipitation of Cu in the ferrite phase in the test specimen labeled with the test number 6.

[0025] It has been believed as described above that increasing the Cr, Mo, and Cu contents increases the pitting resistance. The present inventors have, however, found for the first time that Cu among Cr, Mo, and Cu is instead likely to lower the pitting resistance. The present inventors have further found that reduction in the amount of Cu precipitating in the ferrite phase allows enhancement of the pitting resistance, which is a finding that has not been known at all.

[0026] No detailed reason why Cu precipitated in the ferrite phase lowers the pitting resistance of a duplex stainless steel has been clarified. The present inventors, however, consider the reason as follows: Cu precipitated in the ferrite phase is likely to prevent uniform formation of a passive film. Therefore, in a case where a large amount of Cu has precipitated in the ferrite phase, the large amount of Cu is likely to lower the passive film's effect of suppressing the contact between corrosion factors and the surface of the duplex stainless steel. The present inventors believe that pitting occurs on the surface of the duplex stainless steel as a result of the assumption described above.

[0027] A duplex stainless steel according to the present embodiment attained based on the findings described above has a chemical composition consisting of, in mass%, Cr: more than 27.00% to 29.00%, Mo: 2.50 to 3.50%, Ni: 5.00 to 8.00%, W: 4.00 to 6.00%, Cu: 0.01 to less than 0.10%, N: more than 0.400% to 0.600%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, sol.Al: 0.040% or less, V: 0.50% or less, O: 0.010% or less, P: 0.030% or less, S: 0.020% or less, Ca: 0 to 0.0040%, Mg: 0 to 0.0040%, and B: 0 to 0.0040% with the balance being Fe and impurities and satisfying Formula (1), and a microstructure consisting of 35 to 65 volume% of ferrite phase with the balance being the austenite phase. In the duplex stainless steel according to the present embodiment, the area fraction of Cu precipitated in the ferrite phase is 0.5% or less.

$Cr+4.0\times Mo+2.0\times W+20\times N-5\times ln(Cu)\geq 65.2$ (1)

where, the content in mass% of each of the elements is substituted into the corresponding symbol of the element in Formula (1).

[0028] The duplex stainless steel according to the present embodiment has the chemical composition described above and the microstructure described above, and the area fraction of Cu in the ferrite phase is 0.5% or less. As a result, the duplex stainless steel according to the present embodiment has excellent pitting resistance.

[0029] The chemical composition described above preferably contains, in mass%, one or more types of element selected from the group consisting of Ca: 0.0001 to 0.0040%, Mg: 0.0001 to 0.0040%, and B: 0.0001 to 0.0040%.

[0030] In this case, the duplex stainless steel according to the present embodiment has enhanced hot workability.

[0031] A method for producing a duplex stainless steel according to the present embodiment includes a preparation step, a hot working step, a cooling step, and a solution heat treatment step. In the preparation step, a starting material having the chemical composition described above is prepared. In the hot working step, the starting material is subjected to hot working at 850°C or more. In the cooling step, the starting material subjected to the hot working is cooled at a rate of 5°C/sec or more. In the solution heat treatment step, the cooled starting material is subjected to a solution heat treatment at 1070°C or more.

[0032] The duplex stainless steel produced by the production method according to the present embodiment has the chemical composition described above and the microstructure described above, and the area fraction of Cu in the ferrite phase is 0.5% or less. As a result, the duplex stainless steel produced by the production method according to the present embodiment has excellent pitting resistance.

[0033] The duplex stainless steel according to the present embodiment will be described below in detail.

[Chemical composition]

10

[0034] The chemical composition of the duplex stainless steel according to the present embodiment contains the following elements. The symbol % associated with an element means mass% unless otherwise specified.

[Essential elements]

[0035] The chemical composition of the duplex stainless steel according to the present embodiment essentially contains the following elements:

Cr: more than 27.00% to 29.00%

[0036] Chromium (Cr) forms a passive film as an oxide on the surface of the duplex stainless steel. The passive film prevents contact between corrosion factors and the surface of the duplex stainless steel. As a result, occurrence of pitting on the duplex stainless steel is suppressed. Further, Cr is an element necessary for achievement of the ferrite structure in the duplex stainless steel. Achievement of a sufficient ferrite structure provides stable pitting resistance. Too low a Cr content provides no effects described above. On the other hand, too high a Cr content lowers the hot workability of the duplex stainless steel. The Cr content therefore ranges from more than 27.00% to 29.00%. The lower limit of the Cr content is preferably 27.50%, more preferably 28.00%. The upper limit of the Cr content is preferably 28.50%.

Mo: 2.50 to 3.50%

[0037] Molybdenum (Mo) is contained in the passive film and further enhances the corrosion resistance of the passive film. As a result, the pitting resistance of the duplex stainless steel is enhanced. Too low a Mo content provides no effect described above. On the other hand, too high a Mo content lowers the workability of, for example, the assembly of a steel pipe made of the duplex stainless steel. The Mo content therefore ranges from 2.50 to 3.50%. The lower limit of the Mo content is preferably 2.80%, more preferably 3.00%. The upper limit of the Mo content is preferably 3.30%.

Ni: 5.00 to 8.00%

40

45

50

55

[0038] Nickel (Ni) is an austenite stabilizing element and is an element necessary for achievement of the ferrite/austenite dual phase structure. Too low a Ni content provides no effect described above. On the other hand, too high a Ni content causes imbalance between the ferrite phase and the austenite phase. In this case, the duplex stainless steel is not stably produced. The Ni content therefore ranges from 5.00 to 8.00%. The lower limit of the Ni content is preferably 5.50%, more preferably 6.00%. The upper limit of the Ni content is preferably 7.50%.

W: 4.00 to 6.00%

[0039] Tungsten (W) is contained in the passive film and further enhances the corrosion resistance of the passive film, as in the case of Mo. As a result, occurrence of the pitting on the duplex stainless steel is suppressed. Too low a W content provides no effect described above. On the other hand, too high a W content is likely to cause the σ phase to precipitate easily, resulting in a decrease in toughness. The W content therefore ranges from 4.00 to 6.00%. The lower limit of the W content is preferably 4.50%. The upper limit of the W content is preferably 5.50%.

Cu: 0.01 to less than 0.10%

[0040] Copper (Cu) is an element effective in suppressing the propagation of the pitting (propagation stage). Too low a Cu content provides no effect described above. On the other hand, among Cr, Mo, and Cu, Cu lowers the pitting resistance at the occurrence of pitting (initial stage). The duplex stainless steel according to the present embodiment therefore has a lowered Cu content as compared with the Cu content in a duplex stainless steel of the related art. As a result, the precipitation of Cu in the ferrite phase is suppressed, and occurrence of pitting on the duplex stainless steel (initial stage) is suppressed. Too high a Cu content causes too large an area fraction of Cu in the ferrite phase. In this case, the pitting resistance of the duplex stainless steel lowers. The Cu content therefore ranges from 0.01 to less than 0.10%. The upper limit of the Cu content is preferably 0.07%, more preferably 0.05%.

N: more than 0.400% to 0.600%

[0041] Nitrogen (N) is an austenite stabilizing element and is an element necessary for achievement of the ferrite/austenite dual phase structure. N further enhances the pitting resistance of the duplex stainless steel. Too low a N content provides no effects described above. On the other hand, too high a N content lowers the toughness and the hot workability of the duplex stainless steel. The N content therefore ranges from more than 0.400% to 0.600%. The lower limit of the N content is preferably 0.420%. The upper limit of the N content is preferably 0.500%.

20 C: 0.030% or less

10

15

[0042] Carbon (C) is inevitably contained. That is, the C content is more than 0%. C forms a Cr carbide in the crystal grain boundary, and the Cr carbide increases the corrosion susceptibility in the grain boundary. The C content is therefore 0.030% or less. The upper limit of the C content is preferably 0.025%, more preferably 0.020%. The C content is preferably minimized. Extreme reduction in the C content, however, greatly increases the production cost. The lower limit of the C content is therefore preferably 0.001%, and more preferably 0.005% in consideration of industrial production.

Si: 1.00% or less

[0043] Silicon (Si) deoxidizes steel. In a case where Si is used as a deoxidizer, the Si content is more than 0%. On the other hand, too high a Si content lowers the hot workability of the duplex stainless steel. The Si content is therefore 1.00% or less. The upper limit of the Si content is preferably 0.80%, and more preferably 0.70%. The lower limit of the Si content is not limited to a specific value and is, for example, 0.20%.

35 Mn: 1.00% or less

40

55

[0044] Manganese (Mn) deoxidizes steel. In a case where Mn is used as a deoxidizer, the Mn content is more than 0%. On the other hand, too high a Mn content lowers the hot workability of the duplex stainless steel. The Mn content is therefore 1.00% or less. The upper limit of the Mn content is preferably 0.80%, and more preferably 0.70%. The lower limit of the Mn content is not limited to a specific value and is, for example, 0.20%.

Sol. Al: 0.040% or less

[0045] Aluminum (Al) deoxidizes steel. In a case where Al is used as a deoxidizer, the Al content is more than 0%. On the other hand, too high an Al content lowers the hot workability of the duplex stainless steel. The Al content is therefore 0.040% or less. The upper limit of the Al content is preferably 0.030%, and more preferably 0.025%. The lower limit of the Al content is not limited to a specific value and is, for example, 0.005%. In the present embodiment, the Al content refers to the acid-soluble Al (sol.Al) content.

50 V: 0.50% or less

[0046] Vanadium (V) is inevitably contained. That is, the V content is more than 0%. Too high a V content excessively increases the amount of the ferrite phase, resulting in decreases in toughness and corrosion resistance of the duplex stainless steel in some cases. The V content is therefore 0.50% or less. The upper limit of the V content is preferably 0.40%, and more preferably 0.30%. The lower limit of the V content is not limited to a specific value and is, for example, 0.05%.

O: 0.010% or less

[0047] Oxygen (O) is an impurity. That is, the O content is more than 0%. O lowers the hot workability of the duplex stainless steel. The O content is therefore 0.010% or less. The upper limit of the O content is preferably 0.007%, and more preferably 0.005%. The O content is preferably minimized. Extreme reduction in the O content, however, greatly increases the production cost. The lower limit of the O content is therefore preferably 0.0001%, and more preferably 0.0005% in consideration of industrial production.

P: 0.030% or less

10

20

30

35

40

55

[0048] Phosphorus (P) is an impurity. That is, the P content is more than 0%. P lowers the pitting resistance and toughness of the duplex stainless steel. The P content is therefore 0.030% or less. The upper limit of the P content is preferably 0.025%, and more preferably 0.020%. The P content is preferably minimized. Extreme reduction in the P content, however, greatly increases the production cost. The lower limit of the P content is therefore preferably 0.001%, and more preferably 0.005% in consideration of industrial production.

S: 0.020% or less

[0049] Sulfur (S) is an impurity. That is, the S content is more than 0%. S lowers the hot workability of the duplex stainless steel. The S content is therefore 0.020% or less. The upper limit of the S content is preferably 0.010%, more preferably 0.005%, and still more preferably 0.003%. The S content is preferably minimized. Extreme reduction in the S content, however, greatly increases the production cost. The lower limit of the S content is therefore preferably 0.0001%, and more preferably 0.0005% in consideration of industrial production.

[0050] The balance of the chemical composition of the duplex stainless steel according to the present embodiment is Fe and impurities. The impurities in the chemical composition mean contaminants, for example, from ore as a raw material, scraps, or the production environment in industrial production of the duplex stainless steel that are acceptable to the extent that the contaminants do not adversely affect the duplex stainless steel according to the present embodiment.

[Optional elements]

[0051] The chemical composition of the duplex stainless steel according to the present embodiment may arbitrarily contain the following elements:

Ca: 0 to 0.0040%

[0052] Calcium (Ca) is an optional element and may not be contained. That is, the Ca content may be 0%. When contained, Ca enhances the hot workability of the duplex stainless steel. When Ca is contained even by a trace amount, the effect described above is provided to some extent. On the other hand, too high a Ca content produces a coarse oxide, which lowers the hot workability of the duplex stainless steel. The Ca content is therefore 0 to 0.0040%. The lower limit of the Ca content is preferably 0.0001%, more preferably 0.0005%, and still more preferably 0.0010%. The upper limit of the Ca content is preferably 0.0030%.

Mg: 0 to 0.0040%

[0053] Magnesium (Mg) is an optional element and may not be contained. That is, the Mg content may be 0%. When contained, Mg enhances the hot workability of the duplex stainless steel, as does Ca. When Mg is contained even by a trace amount, the effect described above is provided to some extent. On the other hand, too high a Mg content produces a coarse oxide, which lowers the hot workability of the duplex stainless steel. The Mg content is therefore 0 to 0.0040%. The lower limit of the Mg content is preferably 0.0001%, more preferably 0.0005%, and still more preferably 0.0010%.
The upper limit of the Ca content is preferably 0.0030%.

B: 0 to 0.0040%

[0054] Boron (B) is an optional element and may not be contained. That is, the B content may be 0%. When contained, B enhances the hot workability of the duplex stainless steel, as do Ca and Mg. When B is contained even by a trace amount, the effect described above is provided to some extent. On the other hand, too high a B content lowers the toughness of the duplex stainless steel. The B content is therefore 0 to 0.0040%. The lower limit of the B content is preferably 0.0001%, more preferably 0.0005%, and still more preferably 0.0010%. The upper limit of the Ca content is

preferably 0.0030%.

[Formula (1)]

5

10

20

30

35

40

45

50

55

[0055] The chemical composition of the duplex stainless steel according to the present embodiment satisfies the contents of the elements described above and further satisfies the following Formula (1):

$$Cr+4.0 \times Mo + 2.0 \times W + 20 \times N - 5 \times ln(Cu) \ge 65.2$$
 (1)

where, content in mass% of each of the elements is substituted into the corresponding symbol of the element in Formula (1).

[0056] The following definition is made: F1=Cr+4.0 \times Mo+2.0 \times W+20 \times N-5 \times In(Cu). F1 is an index representing the pitting resistance. When F1 is less than 65.2, the pitting resistance of the duplex stainless steel lowers. The following formula is therefore satisfied: F1 \ge 65.2. The lower limit of F1 is preferably 68.0, more preferably 69.0, and still more preferably 70.0. The upper limit of F1 is not limited to a specific value and is, for example, 90.0.

[Micro structure]

[0057] The microstructure of the duplex stainless steel according to the present embodiment consists of ferrite and austenite. Specifically, the microstructure of the duplex stainless steel according to the present embodiment consists of 35 to 65 volume% of ferrite phase with the balance being the austenite phase. When the volume ratio of the ferrite phase (hereinafter also referred to as ferrite fraction) is less than 35%, stress corrosion cracking is more likely to occur depending on the environment in which the duplex stainless steel is used. On the other hand, when the volume ratio of the ferrite phase is more than 65%, the toughness of the duplex stainless steel is more likely to lower. Therefore, the microstructure of the duplex stainless steel according to the present embodiment consists of 35 to 65 volume% of ferrite phase with the balance being the austenite phase.

[Method for measuring ferrite fraction]

[0058] In the present embodiment, the ferrite fraction of the duplex stainless steel can be determined by the following method: A test specimen for microstructure observation is collected from the duplex stainless steel. When the duplex stainless steel is used to form a steel plate, a cross section of the steel plate that is the cross section perpendicular to the plate width direction of the steel plate (hereinafter referred to as observation surface) is polished. When the duplex stainless steel is used to form a steel pipe, a cross section of the steel pipe that is the cross section (observation surface) containing the axial direction and the wall thickness direction of the steel pipe is polished. When the duplex stainless steel is used to form a steel bar or a wire rod, a cross section of the steel bar or the wire rod that is the cross section (observation surface) containing the axial direction of the steel bar or the wire rod is polished. The polished observation surface is then etched by using a liquid that is the mixture of aqua regia and glycerin.

[0059] Ten visual fields of the etched observation surface are observed under an optical microscope. The area of each of the visual fields is, for example, $2000 \ \mu m^2$ (at magnification of 500). In each of the visual fields, the ferrite and the other phases can be distinguished from each other based on contrast. The ferrite is therefore identified based on the contrast in each observation. The area fraction of the identified ferrite is measured by using a point counting method compliant with JIS G0555 (2003). The measured area fraction is assumed to be equal to the volume fraction, which is then defined as a ferrite fraction (volume%).

[Cu area fraction in ferrite phase]

[0060] The area fraction of Cu precipitated in the ferrite phase of the duplex stainless steel according to the present embodiment is 0.5% or less. It is believed as described above that Cu contained in the duplex stainless steel suppresses the propagation of the pitting on the duplex stainless steel. The duplex stainless steel according to the present embodiment therefore contains Cu by an amount ranging from 0.01 to less than 0.10%. On the other hand, in the duplex stainless steel containing Cu by the amount ranging from 0.01 to less than 0.10%, metal Cu precipitates in the ferrite phase in some cases. It has clearly been shown as described above that Cu precipitated in the ferrite phase lowers the passive film's effect of suppressing occurrence of pitting. That is, metal Cu precipitated in the ferrite phase lowers the pitting resistance of the duplex stainless steel.

[0061] The duplex stainless steel according to the present embodiment has a reduced Cu area fraction in the ferrite

phase to 0.5% or less. The occurrence of pitting on the duplex stainless steel is thus suppressed. The Cu area fraction in the ferrite phase is preferably minimized. The upper limit of the Cu area fraction in the ferrite phase is preferably 0.3%, and more preferably 0.1%. The lower limit of the Cu area fraction in the ferrite phase is 0.0%.

5 [Method for measuring Cu area fraction in ferrite phase]

[0062] In the present specification, the Cu area fraction in the ferrite phase means the area fraction of Cu precipitated in the ferrite phase out of the microstructure of the duplex stainless steel with respect to the ferrite phase. In the present embodiment, the Cu area fraction in the ferrite phase can be measured by the following method: A thin film specimen for observation under a transmission electron microscope (TEM) is prepared by an FIB-micro-sampling method. To prepare the thin film specimen, a focused ion beam processing apparatus (MI4050 manufactured by Hitachi High-Tech Science Corporation) is used. A thin film specimen for TEM observation is prepared from an arbitrary portion of the duplex stainless steel. To prepare the thin film specimen, a mesh made of Mo and a carbon deposit film as a surface protection film are used.

[0063] A field emission transmission electron microscope (JEM-2100F manufactured by JEOL Ltd.) is used for the TEM observation. The TEM observation is performed at an observation magnification of 10000. The ferrite phase and the austenite phase in a visual field differ from each other in terms of contrast. The crystal grain boundary is then identified based on the contrast. The phase of a region surrounded by each crystal grain boundary is identified by X-ray diffraction (XRD). Among the regions surrounded by the crystal grain boundaries, the area of the region identified as the ferrite phase is determined by image analysis.

[0064] Element analysis based on energy dispersive X-ray spectrometry (EDS) is performed on the visual field under observation to generate an element map. Further, a precipitate can be identified based on the contrast. Therefore, whether a precipitate identified based on the contrast in the ferrite phase identified by XRD is metal Cu can be identified by EDS.

²⁵ **[0065]** The area of Cu precipitated in the identified ferrite phase is determined by image analysis. The sum of the areas of Cu precipitated in the ferrite phase is divided by the sum of areas of the ferrite phase. The Cu area fraction (%) in the ferrite phase is thus measured.

[0066] The duplex stainless steel according to the present embodiment satisfies both the chemical composition including Formula (1) and the microstructure including the in-ferrite-phase Cu area fraction described above. The duplex stainless steel according to the present embodiment therefore has excellent pitting resistance.

[Yield strength]

10

15

20

30

35

55

[0067] The yield strength of the duplex stainless steel according to the present embodiment is not limited to a specific value. When the yield strength is 750 MPa or less, however, the cold working can be omitted in the production process. In this case, the production cost can be reduced. The yield strength is therefore preferably 750 MPa or less. The yield strength is more preferably 720 MPa or less. The lower limit of the yield strength is not limited to a specific value and is, for example, 300 MPa.

40 [Method for measuring yield strength]

[0068] The yield strength in the present specification means 0.2% proof stress determined by a method compliant with JIS Z2241 (2011).

45 [Shape of duplex stainless steel]

[0069] The shape of the duplex stainless steel according to the present embodiment is not limited to a specific shape. The duplex stainless steel may be used in a form of, for example, a steel pipe, a steel plate, a steel bar, or a wire rod.

50 [Production method]

[0070] The duplex stainless steel according to the present embodiment can be produced, for example, by the following method: The production method includes a preparation step, a hot working step, a cooling step, and a solution heat treatment step.

[Preparation step]

[0071] In the preparation step, a starting material having the chemical composition described above is prepared. The

starting material may be a cast piece produced by a continuous casting process (including round continuous casting) or a slab produced from the cast piece. The starting material may be a slab produced by performing hot working on an ingot produced by an ingot-making process.

⁵ [Hot working step]

10

20

30

45

50

[0072] The prepared starting material is placed in a heating furnace or a soaking pit and heated at a temperature ranging, for example, from 1150 to 1300°C. The heated starting material is subsequently subjected to hot working. The hot working may be hot forging, hot extrusion using, for example, the Ugine-Sejournet process or the Ehrhardt push bench process, or hot rolling. The hot working may be performed once or multiple times.

[0073] The heated starting material is subjected to hot working at 850°C or more. More specifically, the surface temperature of the steel material at the end of the hot working is 850°C or more. When the surface temperature of the steel material at the end of the hot working is less than 850°C, a large amount of Cu precipitates in the ferrite phase. As a result, even a solution treatment, which will be described later, cannot sufficiently reduce the Cu area fraction in the ferrite phase in some cases. In this case, the pitting resistance of the duplex stainless steel lowers. The surface temperature of the steel material at the end of the hot working is therefore 850°C or more. In a case where the hot working is performed multiple times, the surface temperature of the steel material at the end of the last hot working. The upper limit of the surface temperature of the steel material at the end of the hot working. The upper limit of the surface temperature of the steel material at the end of the hot working is not limited to a specific value and is, for example, 1300°C. The end of the hot working is the point of time within three seconds after the hot working ends.

[Cooling step]

[0074] The starting material after the hot working is subsequently cooled at a rate of 5°C/sec or more. Cu starts precipitating in the ferrite phase at around 850°C. Therefore, if the cooling rate after the hot working is too slow, a large amount of Cu precipitates in the ferrite phase. As a result, even a solution treatment, which will be described later, cannot sufficiently reduce the Cu area fraction in the ferrite phase in some cases. In this case, the pitting resistance of the duplex stainless steel lowers. The cooling rate after the hot working is therefore 5°C/sec or more. In the case where the hot working is performed multiple times, "after the hot working" refers to "after the last hot working." That is, in the present embodiment, the starting material after the last hot working is cooled at the rate of 5°C/sec or more. The upper limit of the cooling rate is not limited to a specific value. The cooling method is, for example, air cooling, water cooling, or oil cooling.

[Solution heat treatment step]

[0075] The cooled starting material is subsequently subjected to a solution heat treatment at 1070°C or more. The solution heat treatment causes the Cu precipitated in the ferrite phase to dissolve. Performing the solution heat treatment at 1070°C or more on the starting material in which the precipitation of Cu in the ferrite phase at the end of the hot working and after the cooling is sufficiently suppressed allows the Cu area fraction in the ferrite phase to be 0.5% or less. The upper limit of the solution heat treatment temperature is not limited to a specific value and is, for example, 1150°C. The treatment period of the solution heat treatment is not limited to a specific value. The treatment period of the solution heat treatment ranges, for example, from 1 to 30 minutes.

[0076] The duplex stainless steel according to the present embodiment can be produced by carrying out the steps described above. In the present embodiment, it is preferable to perform no cold working because cold working increases the production cost.

EXAMPLES

[0077] Alloys having the chemical compositions shown in Table 3 were melted in a 50 kg vacuum furnace, the obtained ingots were heated at 1200°C, and the heated ingots were subjected to hot forging and hot rolling into steel plates having a thickness of 10 mm. The temperatures at the end of rolling shown in Table 4 are the surface temperatures of the steel plates at the end of the hot rolling. The post-rolling cooling rates shown in Table 4 are the cooling rates after the hot rolling. Further, the steel plates were subjected to a solution treatment at the solution temperatures (°C) shown in Table 4 into test specimens labeled with the test numbers.

⁵⁵ [Table 3]

		_														
			7	-	29.8	67.2	69.5	65.1	71.1	74.6	73.0	9.99	65.7	6.99		
5					В	0.0017	0.0019	0.0012	0.0015	0.0013	ı	-	0.0021	0.0011	0.0017	
10				Mg	0.0021	0.0001	0.0002	0.0034	0.0025	ı	-	0.0019	0.0014	0.0034		
				Ca	0.0019	0.0025	0.0015	0.0027	0.0010	ı	-	0.0018	0.0025	0.0013		
15						S	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
20			purities)	Ь	0.019	0.018	0.019	0.017	0.016	0.017	0.017	0.021	0.023	0.018		
			Chemical composition (unit is mass%, balance is Fe and impurities)	0	0.003	0.004	0.004	0.005	0.005	0.003	0.005	0.004	0.003	0.003		
25			ance is F	^	0.10	0.10	0.10	0.10	0.10	0.11	0.11	0.10	0.11	0.09		
		TABLE 3	ss%, bala	sol.Al	0.017	0.013	0.012	0.014	0.017	0.015	0.016	0.014	0.019	0.017		
30		TABI	nit is ma	Mn	0.98	76.0	0.91	0.92	0.92	0.94	76.0	0.91	0.92	96.0		
35			sition (uı	Si	0.50	0.49	0.51	0.52	0.48	0.49	0.48	0.54	0.51	0.47		
			al compo	0	0.015	0.016	0.014	0.017	0.016	0.016	0.014	0.018	0.016	0.019		
40			Chemic	z	0.406	0.421	0.416	0.401	0.419	0.501	0.457	0.401	0.405	0.408		
				no	0.50	0.14	0.08	0.09	0.04	0.07	0.08	0.08	0.07	60.0		
45				Μ	4.10	4.19	4.25	4.00	4.31	5.61	4.37	3.61	4.19	4.27		
ΕO				Z	6.21	5.31	5.76	5.29	6.97	5.34	7.21	6.48	7.62	5.67		
50				Mo	3.21	3.11	2.96	2.50	2.61	3.05	3.45	2.86	2.23	3.01		
55				Cr	27.14	28.10	28.24	27.01	27.53	27.88	28.71	27.30	27.04	26.10		
	[0078]		Stool	ם פו	4	В	ပ	Q	ш	ш	9	т	_	7		
		_														

[Table 4]

[0079]

5

10

15

20

25

30

40

45

50

TABLE 4

		Prod	uction condi	tions	Analysis results						
Test No.	Steel	End of rolling temperature (°C)	Post- rolling cooling rate (°c/sec)	Solution temperature (°C)	Ferrite fraction (volume%)	Cu area fraction in ferrite phase (%)	Pitting potential Vc' ₁₀₀ (mVvs.SCE)	Yield strength (MPa)			
1	Α	980	30	1120	44	0.8	-60	712			
2	В	970	10	1100	48	0.6	71	680			
3	С	1010	30	1050	39	0.7	-12	620			
4	D	930	10	1100	43	0.1	85	719			
5	Е	950	30	1100	50	0.0	346	637			
6	С	1000	30	1090	41	0.0	204	675			
7	F	1020	10	1070	40	0.0	410	617			
8	G	1060	10	1090	47	0.0	384	701			
9	Н	1050	10	1100	51	0.0	70	721			
10	I	1100	30	1090	48	0.1	76	679			
11	J	1040	10	1070	45	0.2	81	665			
12	С	840	10	1070	44	1.1	-150	663			
13	С	1000	3	1090	51	1.6	-71	714			

[Ferrite fraction measurement test]

³⁵ **[0080]** The ferrite fraction (volume%) of each of the test specimens labeled with the test numbers was measured by using the method described above. Table 4 shows the results of the measurement. The balance of the microstructure of each of the test specimens labeled with the test numbers was the austenite phase.

[In-ferrite-phase Cu area fraction measurement test]

[0081] The in-ferrite-phase Cu area fraction (%) of each of the test specimens labeled with the test numbers was measured by using the method described above. Table 4 shows the results of the measurement.

[Pitting potential measurement test]

[0082] The pitting potential of each of the test specimens labeled with the test numbers after the solution treatment was measured. The test specimens were each first machined into a test specimen having a diameter of 15 mm and a thickness of 2 mm. The obtained test specimens were each used to measure the pitting potential in 25% NaClaq. at 80°C. The conditions other than the test temperature and the NaCl concentration were compliant with JIS G0577 (2014). Table 4 shows the results of the measurement of pitting potential Vc'₁₀₀ of the test specimens labeled with the test numbers.

[Tensile test]

⁵⁵ **[0083]** The 0.2% proof stress of the test specimens labeled with the respective test numbers was determined by using a method compliant with JIS Z2241 (2011). Table 4 shows the results of the determination.

[Evaluation results]

10

20

30

35

45

55

[0084] Referring to Tables 3 and 4, the test specimens labeled with test numbers 5 to 8 had appropriate chemical compositions and were produced under appropriate conditions. The test specimens labeled with the test numbers 5 to 8 therefore were the duplex stainless steel having a ferrite fraction ranging from 35 to 65 volume% with the balance being the austenite phase, and the Cu area fraction in the ferrite phase was 0.5% or less. As a result, the pitting potential (mVvs.SCE) of each of the steel plates labeled with the test numbers 5 to 8 was 100 or more, which represented excellent pitting resistance.

[0085] On the other hand, the test specimen labeled with test number 1 has too high a Cu content. Further, F1 of the test specimen labeled with the test number 1 was 59.8, which did not satisfy Formula (1). The Cu area fraction in the ferrite phase of the test specimen labeled with the test number 1 was therefore 0.8%. As a result, the pitting potential (mVvs.SCE) of the test specimen labeled with the test number 1 was -60, which did not represent excellent pitting resistance

[0086] The test specimen labeled with test number 2 has too high a Cu content. The Cu area fraction in the ferrite phase of the test specimen labeled with the test number 2 was therefore 0.6%. As a result, the pitting potential (mVvs.SCE) of the test specimen labeled with the test number 2 was 71, which did not represent excellent pitting resistance.

[0087] The solution temperature of the test specimen labeled with test number 3 was 1050°C, which was too low. The Cu area fraction in the ferrite phase of the test specimen labeled with the test number 3 was therefore 0.7%. As a result, the pitting potential (mVvs.SCE) of the test specimen labeled with the test number 3 was -12, which did not represent excellent pitting resistance.

[0088] The content of each element of the test specimen labeled with test number 4 was appropriate, but F1 was 65.1, which did not satisfy Formula (1). As a result, the pitting potential (mVvs.SCE) of the test specimen labeled with the test number 4 was 85, which did not represent excellent pitting resistance.

[0089] The test specimen labeled with test number 9 had too low a W content. As a result, the pitting potential (mV-vs.SCE) of the test specimen labeled with the test number 9 was 70, which did not represent excellent pitting resistance.

[0090] The test specimen labeled with test number 10 had too low a Mo content. As a result, the pitting potential (mVvs.SCE) of the test specimen labeled with the test number 10 was 76, which did not represent excellent pitting resistance.

[0091] The test specimen labeled with test number 11 had too low a Cr content. As a result, the pitting potential (mVvs.SCE) of the test specimen labeled with the test number 11 was 81, which did not represent excellent pitting resistance.

[0092] The temperature of the test specimen labeled with test number 12 at the end of the hot rolling was 840°C, which was too low. The Cu area fraction in the ferrite phase of the test specimen labeled with the test number 12 was therefore 1.1%. As a result, the pitting potential (mVvs.SCE) of the test specimen labeled with the test number 12 was -150, which did not represent excellent pitting resistance.

[0093] The cooling rate at which the test specimen labeled with test number 13 was cooled at the end of the hot rolling was 3°C/sec, which was too slow. The Cu area fraction in the ferrite phase of the test specimen labeled with the test number 13 was therefore 1.6%. As a result, the pitting potential (mVvs.SCE) of the test specimen labeled with the test number 13 was -71, which did not represent excellent pitting resistance.

[0094] The embodiment of the present invention has been described. The embodiment described above is, however, only an example for implementing the present invention. The present invention is therefore not limited to the embodiment described above, and the embodiment described above can be changed as appropriate to the extent that the change does not depart from the substance of the present invention.

Claims

1. A duplex stainless steel comprising:

a chemical composition consisting of, in mass%,

Cr: more than 27.00% to 29.00%,

Mo: 2.50 to 3.50%, Ni: 5.00 to 8.00%, W: 4.00 to 6.00%.

Cu: 0.01 to less than 0.10%,

N: more than 0.400% to 0.600%,

C: 0.030% or less, Si: 1.00% or less,

Mn: 1.00% or less, sol.Al: 0.040% or less, V: 0.50% or less, O: 0.010% or less, P: 0.030% or less, S: 0.020% or less, Ca: 0 to 0.0040%, Mg: 0 to 0.0040%,

5

10

15

25

35

40

45

50

55

B: 0 to 0.0040%, and with the balance being Fe and impurities, and satisfying Formula (1),

a microstructure consisting of 35 to 65 volume% of ferrite phase with the balance being an austenite phase, wherein an area fraction of Cu precipitates in the ferrite phase is 0.5% or less:

$Cr+4.0\times Mo+2.0\times W+20\times N-5\times ln(Cu)\geq 65.2$ (1)

where, a content in mass% of each of the elements is substituted into a corresponding symbol of the element in Formula (1).

20 2. The duplex stainless steel according to claim 1, wherein the chemical composition contains, in mass%, one or more types of element selected from the group consisting of:

> Ca: 0.0001 to 0.0040%, Mg: 0.0001 to 0.0040%, and B: 0.0001 to 0.0040%.

- 3. A method for producing a duplex stainless steel, the method comprising the steps of:
- preparing a starting material having a chemical composition consisting of, in mass%,

Cr: more than 27.00% to 29.00%,

Mo: 2.50 to 3.50%, Ni: 5.00 to 8.00%, W: 4.00 to 6.00%,

Cu: 0.01 to less than 0.10%,

N: more than 0.400% to 0.600%,

C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, sol.Al: 0.040% or less, V: 0.50% or less,

O: 0.010% or less, P: 0.030% or less,

S: 0.020% or less, Ca: 0 to 0.0040%,

Mg: 0 to 0.0040%, and

B: 0 to 0.0040%

with the balance being Fe and impurities and satisfying Formula (1);

subjecting the starting material to hot working at 850°C or more;

cooling the starting material subjected to the hot working at a rate of 5°C/sec or more; and subjecting the cooled starting material to a solution heat treatment at 1070°C or more:

$$Cr+4.0\times Mo+2.0\times W+20\times N-5\times ln(Cu)\geq 65.2$$
 (1)

where, a content in mass% of each of the elements is substituted into a corresponding symbol of the element in Formula (1).

INTERNATIONAL SEARCH REPORT International application No. PCT/JP2018/042114 A. CLASSIFICATION OF SUBJECT MATTER 5 Int.Cl. C22C38/00(2006.01)i, C21D8/00(2006.01)i, C22C38/54(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. C22C38/00-38/60 10 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2019 Registered utility model specifications of Japan 1996-2019 Published registered utility model applications of Japan 1994-2019 15 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT 20 Citation of document, with indication, where appropriate, of the relevant passages Category* Relevant to claim No. JP 2008-519165 A (SANDVIK INTELLECTUAL PROPERTY AB.) 05 June Α 1 - 32008 & US 2008/0138232 A1 & WO 2006/049572 A1 & EP 1812614 A1 & SE 528782 C2 & CA 2586452 A1 & KR 10-2007-0073870 A & CN 101057002 A & AU 2005301376 A1 & NO 341532 B1 25 JP 2013-253315 A (KOBE STEEL, LTD.) 19 December 2013 Α (Family: none) 1 - 3JP 61-243117 A (SUMITOMO METAL INDUSTRIES, LTD.) 29 October 1986 & US 4721600 A & GB 2173816 A & SE 8601468 L 1 - 3Α 30 JP 58-1062 A (MITSUBISHI HEAVY INDUSTRIES, LTD.) 06 January 1983 (Family: none) Α 1 - 335 Further documents are listed in the continuation of Box C. See patent family annex. 40 later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other "L" 45 document of particular relevance; the claimed invention cannot be special reason (as specified) considered to involve an inventive step when the document is combined with one or more other such documents, such combination document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed being obvious to a person skilled in the art document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 50 10 January 2019 (10.01.2019) 22 January 2019 (22.01.2019) Name and mailing address of the ISA/ Authorized officer Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan 55 Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2013191208 A [0004] [0008]
- WO 2010082395 A **[0005] [0008]**

- JP 2007084837 A [0006] [0008]
- WO 2005520934 A [0007] [0008]