(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 476 771 A1

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

(43) Date of publication:
18.07.2012 Bulletin 2012/29

(21) Application number: **10815306.5**

(22) Date of filing: **01.09.2010**

(51) Int Cl.:
C22C 38/00 $^{(2006.01)}$ ***C22C 38/58*** $^{(2006.01)}$

(86) International application number:
PCT/JP2010/064953

(87) International publication number:
WO 2011/030709 (17.03.2011 Gazette 2011/11)

(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 SE SI SK SM TR

(30) Priority: **10.09.2009 JP 2009209160**

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(54) TWO-PHASE STAINLESS STEEL

(57) [Problem to be Solved]

To provide a duplex stainless steel excellent in the weldability during large heat input welding and excellent in the stress corrosion cracking resistance in a chloride environment containing corrosive associated gases.

[Solution]

A duplex stainless steel that has a chemical composition consisting, by mass%, of C: 0.03% or less, Si: 0.2 to 1%, Mn: 5.0% or less, P: 0.040% or less, S: 0.010% or less, sol. Al: 0.040% or less, Ni: 4 to 8%, Cr: 20 to 28%, Mo: 0.5 to 2.0%, Cu: more than 2.0% and 4.0% or less and N: 0.1 to 0.35%, and optionally contains one or more selected from among V, Ca, Mg, B and a rare earth metal(s), with the balance being Fe and impurities; wherein the duplex stainless steel satisfies the relations of the following formulas (1) and (2):

$$2.2\mathrm{Cr} + 7\mathrm{Mo} + 3\mathrm{Cu} > 66 \qquad (1)$$

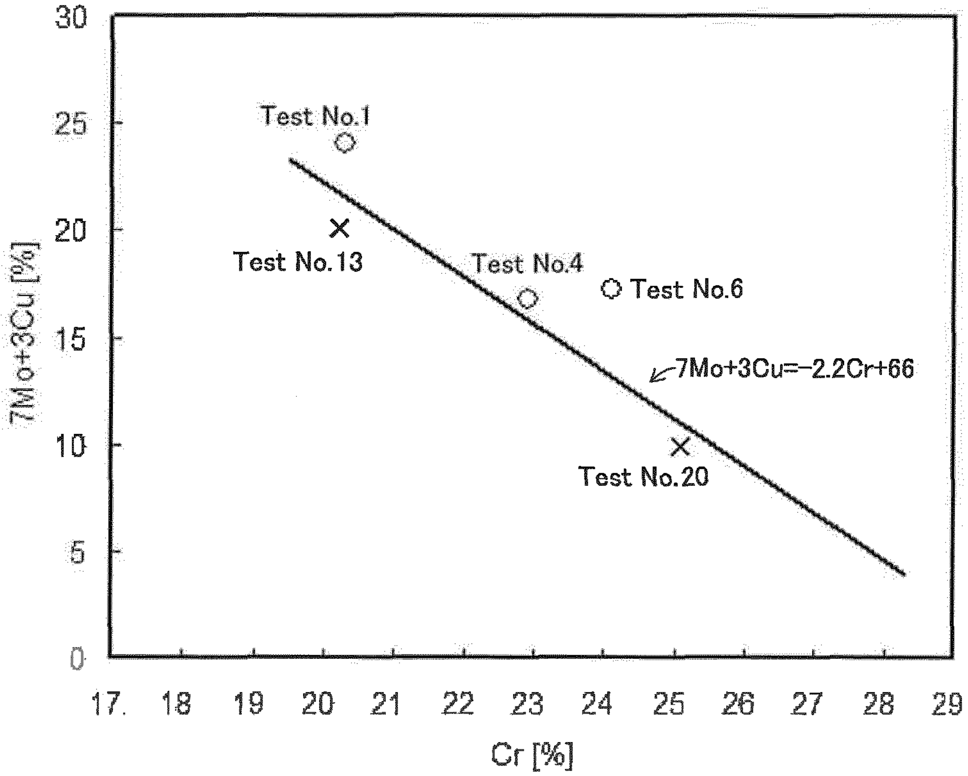
$$\mathrm{Cr} + 11\mathrm{Mo} + 10\mathrm{Ni} < 12(\mathrm{Cu} + 30\mathrm{N}) \qquad (2)$$

wherein the symbols of elements in formulas (1) and (2) respectively represent the contents (unit: mass%) of the elements in the steel.

Printed by Jouve, 75001 PARIS (FR)

(Cont. next page)

[Fig.4]


30
25
20
15
10
5
0
7Mo+3Cu [%]
Test No.1
Test No.13
Test No.4
Test No.6
7Mo+3Cu=−2.2Cr+66
Test No.20
17.
18
19
20
21
22
23
24
25
26
27
28
29
Cr [%]

Description

[Technical Field]

[0001] The present invention relates to a ferrite-austenite duplex stainless steel excellent in stress corrosion cracking resistance, in particular to a duplex stainless steel suitable as a steel material for line pipes transporting petroleum, natural gas or the like.

[Background Art]

[0002] In petroleum and natural gas produced from oil fields and gas fields, such corrosive gasses as carbon dioxide gas (CO_2) and hydrogen sulfide (H_2S) are present as associated gases. In line pipes transporting such highly corrosive petroleum and natural gas, stress corrosion cracking (SCC), sulfide stress cracking (SSC), and general corrosion functioning as a factor for wall thickness reduction and the like offer problems. In particular, stress corrosion cracking (SCC) and sulfide stress cracking (SSC) are fast in rate of progression, hence the time in which the crack penetrates line pipes is short, and such penetration occurs locally to offer more serious problems. Accordingly, the steel materials for such line pipes as aforementioned are required to have excellent corrosion resistance.

[0003] As steel materials excellent in corrosion resistance, what is called duplex stainless steels composed of ferrite-austenite phases have hitherto been used. For example, Patent Document 1 describes a duplex stainless steel containing Cu in a content of 1 to 3% and improved in corrosion resistance in chloride and sulfide environments. Patent Document 2 describes a duplex stainless steel in which the strength, toughness and seawater resistance are improved by appropriately regulating the contents of Cr, Ni, Cu, Mo, N and W and by controlling the area fraction of the ferrite phase to 40% through 70%.

[Citation List]

[0004]

[Patent Document 1] WO 96/18751
[Patent Document 2] JP2003-171743A

[Summary of Invention]

[Technical Problem]

[0005] In the duplex stainless steel described in Patent Document 1, the degradation of the corrosion resistance of the weld zone tends to occur during large heat input welding. In the duplex stainless steel described in Patent Document 2, intermetallic compounds precipitate in the weld zone during large heat input welding, and hence embrittlement and degradation of the corrosion resistance tend to occur in the weld zone, and additionally, on the assumption of the transportation of petroleum or natural gas, insufficient is the stress corrosion cracking resistance in a chloride environment containing corrosive associated gases such as carbon dioxide gas and hydrogen sulfide.

[0006] The present invention has been performed for the purpose of solving the aforementioned problems, and an object of the present invention is to provide a duplex stainless steel excellent in the weldability during large heat input welding and excellent in the stress corrosion cracking resistance in the chloride environment containing corrosive associated gases.

[Solution to Problem]

[0007] The present inventors performed a series of various experiments and detailed studies for the purpose of actualizing in a duplex stainless steel the improvement of the weldability during large heat input welding and the improvement of the stress corrosion cracking resistance in the chloride environment. Consequently, the present inventors have obtained the following findings (a) to (f).

[0008]

(a) The stress corrosion cracking resistance of a duplex stainless steel can be improved by strengthening with Mo the passivation film mainly composed of Cr. On the other hand, for the purpose of preventing the precipitation of intermetallic compounds during large heat input welding, it is necessary to regulate the contents of Cr and Mo. However, in a high-temperature chloride environment containing carbon dioxide gas and hydrogen sulfide, when the contents of Cr and Mo are reduced, it is impossible to obtain any excellent stress corrosion cracking resistance in the vicinity of a weld zone.

[0009]

(b) For the purpose of improving the stress corrosion cracking resistance while the contents of Cr and Mo are being regulated, it is only required that the passivation film mainly composed of Cr be able to be strengthened with an element other than Mo. In this connection, Cu is an element having a function to reduce the corrosion rate of a steel material in an acidic environment. Accordingly, the inclusion of Cu in an appropriate content in addition to Cr and Mo enables to stabilize the passivation film and to strengthen the passivation film.

[0010] Figure 4 is a graph in which for duplex stainless steels having various chemical compositions, used in Examples described later, the content (mass%) of "Cr" is plotted on the X-axis and the content (mass%) of "7Mo + 3Cu" is plotted on the Y-axis. With the straight line of "7Mo + 3Cu = -2.2Cr + 66" as a boundary, the graph can be divided into the upper right section of the "determination (○) of non-occurrence of stress corrosion cracking" and the lower left section of the "determination (×) of occurrence of stress corrosion cracking."

[0011] Accordingly, it can be derived that by containing Cr, Mo and Cu so as to satisfy the relation of the following formula (1), the passivation film can be strengthened:

$$2.2\mathrm{Cr} + 7\mathrm{Mo} + 3\mathrm{Cu} > 66 \qquad (1)$$

wherein the symbols of elements in formula (1) respectively represent the contents (unit: mass%) of the elements in the steel.

[0012] When the content of Cu is 2% or less by mass%, no sufficient corrosion resistance is obtained. Accordingly, Cu is required to be contained in a content exceeding 2%.

[0013]

(c) When a duplex stainless steel is welded, the micro-structure in the vicinity of the weld zone is heated in a short time and then cooled in a short time. For the purpose of preventing the precipitation of the intermetallic compound (the sigma phase) in such a micro-structure in which heating and cooling are conducted in a short time, it is important to suppress the nucleation and the nuclear growth of the sigma phase.

[0014]

(d) The driving force for the nucleation of the sigma phase is increased with the increase of the content of Ni. Accordingly, when only the suppression of the production of the sigma phase is considered, Ni has only not to be contained. However, when Ni is not contained, the ratio between the ferrite phase and the austenite phase largely deviates from 1:1, and the toughness and the corrosion resistance are degraded. Accordingly, for the purpose of suppressing the production of the sigma phase while the degradation of the toughness and the degradation of the corrosion resistance are being prevented, Ni is required to be contained in an appropriate content depending on the contents of Cu and N. Specifically, by containing Ni so as to satisfy the relation of the following formula (2), the production of the sigma phase can be suppressed without degrading the toughness and the corrosion resistance:

$$\mathrm{Cr} + 11\mathrm{Mo} + 10\mathrm{Ni} < 12(\mathrm{Cu} + 30\mathrm{N}) \qquad (2)$$

wherein the symbols of elements in formula (2) respectively represent the contents (unit: mass%) of the elements in the steel.

[0015] The left hand side of formula (2) represents the driving force for the precipitation of the sigma phase; among the components constituting the duplex stainless steel, Cr, Mo and Ni are the elements to increase the driving force for the nucleation of the precipitation of the sigma phase; on the basis of various tests, it has been found that the degrees of contribution of Mo and Ni are 11 times and 10 times the degree of contribution of Cr, respectively.

[0016] On the other hand, the right hand side of formula (2) conversely represents the deterrent force against the precipitation of the sigma phase, and on the basis of various tests, it has been found that the degree of contribution of

N is 30 times the degree of contribution of Cu, and the deterrent force of Cu is 12 times the driving force of Cr.

[0017] The manifestation mechanism of the deterrent force against the precipitation of the sigma phase due to Cu and N is as follows. The presence of a Cu atom or an N atom in the vicinity of each of the Ni atoms present in the crystal lattice suppresses the decrease of the interface energy in the ferrite/austenite phase interface, which is the site of the nucleation of the sigma phase; thus, the decrease amount of the free energy at the time of the precipitation reaction of the sigma phase is made small, and hence the driving force for the crystal nucleation can be made small to be associated with the aforementioned manifestation mechanism. Additionally, Cu precipitates in the matrix as a Cu concentrated phase in an ultrafine manner, hence a large number of nucleation sites of the sigma phase are dispersed so as to compete against the ferrite/austenite phase interface which is the proper nucleation site, and consequently, there occurs an effect to retard the sigma phase production, otherwise fast in growth, in the ferrite/austenite phase boundary.

[0018]

(e) By containing an appropriate amount of Ni to satisfy the relation of the aforementioned formula (2), Cu atoms and N atoms can be located in the vicinities of the Ni atoms present in the crystal lattice. In this case, it is possible to suppress the decrease amount of the interface energy in the ferrite phase/austenite phase interface, which is the nucleation site of the sigma phase. Accordingly, it is possible to reduce the decrease amount of the free energy at the time of the precipitation reaction of the sigma phase, and it is possible to reduce the driving force for the nucleation of the sigma phase. Consequently, it is possible to suppress the production of the sigma phase.

[0019]

(f) The nuclear growth of the sigma phase can be suppressed by containing an appropriate amount of Cu. Specifically, the inclusion of an appropriate amount of Cu enables the precipitation of an ultrafine Cu concentrated phase in the matrix during large heat input welding. The Cu concentrated phase serves as the nucleation site of the sigma phase, and hence by precipitating a large number of Cu concentrated phases in a dispersed manner, the Cu concentrated phases can be made to compete against the ferrite phase/austenite phase interface, which is the proper nucleation site. Consequently, the growth of the sigma phase in the ferrite phase/austenite phase interface can be retarded.

[0020] The present invention has been perfected on the basis of the aforementioned findings, and the gist of the present invention resides in the following items (1) to (4) regarding duplex stainless steel.

[0021]

(1) A duplex stainless steel that has a chemical composition consisting, , by mass%, of C: 0.03% or less, Si: 0.2 to 1%, Mn: 5.0% or less, P: 0.040% or less, S: 0.010% or less, sol. Al: 0.040% or less, Ni: 4 to 8%, Cr: 20 to 28%, Mo: 0.5 to 2.0%, Cu: more than 2.0% and 4.0% or less and N: 0.1 to 0.35%, with the balance being Fe and impurities; wherein the duplex stainless steel satisfies the relations of the following formulas (1) and (2):

$$2.2\mathrm{Cr} + 7\mathrm{Mo} + 3\mathrm{Cu} > 66 \qquad (1)$$

$$\mathrm{Cr} + 11\mathrm{Mo} + 10\mathrm{Ni} < 12(\mathrm{Cu} + 30\mathrm{N}) \qquad (2)$$

wherein the symbols of elements in formulas (1) and (2) respectively represent the contents (unit: mass%) of the elements in the steel.

[0022]

(2) The duplex stainless steel according to the item (1) above, which further contains, by mass%, V: 1.5% or less, in place of part of Fe.

[0023]

(3) The duplex stainless steel according to the item (1) or (2) above, which further contains, by mass%, one or more selected from among Ca: 0.02% or less, Mg: 0.02% or less and B: 0.02% or less, in place of part of Fe.

[0024]

(4) The duplex stainless steel according to any one of the items (1) to (3) above, which further contains, by mass%, rare earth metal(s): 0.2% or less, in place of part of Fe.

[Advantageous Effects of Invention]

[0025] The duplex stainless steel according to the present invention is excellent in the weldability during large heat input welding and excellent in the stress corrosion cracking resistance in a chloride environment.

[Brief Description of Drawings]

[0026]

[Figure 1] Figure 1 is a view illustrating a plate material prepared by mechanical working, (a) being a plane view and (b) being a front view.
[Figure 2] Figure 2 is a view illustrating a weld joint, (a) being a plane view and (b) being a front view.
[Figure 3] Figure 3 is an oblique perspective view illustrating a specimen.
[Figure 4] Figure 4 is a graph showing the relations between the chemical compositions of the duplex stainless steels according to Examples, wherein the mark ○ represents the "determination of non-occurrence of stress corrosion cracking" and the mark × represents the "determination of occurrence of stress corrosion cracking."

[Description of Embodiments]

[0027] Hereinafter, the functional effect of the chemical composition of the duplex stainless steel according to the present invention is described, together with the reasons for limiting the contents in the chemical composition. In this connection, "%" related to the contents means "mass%."

C: 0.03% or less

[0028] C is an element effective in stabilizing the austenite phase. However, when the content of C exceeds 0.03%, carbides tend to precipitate, and the corrosion resistance is degraded. Accordingly, the content of C is set at 0.03% or less.

Si: 0.2 to 1%

[0029] Si is able to ensure the fluidity of the molten metal during welding, and hence is an element effective in preventing weld defects. For the purpose of obtaining this effect, Si is required to be contained in a content of 0.2% or more. On the other hand, when the content of Si exceeds 1%, intermetallic compounds (such as the sigma phase) tend to be produced. Accordingly, the content of Si is set at 0.2 to 1%. The content of Si is preferably 0.2 to 0.5%.

Mn: 5.0% or less

[0030] Mn is a component effective in improving the hot workability through the desulfurization and deoxidation effects during melting of the duplex stainless steel. Mn also has a function to increase the solubility of N. However, when the content of Mn exceeds 5.0%, the corrosion resistance is degraded. Accordingly, the content of Mn is set at 5.0% or less.

P: 0.040% or less

[0031] P is mixed in the steel as an impurity, and degrades the corrosion resistance and the toughness of the steel. Accordingly, the content of P is set at 0.040% or less.

S: 0.010% or less

[0032] S is mixed in the steel as an impurity, and degrades the hot workability of the steel. Sulfides offer the origins of the occurrence of pitting and degrade the pitting resistance of the steel. For the purpose of avoiding these adverse effects, the content of S is set at 0.010% or less. The content of S is preferably 0.007% or less.

sol. Al: 0.040% or less

[0033] Al is a component effective as a deoxidizer of the steel. On the other hand, when the content of N in the steel is large, Al precipitates as AlN (aluminum nitride), and degrades the toughness and the corrosion resistance of the steel. Accordingly, the content of Al is set at 0.040% or less. The content of Al as referred to in the present invention means the content of acid-soluble Al (what is called sol. Al). Al is used as a deoxidizer in the duplex stainless steel according to the present invention, because the content of Si as a component effective deoxidizer is suppressed , and hence. However, when the duplex stainless steel is produced by vacuum melting, it is not necessary to contain Al.

Ni: 4 to 8%

[0034] Ni is a component effective in stabilizing austenite. When the content of Ni exceeds 8%, the resultant decrease of the amount of ferrite makes it difficult to ensure the fundamental properties of the duplex stainless steel and also facilitates the production of intermetallic compounds (such as the sigma phase). On the other hand, when the content of Ni is less than 4%, the amount of ferrite comes to be too large and thus the features of the duplex stainless steel are lost. The solubility of N in ferrite is small, and hence due to the amount of ferrite becoming too large, nitrides precipitate and the corrosion resistance is degraded. Accordingly, the content of Ni is set at 4 to 8%.

Cr: 20 to 28%

[0035] Cr is a component effective in maintaining the corrosion resistance. For the purpose of obtaining the SCC resistance in a chloride environment, Cr is required to be contained in a content of 20% or more. On the other hand, when the content of Cr exceeds 28%, the precipitation of intermetallic compounds (such as the sigma phase) comes to be remarkable, and the degradation of the hot workability and the degradation of the weldability are caused. Accordingly, the content of Cr is set at 20 to 28%.

Mo: 0.5 to 2.0%

[0036] Mo is an element extremely effective in improving the SCC resistance. For the purpose of obtaining this effect, Mo is required to be contained in a content of 0.5% or more. On the other hand, when the content of Mo exceeds 2.0%, the precipitation of intermetallic compounds is remarkably accelerated during large heat input welding, and the degradation of the hot workability and the degradation of the weldability are caused. Accordingly, the content of Mo is set at 0.5 to 2.0%. The content of Mo is preferably 0.7 to 1.8% and more preferably 0.8 to 1.5%.

Cu: more than 2.0% and 4.0% or less

[0037] Cu is a component effective in strengthening the passivation film mainly composed of Cr in a chloride environment containing corrosive acidic gasses (such as carbon dioxide gas and hydrogen sulfide gas). Additionally, Cu precipitates in the matrix in an ultrafine manner during large heat input welding to become nucleation sites of intermetallic compounds (the sigma phase) so as to compete against the ferrite/austenite phase interface which is the proper nucleation site. Consequently, there occurs retardation of the sigma phase production, otherwise fast in growth, in the ferrite/austenite phase interface. For the purpose of obtaining these effects, Cu is required to be contained in a content exceeding 2.0%. On the other hand, when Cu is contained in a content exceeding 4.0%, the hot workability of the steel is impaired. Accordingly, the content of Cu is set to be more than 2.0% and 4.0% or less.

N: 0.1 to 0.35%

[0038] N is a powerful austenite former, and is effective in improving the thermal stability and the corrosion resistance of the duplex stainless steel. The duplex stainless steel according to the present invention contains Cr and Mo, which are ferrite formers, in large amounts, and hence N is required to be contained in a content of 0.1% or more for the purpose of establishing an appropriate balance between ferrite and austenite. On the other hand, when the content of N exceeds 0.35%, the toughness and the corrosion resistance of the steel are degraded due to the occurrence of blow holes as weld defects, the nitride production caused by the thermal effects during welding or the like. Accordingly, the content of N is set at 0.1 to 0.35%.

[0039] In addition to the aforementioned chemical composition, Cr, Mo, Ni, Cu and N are required to satisfy the following formulas (1) and (2):

$$2.2Cr + 7Mo + 3Cu > 66 \qquad (1)$$

$$Cr + 11Mo + 10Ni < 12(Cu + 30N) \qquad (2)$$

wherein the symbols of elements in formulas (1) and (2) respectively represent the contents (unit: mass%) of the elements in the steel.

[0040] In the duplex stainless steel according to the present invention, the contents of Cr and Mo are regulated for the purpose of suppressing the precipitation of the intermetallic compounds. Accordingly, for the purpose of strengthening the passivation film mainly composed of Cr, Cu is required to be contained in an appropriate amount in addition to Mo. In this connection, when the value of "2.2Cr + 7Mo + 3Cu" is 66 or less, a sufficient resistance against the stress corrosion cracking (SCC) in a chloride environment cannot be ensured as the case may be. Accordingly, the requirement of the above presented formula (1) is specified.

[0041] When the value of "Cr + 11Mo + 10Ni" is equal to or larger than the value of "12(Cu + 30N)," the production of the intermetallic compounds in the ferrite/austenite phase boundary during large heat input welding cannot be sufficiently suppressed as the case maybe. In consideration of this point, the requirement of the above presented formula (2) is specified.

[0042] The duplex stainless steel according to the present invention has the aforementioned chemical composition, and the balance is composed of Fe and impurities. The impurities as referred to herein mean the components which are mixed due to various factors in the production process including raw materials such as ores and scraps when the duplex stainless steel is industrially produced, and are tolerated within the range not adversely affecting the present invention.

[0043] The duplex stainless steel according to the present invention may contain, in addition to the aforementioned elements, one or more of the elements selected from at least one group of the following first to third groups.

[0044]

First group: V: 1.5% or less
Second group: Ca, Mg, B: 0.02% or less
Third group: rare earth metal (REM): 0.2% or less

Hereinafter, these optional elements are described in detail.

First group: V: 1.5% or less

[0045] V may be contained if necessary. V is effective in improving the corrosion resistance (in particular, the corrosion resistance in an acidic environment) of the duplex stainless steel. More specifically, by containing V in combination with Mo and Cu, the crevice corrosion resistance can be improved. However, when the content of V exceeds 1.5%, there is an adverse possibility that the amount of ferrite is excessively increased, and the toughness and the corrosion resistance are degraded; accordingly, the content of V is set at 1.5% or less. For the purpose of stably displaying the improvement effect due to V of the corrosion resistance of the duplex stainless steel, it is preferable to contain V in a content of 0.05% or more.

Second group: One or more selected from among Ca: 0.02% or less, Mg: 0.02% or less and B: 0.02% or less

[0046] One or more selected from among Ca, Mg and B may be contained if necessary. Each of Ca, Mg and B has an effect to fix S (sulfur) and O (oxygen) to improve the hot workability. In the duplex stainless steel according to the present invention, the content of S is regulated so as to be low, and hence the hot workability can be satisfactory even when Ca, Mg or B is not contained. However, in the case where further hot workability is demanded under severe working conditions such as the case of the production of seamless pipes based on a skew rolling method, it is possible to further improve the hot workability of the duplex stainless steel by containing one or more selected from among Ca, Mg and B. On the other hand, when the content of each of these elements exceeds 0.02%, there is an adverse possibility that the amount of nonmetallic inclusions (such as the oxides and sulfides of Ca, Mg or B) is increased and such inclusions offer the origins of pitting and the degradation of the corrosion resistance occurs. Accordingly, when these elements are contained, the content of each of these elements is set at 0.02% or less. When two selected from among Ca, Mg and B are contained, the upper limit of the total content is 0.04%; and when three of Ca, Mg and B are contained, the upper limit of the total content is 0.06%. For the purpose of stably displaying the improvement effect of the hot workability due to Ca, Mg or B, it is preferable to contain Ca, Mg and B each alone or in total, in a content of "S(mass%) + (1/2)·O (mass%)" or more.

Third group: rare earth metal (REM): 0.2% or less

[0047] REM may be contained if necessary. Similarly to Ca, Mg and B, a rare earth metal also has an effect to fix S or O to enable further improvement of the hot workability of the duplex stainless steel. On the other hand, when the content of the rare earth metal exceeds 0.2%, there is an adverse possibility that the amount of nonmetallic inclusions (such as the oxides and sulfides of the rare earth metal) is increased and such inclusions offer the origins of pitting and the degradation of the corrosion resistance occurs. Accordingly, when the rare earth metal is contained, the content of the rare earth metal is set at 0.2% or less. For the purpose of stably displaying the improvement effect of the hot workability due to REM, it is preferable to contain REM in a content of "S(mass%) + (1/2)·O(mass%)" or more.

[0048] REM as referred to herein is a generic name of the 17 elements consisting of the 15 lanthanoid elements and Y and Sc, and one or more of these elements may be contained. The content of REM means the total content of such elements.

[0049] The duplex stainless steel according to the present invention can be produced by the production equipment and the production method used for the usual commercial production. For example, for the melting of the duplex stainless steel, there can be used an electric furnace, an $Ar\text{-}O_2$ mixed gas bottom blowing decarburization furnace (AOD furnace), a vacuum decarburization furnace (VOD furnace) or the like. The molten steel obtained by melting may be cast into ingots, or may be cast into rod-like billets or the like by a continuous casting method.

[Examples]

[0050] The duplex stainless steels (Present Inventions: Test Nos. 1 to 11, the Comparative: Test Nos. 12 to 25) having the chemical compositions shown in below-presented Table 1 were melted by using a vacuum furnace of 150 kg in capacity, and cast into ingots. Next, each of the ingots was heated to 1250˚C, and forged into a 40-mm thick plate material. Subsequently, each of the plate materials was again heated to 1250˚C, and rolled so as to have a thickness of 15 mm by hot rolling (the working temperature: 1050˚C or higher); then each of the plate materials after rolling was subjected to a solid solution heat treatment (a treatment of water cooling after being maintained in a soaked manner at 1070˚C for 30 minutes) to prepare a test steel plate.

[0051] [Table 1]

Table 1

		Chemical composition (mass%, the balance: Fe and impurities)															
	Test No.	C	Si	Mn	P	S	Ni	sol-Al	N	Cr	Mo	Cu	V	Ca	Mg	B	REM
Inventions	1	0.015	0.50	1.51	0.010	0.0008	4.21	0.020	0.152	20.3	1.98	3.41	-	-	-	-	-
	2	0.015	0.50	1.50	0.015	0.0010	5.50	0.020	0.211	22.1	1.95	2.92	0.15	-	-	-	-
	3	0.015	0.50	1.48	0.014	0.0007	4.51	0.020	0.181	23.2	1.97	2.08	0.07	-	-	-	-
	4	0.015	0.50	1.55	0.014	0.0008	5.09	0.020	0.156	22.9	1.05	3.15	-	-	-	-	-
	5	0.015	0.50	1.52	0.016	0.0011	4.08	0.020	0.192	23.9	1.96	2.20	0.06	0.0015	-	-	-
	6	0.021	0.42	1.53	0.017	0.0005	5.19	0.022	0.210	24.1	1.55	2.12	-	-	-	-	-
	7	0.017	0.51	1.52	0.012	0.0004	7.82	0.013	0.305	25.2	1.02	2.51	-	-	0.0200	-	-
	8	0.017	0.51	1.03	0.011	0.0008	5.19	0.013	0.215	24.9	1.02	3.24	-	-	-	0.0005	-
	9	0.015	0.50	1.03	0.014	0.0006	5.22	0.014	0.228	26.0	0.51	2.07	-	-	-	-	0.0012
	10	0.016	0.50	1.03	0.015	0.0009	5.22	0.014	0.202	27.1	0.50	2.15	0.08	-	-	0.0008	-
	11	0.016	0.50	1.02	0.013	0.0007	5.18	0.012	0.223	27.0	0.52	3.20	0.01	-	-	-	0.0010
Comparative	12	0.016	0.49	1.52	0.011	0.0008	5.21	0.012	0.232	18.1*	1.94	3.22	-	-	-	-	-
	13	0.016	0.50	1.55	0.015	0.0005	5.22	0.008	0.085*	20.2	1.99	2.05	-	-	-	-	-
	14	0.015	0.49	4.90	0.014	0.0005	4.04	0.019	0.224	20.1	1.03	3.10	-	-	-	-	-
	15	0.016	0.46	7.11*	0.014	0.0008	2.01*	0.023	0.208	22.2	0.95	2.89	-	-	-	-	-
	16	0.015	0.48	5.08*	0.015	0.0009	3.52*	0.023	0.262	23.2	0.52	3.11	-	-	-	-	-
	17	0.036*	0.68	4.94	0.012	0.0004	1.49*	0.027	0.238	24.0	0.96	2.10	-	-	-	-	-
	18	0.015	0.48	1.02	0.011	0.0001	5.08	0.028	0.231	24.2	0.52	1.90*	-	-	-	-	-
	19	0.015	0.50	1.03	0.011	0.0005	5.02	0.032	0.302	25.1	1.05	1.15*	-	-	-	-	-
	20	0.015	0.43	0.98	0.011	0.0003	5.06	0.019	0.148	25.1	0.51	2.10	-	-	-	-	-
	21	0.015	0.49	1.03	0.016	0.0006	5.08	0.020	0.185	24.8	2.11*	1.21*	-	-	-	-	-
	22	0.016	0.50	1.01	0.013	0.0005	5.56	0.019	0.182	25.1	0.11*	2.10	-	-	-	-	-
	23	0.015	0.50	1.02	0.012	0.0008	6.10	0.015	0.182	26.2	0.02*	2.12	-	-	-	-	-
	24	0.011	0.48	1.54	0.012	0.0009	5.12	0.020	0.155	26.7	1.04	1.55*	-	-	-	-	-
	25	0.014	0.49	1.56	0.015	0.0008	4.98	0.015	0.164	26.8	0.02*	2.10	-	-	-	-	-

* shows out of scope of the invention.

[0052] For the purpose of evaluating the weldability of each of these test steel plates, first prepared were plate materials of 12 mm in thickness, 100 mm in width and 200 mm in length, each having on a long side a V-type groove of a groove angle of 30 degrees. Figure 1 shows a plate material 10 which is prepared by mechanical working. In Figure 1, (a) is a plan view and (b) is a front view.

[0053] Next, as shown in Figure 2, for each of the test steels, two pieces of the plate material 10 having a shape shown in Figure 1 were prepared and arranged so as for the groove faces to butt each other; then, a weld joint 20 was prepared by performing multilayer welding based on tungsten inert gas (TIG) welding from the one side of each of the plate materials. Figure 2(a) is a plan view and Figure 2(b) is a front view of the weld joint 20. As the welding material 30 of each of the weld joints 20, a welding material of 2 mm in outer diameter prepared from the Test No. 1 in Table 1 was used commonly for all the test steels. The welding was performed under the condition of the heat input amount of 30 kJ/cm, which was particularly highly efficient for a common welding working of stainless steel.

[0054] Next, a specimen was sampled from the back side (the first layer side of the weld bead) of each of the weld joints 20 obtained as described above. Specifically, under the conditions that the penetration bead and the scales during welding were allowed to remain, a specimen of 2 mm in thickness, 10 mm in width and 75 mm in length was sampled. Figure 2 shows the region to be sampled as a specimen with a dotted line.

[0055] Figure 3 shows an oblique perspective view of a sampled specimen 40. In the specimen 40 shown in Figure 3, the upper surface is the rolled surface (the lower surface of the weld joint in Figurer 2). As shown in Figure 3, the longitudinal direction of the specimen 40 is a direction perpendicular to the weld line. Each of the specimens 40 was sampled in such a way that one of the two boundary lines between the welding material 30 and the plate material 10, on the surface (the rolled surface) of the concerned specimen 40, was to be located in the center of the surface of the concerned specimen 40.

[0056] By using each of the obtained specimens, a four-point bending test was performed. In the four-point bending test, a stress corresponding to the yield stress of the specimen was applied to the specimen in a NaCl aqueous solution (150˚C) having a concentration of 25 mass% into which CO_2 at 3 MPa had been injected under pressure. The test time of the four-point bending test was 720 hours.

[0057] After the four-point bending test, for each of the specimens, the occurrence/nonoccurrence of the stress corrosion cracking was examined by visually observing the exterior appearance and also by the observation (magnification of field of vision: 500 times) with an optical microscope in the cross-sectional direction (the direction perpendicular to the upper surface of the specimen in Figure 3). The results of the observation are shown in Table 2. In Table 2, the cases where no stress corrosion cracking occurred are marked with "○" and the cases where the stress corrosion cracking occurred are marked with "×."

[0058] [Table 2]

Table 2

	Test No.	2.2Cr+7Mo+3Cu	Stress corrosion cracking	(Cr+11Mo+10Ni)-12(Cu+30N)	Precipitation of the sigma phase
Inventions	1	68.75	○	-11.46	○
	2	71.03	○	-12.45	○
	3	71.07	○	-0.15	○
	4	67.18	○	-8.61	○
	5	72.9	○	-9.26	○
	6	70.23	○	-7.99	○
	7	70.11	○	-25.3	○
	8	71.64	○	-28.26	○
	9	66.98	○	-23.11	○
	10	69.57	○	-13.72	○
	11	72.64	○	-34.16	○
Comparative	12	63.06*	×	-30.62	○
	13	64.52*	×	39.09*	×
	14	60.73*	×	-46.01	○
	15	64.16*	×	-56.81	○
	16	64.01*	×	-67.52	○
	17	65.82*	×	-61.42	○
	18	62.58*	×	-25.24	○
	19	66.02	×	-35.67	○
	20	65.09*	×	2.83*	×
	21	72.96	×	17.69*	×
	22	62.29*	×	-8.81	○
	23	64.14*	×	-3.54	○
	24	70.67	×	14.94*	×
	25	65.4*	×	-7.42	○

* shows out of scope of the invention.

[0059] In each of the weld joints (see Figure 2), the cross-section perpendicular to the weld line and the rolled surface was mirror polished and etched, and then an image analysis of the cross-section was performed by using an optical microscope with a magnification of field of vision of 500 times. Thus, the area fraction of a trace amount of the sigma phase in HAZ (weld heat affected zone) was measured, and the case where the area fraction of the sigma phase is 1% or more was determined that the precipitation of the sigma phase occurred. The determination results are shown in Table 2. In Table 2, the cases determined that no precipitation of the sigma phase occurred are marked with "○" and the cases determined that the precipitation of the sigma phase occurred are marked with "×."

[0060] Figure 4 is a graph showing the relation between "7Mo (mass%) + 3Cu (mass%)" and "Cr (mass%)" for the duplex stainless steels of Test Nos. 1, 4, 6, 13 and 20. In this connection, as shown in Table 2, no stress corrosion cracking occurred in the specimens prepared from the duplex stainless steels of Test Nos. 1, 4 and 6, whereas the stress corrosion cracking occurred in the specimens prepared from the duplex stainless steels of Test Nos. 13 and 20. Accordingly, as shown in Figure 4, when a border line is drawn between the "7Mo (mass%) + 3Cu (mass%)" values of the duplex stainless steels of Test Nos. 1, 4 and 6 and the "7Mo (mass%) + 3Cu (mass%)" values of the duplex stainless steels of Test Nos. 13 and 20, the border line is represented by the following formula (3):

$$7\mathrm{Mo}\ (\mathrm{mass\%}) + 3\mathrm{Cu}\ (\mathrm{mass\%}) = -2.2\mathrm{Cr}\ (\mathrm{mass\%}) + 66 \qquad (3)$$

[0061] From the relation shown in Figure 4, it can be seen that in the case where the " 7Mo + 3Cu" value is larger than the "-2.2Cr + 66" value, namely, the case where the duplex stainless steel satisfies the relation of the aforementioned formula (1), it is possible to prevent the occurrence of the stress corrosion cracking. In other words, as shown in Tables 1 and 2, no stress corrosion cracking occurred in the specimens prepared from the duplex stainless steels of Test Nos. 1 to 11 in which the requirements for the chemical composition specified in the present invention and the aforementioned relation of formula (1) were satisfied. On the other hand, the stress corrosion cracking occurred in the specimens prepared from the duplex stainless steels of Test Nos. 12 to 18, 20, 22, 23 and 25. The stress corrosion cracking occurred in these duplex stainless steels of Test Nos. 19, 21 and 24 probably because the duplex stainless steels of Test Nos. 19, 21 and 24 satisfied the relation of formula (1), but the contents of Cu (see Table 1) in these duplex stainless steels did not satisfy the requirement of the present invention.

[0062] Also, as shown in Table 2, no trace amount of the sigma phase precipitated in the HAZ in the weld joints prepared from the duplex stainless steels of Test Nos. 1 to 12, 14 to 19, 22, 23 and 25 satisfying the aforementioned relation of formula (2). On the other hand, a trace amount of the sigma phase precipitated in each of the weld joints prepared from the duplex stainless steels of Test Nos. 13, 20, 21 and 24 not satisfying the relation of formula (2).

[0063] As can be seen clearly from the above-described results, the duplex stainless steels satisfying the requirements of the present invention can suppress the precipitation of the intermetallic compounds during large heat input welding, and each have an excellent stress corrosion cracking resistance in chloride environments.

[Industrial Applicability]

[0064] The duplex stainless steels according to the present invention are excellent in weldability during large heat input welding and excellent in the stress corrosion cracking resistance in chloride environments.

[Reference Signs List]

[0065]

10:	Plate material
20:	Weld joint
30:	Welding material
40:	Specimen

Claims

1. A duplex stainless steel that has a chemical composition consisting, by mass%, of C: 0.03% or less, Si: 0.2 to 1%, Mn: 5.0% or less, P: 0.040% or less, S: 0.010% or less, sol. Al: 0.040% or less, Ni: 4 to 8%, Cr: 20 to 28%, Mo: 0.5 to 2.0%, Cu: more than 2.0% and 4.0% or less and N: 0.1 to 0.35%, with the balance being Fe and impurities;

wherein the duplex stainless steel satisfies the relations of the following formulas (1) and (2):

$$2.2\mathrm{Cr} + 7\mathrm{Mo} + 3\mathrm{Cu} > 66 \qquad (1)$$

$$\mathrm{Cr} + 11\mathrm{Mo} + 10\mathrm{Ni} < 12(\mathrm{Cu} + 30\mathrm{N}) \qquad (2)$$

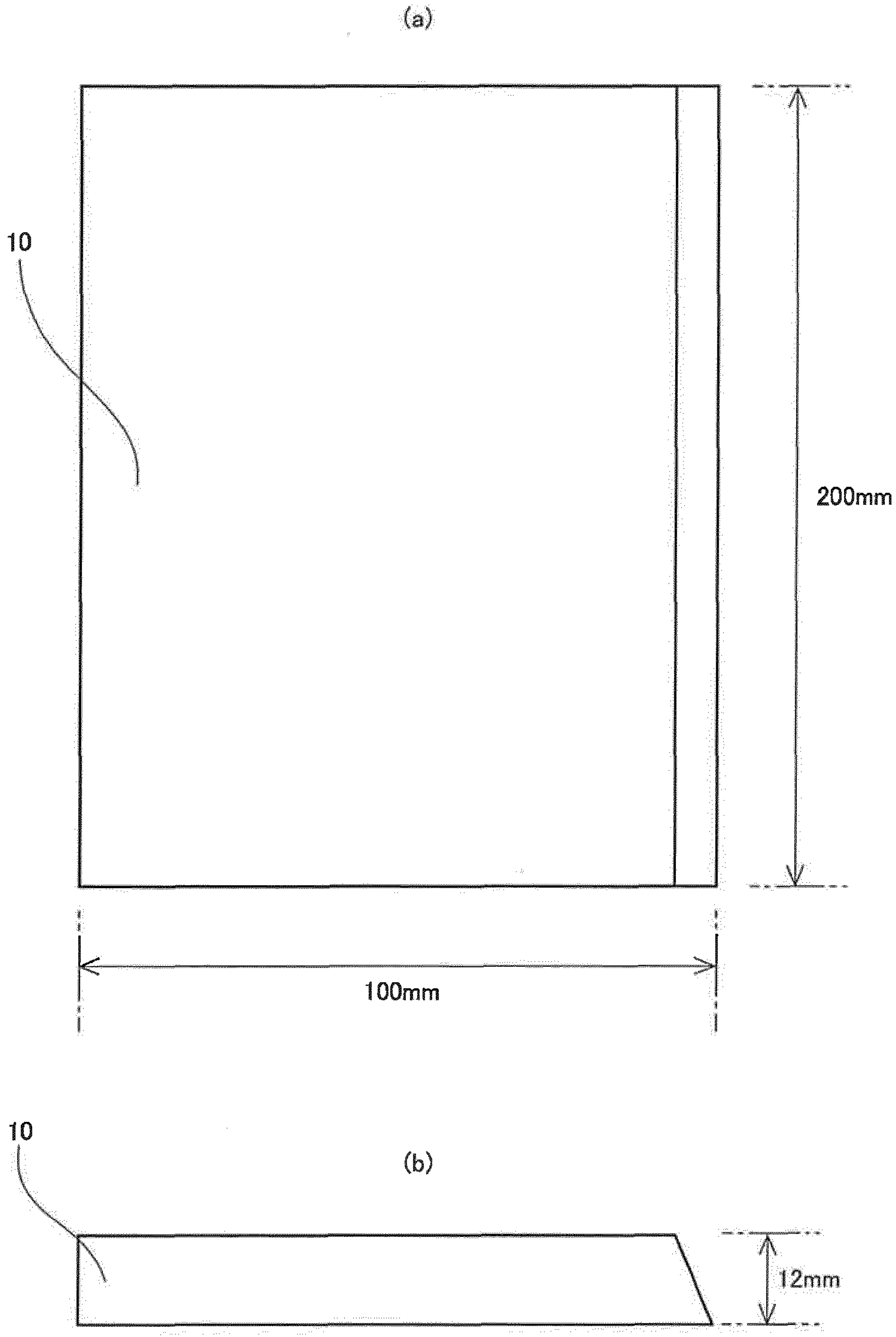
wherein the symbols of elements in formulas (1) and (2) respectively represent the contents (unit: mass%) of the elements in the steel.

2. The duplex stainless steel according to Claim 1, which further contains, by mass%, V: 1.5% or less, in place of part of Fe.

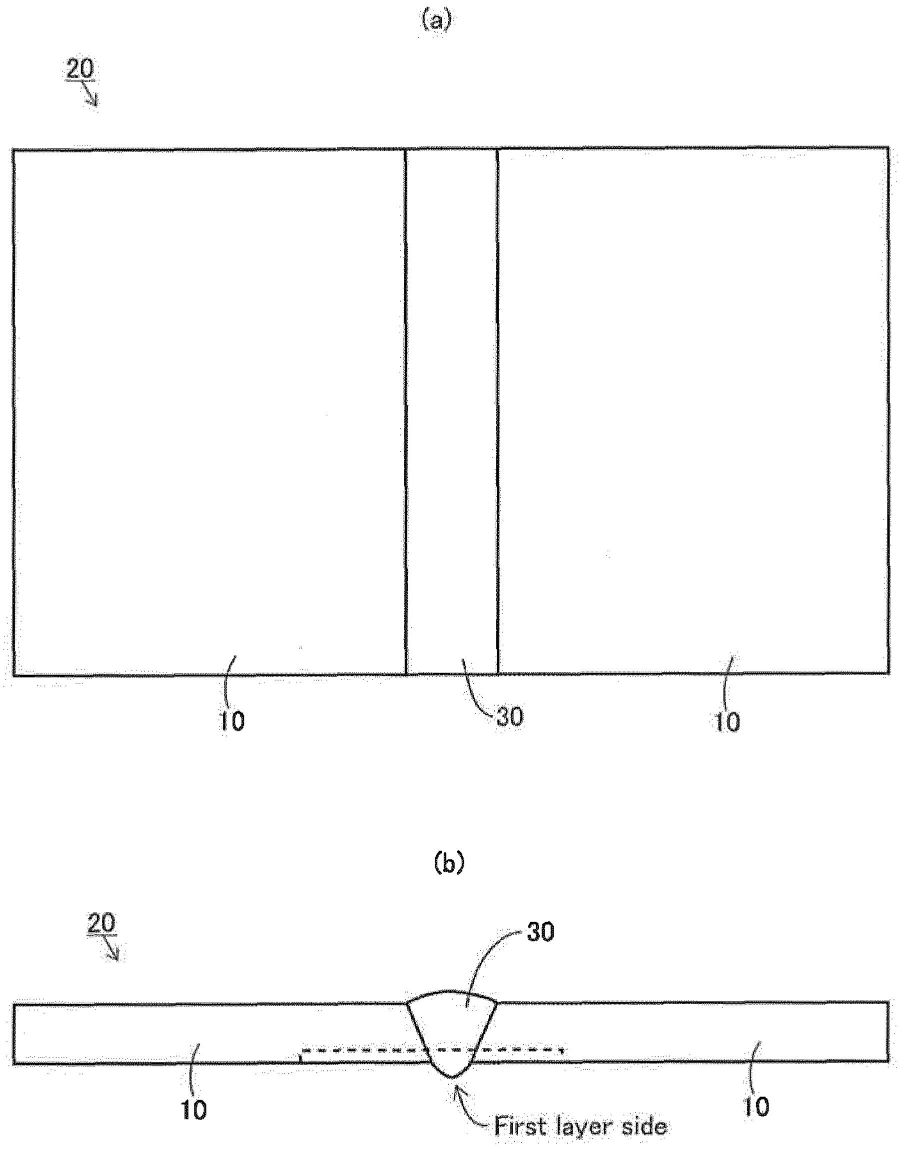
3. The duplex stainless steel according to Claim 1 or 2, which further contains, by mass%, one or more selected from among Ca: 0.02% or less, Mg: 0.02% or less and B: 0.02% or less, in place of part of Fe.

4. The duplex stainless steel according to any one of Claims 1 to 3, which further contains, by mass%, rare earth metal (s): 0.2% or less, in place of part of Fe.

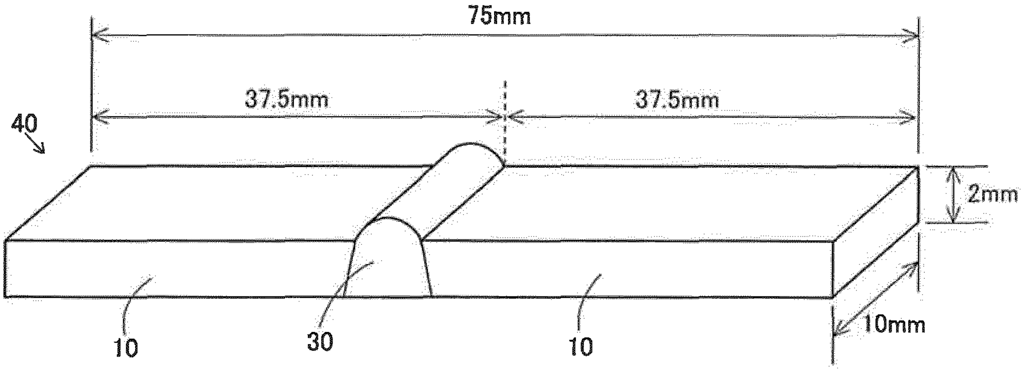
[Fig.1]



[Fig.2]



[Fig.3]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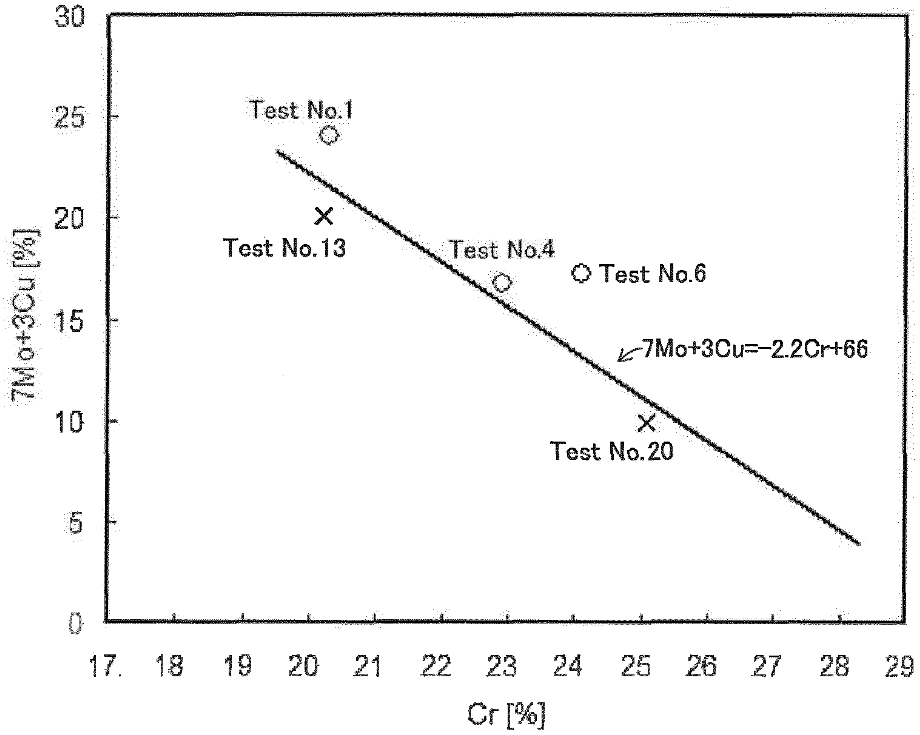
37.5mm
40
2mm
10
30
10
10mm

[Fig.4]


30
25
20
15
10
5
0
7Mo+3Cu [%]
17.
18
19
20
21
22
23
24
25
26
27
28
29
Cr [%]
Test No.1
Test No.13
Test No.4
Test No.6
7Mo+3Cu=-2.2Cr+66
Test No.20

INTERNATIONAL SEARCH REPORT	International application No. PCT/JP2010/064953

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	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2009-91636 A (Nippon Steel & Sumikin Stainless Steel Corp.), 30 April 2009 (30.04.2009), & EP 2199421 A & WO 2009/048137 A1 & KR 10-2010-0059956 A & CN 101815803 A	1-4
A	JP 2004-277767 A (Nisshin Steel Co., Ltd.), 07 October 2004 (07.10.2004), (Family: none)	1-4
A	JP 10-60598 A (NKK Corp.), 03 March 1998 (03.03.1998), (Family: none)	1-4

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

* Special categories of cited documents:

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"&"	document member of the same patent family

Date of the actual completion of the international search 27 October, 2010 (27.10.10)	Date of mailing of the international search report 09 November, 2010 (09.11.10)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 9618751 A **[0004]**
- JP 2003171743 A **[0004]**