US 20130129560A1

(19) United States

(12) Patent Application Publication

Matsuhashi et al.

(10) Pub. No.: US 2013/0129560 A1

(43) Pub. Date: May 23, 2013

(54) **FERRITIC STAINLESS STEEL**

(76) Inventors: **Tooru Matsuhashi**, Shunan-shi (JP); **Michio Nakata**, Hikari-shi (JP)

(21) Appl. No.: **13/813,511**

(22) PCT Filed: **Aug. 4, 2011**

(86) PCT No.: **PCT/JP2011/067850**

§ 371 (c)(1), (2), (4) Date: **Jan. 31, 2013**

(30) **Foreign Application Priority Data**

Aug. 6, 2010 (JP) 2010-177998

Publication Classification

(51) **Int. Cl.**

C22C 38/54	(2006.01)
C22C 38/48	(2006.01)
C22C 38/46	(2006.01)
C22C 38/44	(2006.01)
C22C 38/00	(2006.01)
C22C 38/32	(2006.01)
C22C 38/28	(2006.01)
C22C 38/26	(2006.01)
C22C 38/22	(2006.01)
C22C 38/02	(2006.01)
C22C 38/50	(2006.01)
C22C 38/42	(2006.01)

(52) **U.S. Cl.**

CPC ***C22C 38/54*** (2013.01); ***C22C 38/50*** (2013.01); ***C22C 38/48*** (2013.01); ***C22C 38/46*** (2013.01); ***C22C 38/44*** (2013.01); ***C22C 38/42*** (2013.01); ***C22C 38/32*** (2013.01); ***C22C 38/28*** (2013.01); ***C22C 38/26*** (2013.01); ***C22C 38/22*** (2013.01); ***C22C 38/02*** (2013.01); ***C22C 38/001*** (2013.01)

USPC **420/41**

(57) **ABSTRACT**

A ferritic stainless steel that generates only a small amount of black spots in weld zone, the steel containing, in mass %, 0.020% or less of C, 0.025% or less of N, 1.0% or less of Si, 1.0% or less of Mn, 0.035% or less of P, 0.01% or less of S, 16.0 to 25.0% of Cr, 0.12% or less of Al, 0.05 to 0.35% of Ti, and 0.0015% or less of Ca, and the balance consisting of Fe and unavoidable impurities, wherein the following formula 1 is satisfied.

$$BI=3Al+Ti+0.5Si+200Ca \leqq 0.8 \qquad (1)$$

where Al, Ti, Si, and Ca in the formula 1 each denotes an amount of each element in mass % of the steel.

FIG. 1A

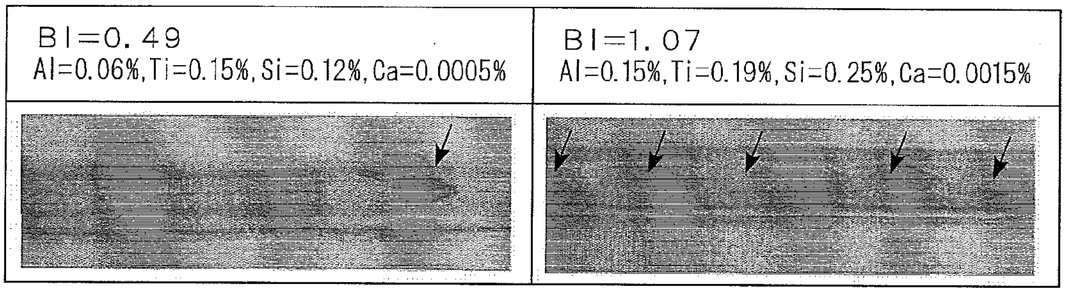

BI=0. 49
Al=0.06%,Ti=0.15%,Si=0.12%,Ca=0.0005%
BI=1. 07
Al=0.15%,Ti=0.19%,Si=0.25%,Ca=0.0015%

FIG. 1B

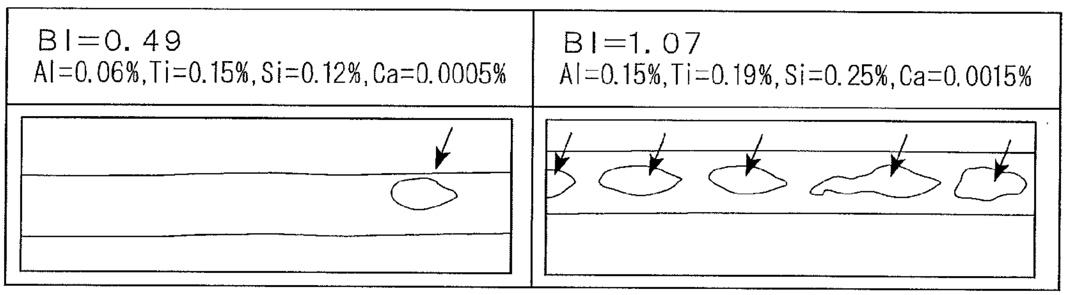

BI=0. 49
Al=0.06%,Ti=0.15%,Si=0.12%,Ca=0.0005%
BI=1. 07
Al=0.15%,Ti=0.19%,Si=0.25%,Ca=0.0015%

FIG. 2A

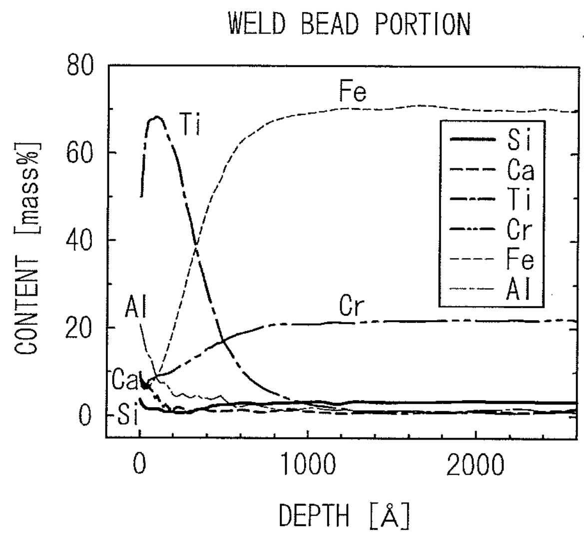

WELD BEAD PORTION
CONTENT [mass%]
DEPTH [Å]
80
60
40
20
0
0
1000
2000
Fe
Ti
Cr
Al
Ca
Si
Si
Ca
Ti
Cr
Fe
Al

FIG. 2B

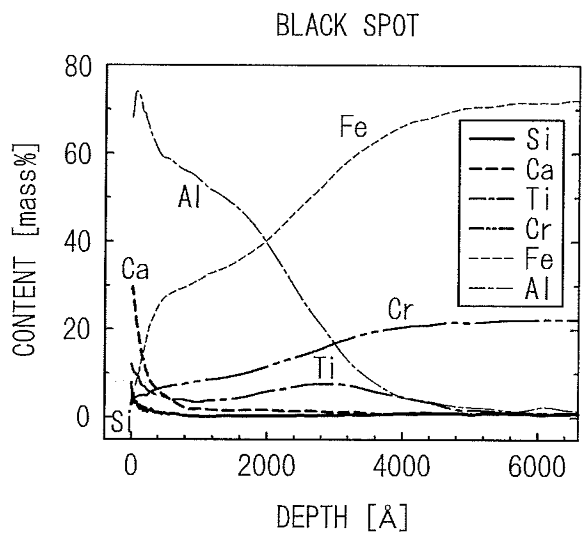

BLACK SPOT
CONTENT [mass%]
DEPTH [Å]
80
60
40
20
0
0
2000
4000
6000
Fe
Al
Ca
Cr
Ti
Si
Si
Ca
Ti
Cr
Fe
Al

FIG. 3

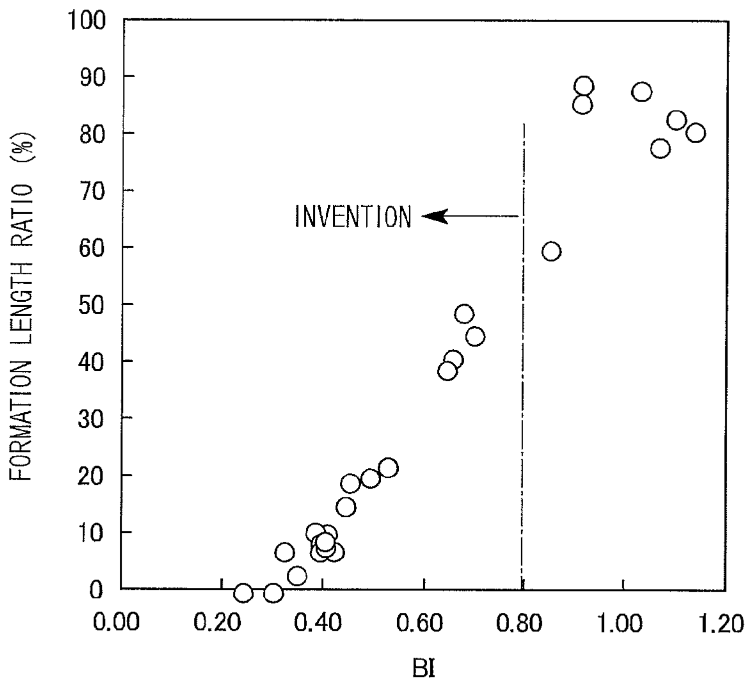
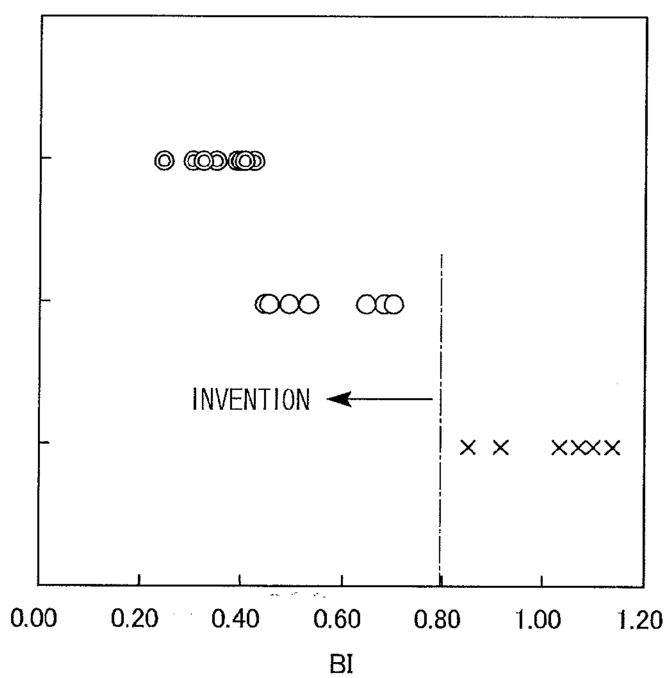

100
90
80
70
60
50
40
30
20
10
0
FORMATION LENGTH RATIO (%)
INVENTION
0.00
0.20
0.40
0.60
0.80
1.00
1.20
BI

FIG. 4


INVENTION
0.00
0.20
0.40
0.60
0.80
1.00
1.20
BI

FERRITIC STAINLESS STEEL

TECHNICAL FIELD

[0001] The present invention relates to a ferritic stainless steel that generates only a small amount of black spots in the TIG weld zone.

[0002] Priority is claimed on Japanese Patent Application No. 2010-177998 filed on Aug. 6, 2010, the content of which is incorporated herein by reference.

BACKGROUND ART

[0003] Ferritic stainless steel generally has properties such as a small expansion coefficient relative to the austenitic stainless steel and excellent resistance to stress corrosion cracking in addition to excellent corrosion resistance. Therefore, the ferritic stainless steel is widely used in tableware, kitchen equipment, building exterior materials such as roof materials, water or hot water container materials or the like. Further, there is increasing demand for replacement of austenitic stainless steel due to recent increasing price of nickel raw material, and the uses of ferritic stainless steel have expanded.

[0004] Welding is an inevitable process in forming the above-described structure of stainless steel. Originally, ferritic stainless steel included a problem of sensitization in weld zone resulting in reduction of corrosion resistance due to the small solid-solubility limit of C and N. In order to solve the above-described problem, there has been proposed and widely practicalized a method of suppressing the sensitization of a weld metal zone by reduction of C and N contents, or by fixing of C and N by addition of stabilizing elements such as Ti and Nb, or the like (for example, see Patent Reference 1).

[0005] The following have been known with regards to the corrosion resistance of weld zone in the ferritic stainless steel. Corrosion resistance is deteriorated in the scale portion generated by heat input during the welding, and therefore, it is important to perform sufficient shielding with an inert gas compared to the austenitic stainless steel. Patent Reference 2 discloses a technique of adding Ti and Al such that the formula, $P1=5Ti+20(Al-0.01)\geqq 5$ (wherein Ti and Al in the formula denote amounts of respective elements in the steel) is satisfied, thereby forming an Al oxide film on the surface portion of the steel during welding to improve corrosion resistance of the weld-heat affected zone.

[0006] Patent Reference 3 discloses a technique of improving crevice corrosion resistance of the weld zone by adding a certain amount or more of Si in addition to combined addition of Al and Ti.

[0007] Patent Reference 4 discloses a technique to improve the corrosion resistance of a weld zone by satisfying $4Al+Ti\leqq 0.32$ (wherein each of Ti and Al denotes amount of each component in the steel), thereby reducing heat input during the welding and suppressing generation of scale in the weld zone, and improving corrosion resistance of the weld zone.

[0008] The above-described prior arts have objects of improving corrosion resistance of the weld zone and weld heat affected zone.

[0009] In another method, there is a technique to improve the weather resistance and crevice corrosion resistance of not the weld zone but the material itself by intentionally adding P and appropriate amounts of Ca and Al (for example, see Patent Reference 5). In Patent Reference 5, Ca and Al are added to control the shapes and distribution of non-metallic inclusions in the steel. The most important feature of Patent Reference 5 is the addition of P in excess of 0.04%, and Patent Reference 5 describes nothing about an effect during welding.

PRIOR ART REFERENCE

Patent Reference

[0010] Patent Reference 1: Japanese Examined Patent Application, Second Publication No. S55-21102.

[0011] Patent Reference 2: Japanese Unexamined Patent Application, First Publication No. 1105-70899.

[0012] Patent Reference 3: Japanese Unexamined Patent Application, First Publication No. 2006-241564.

[0013] Patent Reference 4: Japanese Unexamined Patent Application, First Publication No. 2007-270290.

[0014] Patent Reference 5: Japanese Unexamined Patent Application, First Publication No. H07-34205.

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0015] In the conventional ferritic stainless steel, dark spots (so called black spots or slag spots) occasionally occurred on the surfaces of back beads after the welding even though shielding conditions in the weld zone were controlled appropriately. Elements such as Al, Ti, Si, Ca have a strong affinity to oxygen. Black spots are oxides of these elements that are solidified on the surface of the weld metal during the solidification process of the weld metal formed by Tungsten Inert Gas (TIG) welding. Weld conditions, especially the conditions of shielding with the inert gas have a strong influence on the generation of the black spots. Many black spots occur where the shielding is insufficient.

[0016] Since the black spot itself is an oxide, there is no problem in corrosion resistance and workability of the weld zone even when the weld zone is dotted with a small amount of black spots. However, where the black spots are generated in a large amount or generated in a continuously linked manner, the appearance of the weld material used without polishing the weld zone is worsened. In addition, exfoliation of the black spots portion occasionally occurs during working of the weld zone. Where the black spot portion is exfoliated, problems such as deterioration of workability and/or occurrence of crevice corrosion in the interstitial area between the weld metal and the exfoliated black spots occasionally occur. Even when the steel member is not worked after the welding, where a thick portion is formed by the black spots, exfoliation of the black spots and the resultant deterioration of corrosion resistance occasionally occur in the member having a structure in which stress is loaded on the weld zone.

[0017] Therefore, in order to improve the corrosion resistance of the TIG weld zone, it is important to not only improve the corrosion resistance of the weld bead portion itself and weld scale portion itself, but also to control the occurrence of black spots in the weld zone. The scale that is generated during the welding and accompanies the change of color can be mostly suppressed by the method of enhancing shielding conditions during welding. However, the black spots generated in the TIG weld zone could not be suppressed sufficiently in accordance with the prior arts even when the shielding conditions were enhanced.

[0018] In consideration of the above-explained circumstances, an object of the present invention is to provide a ferritic stainless steel that is resistant to the generation of black spots in the TIG weld zone and exhibits excellent corrosion resistance and workability in the weld zone.

SOLUTION TO THE PROBLEMS

[0019] As described below, the inventors performed extensive research to suppress the amount of generation of black spots. As a result, the inventors found that the generation of black spots in the TIG weld zone could be suppressed by optimizing the amounts of Al, Ti , Si, and Ca, and reached the invention of the ferritic stainless steel in which black spots are generated only in a small amount.

[0020] The followings are summary of the present invention.

[0021] A first aspect of the present invention is a ferritic stainless steel containing, in mass %, 0.020% or less of C, 0.025% or less of N, 1.0% or less of Si, 1.0% or less of Mn, 0.035% or less of P, 0.01% or less of S, 16.0 to 25.0% of Cr, 0.12% or less of Al, 0.05 to 0.35% of Ti, and 0.0015% or less of Ca, and the balance consisting of Fe and unavoidable impurities, wherein the following formula 1 is satisfied.

$$BI=3Al+Ti+0.5Si+200Ca\leqq 0.8 \quad (1)$$

[0022] where Al, Ti, Si, and Ca in the formula 1 each denotes an amount of each element in mass % of the steel.

[0023] In the above-described ferritic stainless steel, only a small amount of black spots is generated in the weld zone.

[0024] A second aspect of the present invention is a ferritic stainless steel according to the above-described first aspect, and further contains, in mass %, 0.6% or less of Nb.

[0025] A third aspect of the present invention is a ferritic stainless steel according to the above-described first or second aspect, and further contains, in mass %, 3.0% or less of Mo.

[0026] A fourth aspect of the present invention is a ferritic stainless steel according to any one of the above-described first to third aspects, and further contains, in mass %, one or two selected from 2.0% or less of Cu and 2.0% or less of Ni.

[0027] A fifth aspect of the present invention is a ferritic stainless steel according to any one of the above-described first to fourth aspects, and further contains, in mass %, one or two selected from 0.2% or less of V and 0.2% or less of Zr.

[0028] A sixth aspect of the present invention is a ferritic stainless steel according to any one of the above-described first to fifth aspects, and further contains, in mass %, 0.005% or less of B.

EFFECT OF THE INVENTION

[0029] According to the present invention, it is possible to provide a ferritic stainless steel in which black spots do not easily occur and that is excellent in corrosion resistance and workability of the weld zone.

BRIEF EXPLANATION OF DRAWINGS

[0030] FIG. **1**A is a photograph that shows appearance of black spots that were generated in the back side during TIG welding.

[0031] FIG. **1**B is a schematic drawing that corresponds to the photograph of FIG. **1**A and shows an appearance of black spots that were generated in the back side during TIG welding.

[0032] FIG. **2**A is a graph that shows a result of AES measurement of depth profile of elements (concentration distributions of elements in the depth direction) of the weld bead portion in the back side of a test piece.

[0033] FIG. **2**B is a graph that shows a result of AES measurement of depth profile of elements (concentration distributions of elements in the depth direction) of a black spot in the back side of a test piece.

[0034] FIG. **3** is a graph that shows a relationship between the BI value and the formation length ratio of black spots.

[0035] FIG. **4** is a graph showing the relationship between the BI value and corrosion, where concentric double circles (◎) show excellent results, circles (○) show good results, and crosses (x) show bad results.

MODE FOR CARRYING OUT THE INVENTION

[0036] In the following, the present invention is explained in detail.

[0037] A ferritic stainless steel according to the present invention that generates only a small amount of black spot satisfies the below described formula 1.

$$BI=3Al+Ti+0.5Si+200Ca\leqq 0.8 \quad (1)$$

[0038] where Al, Ti, Si, and Ca in the formula 1 each denotes an amount of each element in the steel in mass %.

[0039] Al, Ti, Si, and Ca are elements that have a specifically strong affinity with oxygen and that generate black spots at the time of TIG welding. As the amount of Al, Ti, Si, and Ca contained in the steel increases, black spots are easily generated. The coefficients of the amounts of Al, Ti, Si, and Ca in the above-described formula 1 are determined based on the degree (strength) of the effect of enhancing the generation of black spots and the amounts in the steel. Specifically, as it is shown in the following experimental example, Al is an element that is included in the black spot at the highest concentration and has a specifically large effect of enhancing the generation of black spots. Therefore, coefficient of the Al content in the above-described formula 1 is determined to be 3.

[0040] Ca is an element that is included in the black spot at a high concentration regardless of its small content in the steel and that has a large effect of enhancing the generation of black spots. Therefore, the coefficient of the Ca content is determined to be 200.

[0041] Where the above-described BI value exceeds 0.8, the generation of black spots is prominent. On the other hand, where the BI value is 0.8 or less, the generation of black spots in the TIG weld zone is sufficiently reduced, and an excellent corrosion resistance is obtained. Where the BI value is 0.6 or less, it is possible to suppress the generation of black spots more effectively. Further, where the BI value is 0.4 or less, the generation of black spots is mostly suppressed, and it is possible to further improve the corrosion resistance of the TIG weld zone.

[0042] Under conditions in which a large amount of black spots tend to occur, the black spot portion has a large thickness. It is considered that such a portion is easily exfoliated at the time of working, and that severe working such as bulging causes the exfoliation and provides a starting point for corrosion. On the contrary, the black spots have thin thickness under conditions in which black spots are generated in a small amount. Therefore, it is considered that even when black spots are generated, the black spots are not exfoliated easily. Therefore, it is considered that corrosion resistance of the weld zone can be suppressed by suppressing the generation of black spots.

[0043] Next, component compositions of the ferritic stainless steel according to the present invention are explained in detail.

[0044] Firstly, each of the elements for regulating the above described formula 1 is explained.

[0045] Aluminum (Al): 0.012% by Mass or Less

[0046] Al is important as an deoxidizing element and has an effect in grain-refinement of the microstructure of the steel by controlling the composition of non-metallic inclusion. However, Al is an element that has the largest contribution to the generation of black spots. In addition, excessive addition of Al causes coarsening of the non-metallic inclusions that may act as starting points of scratching in the product. Therefore, the upper limit of the amount of Al was determined to be 0.12%. It is preferable for the steel to contain 0.01% or more of Al with the purpose of deoxidization. More preferably, the amount of Al is 0.03% to 0.10%.

[0047] Titanium (Ti): 0.05% to 0.35% by Mass

[0048] Ti is an very important element for fixing C and N and suppressing grain boundary corrosion in the weld zone, thereby improving workability. However, excessive addition of Ti results in not only generation of black spots but also occurrence of surface scratches during the production process. Therefore, the range of the amount of Ti was determined to be 0.05% to 0.35%. More preferable range is 0.07% to 0.20%.

[0049] Silicon (Si): 1.0% by Mass or Less

[0050] Si is an important element as an deoxidizing element and is effective in improvement of corrosion resistance and oxidation resistance. However, excessive addition of Si results in not only enhancement of generation of black spots but also deterioration of workability and productivity. Therefore, the upper limit of the amount of Si was determined to be 1.0%. It is preferable to make the steel contain 0.01% or more of Si for the purpose of deoxidization. Preferably, the amount of Si is 0.05% to 0.55%.

[0051] Calcium (Ca): 0.0015% by Mass or Less

[0052] Ca is very important as an deoxidizing element and is contained in the steel in small amount in the form of non-metallic inclusion. On the other hand, since Ca is oxidized very easily, Ca behaves as strong cause of generation of black spots in the time of welding. In addition, there is a case in that Ca causes generation of water-soluble inclusion, thereby deteriorating corrosion resistance. Therefore, it is preferable to control the amount of Ca to be as small as possible, and the upper limit of the amount of Ca was determined to be 0.0015%. More preferably, the amount of Ca is 0.0012% or less.

[0053] Next, the other elements constituting the ferritic stainless steel according to the present invention is explained.

[0054] Carbon (C): 0.020% or Less by Mass

[0055] The amount of C must be suppressed since C deteriorates grain boundary corrosion resistance and workability. Therefore the upper limit of C was determined to be 0.020%. On the other hand, excessive reduction of C causes an increase in the refining cost. Therefore, the amount of C is preferably 0.002% to 0.015%.

[0056] Nitrogen (N): 0.025% or Less by Mass

[0057] In the same manner as C, N deteriorates grain boundary corrosion resistance and the workability of the steel. Therefore, it is necessary to reduce the amount of N. Therefore, upper limit of the amount of N was determined to be 0.025%. On the other hand, excessive reduction of N causes an increase in the refining cost. Therefore, the amount of N is preferably 0.002% to 0.015%.

[0058] Manganese (Mn): 1.0% or Less by Mass

[0059] Although Mn is an important element as a deoxidizing element, excessive addition of Mn tends to cause generation of MnS that acts as a starting point of corrosion, and destabilizes the ferrite microstructure. Therefore, the amount of Mn was controlled to be 1.0% or less. For the purpose of deoxidization, it is preferable for the steel to contain 0.01% or more of Mn. Preferably, the amount of Mn is 0.05% to 0.5%, and more preferably, 0.05% to 0.3%.

[0060] Phosphorous (P): 0.035% or Less by Mass

[0061] The amount of P must be suppressed to low value since P deteriorates weldability and workability and makes the grain boundary corrosion easily occur. Therefore, the amount of P was controlled to be 0.035% or less. A more preferable amount of P is 0.001% to 0.02%.

[0062] Sulfur (S): 0.01% or Less by Mass

[0063] The amount of S must be reduced since S generates water-soluble inclusions such as CaS and MnS that act as starting points of corrosion. Therefore, the amount of S is controlled to be 0.01% or less. On the other hand, excessive reduction of S results in deterioration of the cost. Therefore, the amount of S is preferably 0.0001% to 0.005%.

[0064] Chromium (Cr): 16.0% to 25.0% by Mass

[0065] Cr is the most important element for ensuring corrosion resistance of the stainless steel. In order to stabilize the ferrite microstructure, it is necessary for the steel to contain 16.0% or more of Cr. On the other hand Cr deteriorates the workability and productivity of the steel. Therefore, the upper limit of Cr content was determined to be 25.0%. Preferably, the amount of Cr is 16.5% to 23.0%, and more preferably, 18.0% to 22.5%.

[0066] Niobium (Nb): 0.6% by Mass or Less

[0067] Nb has properties such that Nb may be added alone, or in combination with Ti. Where Nb and Ti are added in combination, it is preferable that the formula: $(Ti+Nb)/(C+N)\geqq 6$ is satisfied, where Ti, Nb, C, and N in the formula each denote the amount in mass % of each element in the steel.

[0068] In the same manner as Ti, Nb fixes C and N, suppress grain boundary corrosion of weld-zone, and improves workability. On the other hand, excessive addition of Nb deteriorates workability of the steel. Therefore, it is preferable to control the upper limit of the amount of Nb to be 0.6%. In order to improve the above-described properties by the content of Nb, it is preferable for the steel to contain 0.05% or more of Nb. Preferably, the amount of Nb is 0.15% to 0.55%.

[0069] Molibdenum (Mo): 3.0% or Less by Mass

[0070] Mo is an element that has an effect of repairing the passive film and is very effective in improvement of corrosion resistance. By being added in combination with Cr, Mo has an effect of improving pitting corrosion resistance of the steel. By being added in combination with Ni, Mo has an effect of improving the resistance to outflow rust. On the other hand, increased Mo reduces workability and increases the cost. Therefore, it is preferable to control the upper limit of the amount of Mo to be 3.0%. In order to improve the above-described properties by the content of Mo, it is preferable for the steel to contain 0.30% or more of Mo. Preferably, the amount of Mo is 0.60% to 2.5%, more preferably, 0.9% to 2.0%.

[0071] Nickel (Ni): 2.0% or Less by Mass

[0072] Ni has an effect of suppressing active dissolution rate, and is excellent in repassivation properties because of the small hydrogen overvoltage. On the other hand, excessive addition of Ni deteriorates workability and destabilizes the ferrite microstructure. Therefore, it is preferable to control the upper limit of the amount of Ni to be 2.0%. In order to improve the above-described properties by the content of Ni, it is preferable for the steel to contain 0.05% or more of Ni. Preferably, the amount of Ni is 0.1% to 1.2%, more preferably, 0.2% to 1.1%.

[0073] Copper (Cu): 2.0% or Less by Mass

[0074] In the same manner as Ni, Cu reduces the active dissolution rate, and has an effect of enhancing repassivation. However, an excessive addition of Cu deteriorates the workability. Therefore, where Cu is added, it is preferable to control the upper limit of the amount to be 2.0%. In order to improve the above-described property by the content of Cu, it is preferable for the steel to contain 0.05% or more of Cu. Preferably, the amount of Cu is 0.2% to 1.5%, more preferably, 0.25% to 1.1%.

[0075] Vanadium (V) and/or Zirconium (Zr): 0.2% by Mass or Less

[0076] V and Zr improve weather resistance and crevice corrosion resistance. In addition, where V is added while suppressing the use of Cr and Mo, it is possible to ensure an excellent workability. On the other hand, excessive addition of V and/or Zr deteriorates workability, and saturates the effect of improving corrosion resistance. Therefore, where V and/or Zr is contained, it is preferable to control the upper limit of the amount to be 0.2%. In order to improve the above-described properties by the content of V and/or Zr, it is preferable for the steel to contain 0.03% or more of V and/or Zr. More preferably, the amount of V and/or Zr is 0.05% to 0.1%.

[0077] Boron (B): 0.005% or Less by Mass

[0078] B is an element that strengthens grain boundary and is effective in improvement of secondary working embrittlement. On the other hand, excessive addition of B causes reduction of ductility by solution-strengthening of ferrite. Therefore, where B is added, it is preferable to control the lower limit to be 0.0001%, and the upper limit to be 0.005%. More preferably, the amount of B is controlled to be 0.0002% to 0.0020%.

EXAMPLE

[0079] Test pieces composed of ferritic stainless steel each having a chemical component (composition) shown in Table 1 were produced in accordance with the below described method. Firstly, a cast steel having a chemical component (composition) shown in Table 1 was molten by vacuum melting, and an ingot having a thickness of 40 mm was produced from the melt. The ingot was rolled to a thickness of 5 mm by hot rolling. After that, in accordance with the recrystallization behavior of each steel, the rolled steel was heat treated for one minute at a temperature of 800 to 1000° C. After removing a scale by grinding, steel plates having a thickness of 0.8 mm were produced by cold rolling After removing the surface oxide scale by pickling (acid cleaning), test materials were obtained. Using the test materials, test pieces of Nos. 1 to 28 were produced. In the chemical component (composition) shown in Table 1, the amount of each element is shown in mass %, and the balance is iron and unavoidable impurities. The under-line shows that the value is outside the range of the present invention.

TABLE 1

No.	C	Si	Mn	P	S	Cr	Al	Ti	Ca	N	Mo
1	0.004	0.10	0.11	0.007	0.001	18.0	0.04	0.20	0.0002	0.008	
2	0.005	0.11	0.20	0.015	0.003	18.2	0.06	0.12	0.0002	0.007	0.52
3	0.008	0.09	0.20	0.011	0.002	19.7	0.04	0.12	0.0003	0.012	
4	0.011	0.10	0.11	0.009	0.001	22.9	0.03	0.10	0.0003	0.010	
5	0.012	0.11	0.18	0.009	0.001	18.7	0.03	0.16	0.0004	0.011	1.81
6	0.005	0.08	0.20	0.008	0.001	22.5	0.07	0.09	0.0002	0.008	1.18
7	0.007	0.10	0.14	0.010	0.002	19.0	0.04	0.14	0.0004	0.010	0.99
8	0.010	0.13	0.15	0.010	0.002	18.4	0.04	0.16	0.0002	0.010	1.90
9	0.004	0.12	0.18	0.009	0.003	22.6	0.05	0.13	0.0003	0.011	0.82
10	0.007	0.51	0.25	0.010	0.002	19.1	0.01	0.07	0.0002	0.009	
11	0.004	0.10	0.16	0.009	0.001	20.9	0.03	0.06	0.0002	0.009	
12	0.007	0.12	0.25	0.010	0.002	19.1	0.06	0.12	0.0002	0.009	0.95
13	0.014	0.04	0.22	0.020	0.003	17.5	0.04	0.08	0.0005	0.014	
14	0.003	0.45	0.27	0.011	0.002	19.4	0.05	0.09	0.0003	0.006	
15	0.009	0.08	0.09	0.008	0.002	18.5	0.08	0.08	0.0004	0.008	
16	0.004	0.12	0.20	0.022	0.002	23.0	0.12	0.19	0.0002	0.008	0.55
17	0.005	0.15	0.21	0.020	0.003	19.2	0.04	0.30	0.0009	0.009	
18	0.004	0.10	0.14	0.007	0.001	17.1	0.04	0.22	0.0003	0.009	
19	0.004	0.12	0.12	0.008	0.003	23.7	0.06	0.15	0.0005	0.011	1.85
20	0.013	0.62	0.25	0.020	0.003	17.6	0.06	0.07	0.0004	0.014	
21	0.005	0.09	0.28	0.015	0.002	23.8	0.08	0.21	0.0010	0.010	
22	0.010	0.25	0.20	0.030	0.003	23.0	0.15	0.19	0.0015	0.012	
23	0.006	0.65	0.21	0.015	0.002	18.5	0.05	0.02	0.0010	0.009	
24	0.004	0.20	0.22	0.020	0.003	21.5	0.09	0.34	0.0010	0.010	1.05
25	0.006	0.26	0.16	0.025	0.001	15.9	0.09	0.21	0.0009	0.014	
26	0.010	0.25	0.20	0.020	0.002	17.9	0.03	0.40	0.0015	0.011	2.01
27	0.015	1.01	0.31	0.002	0.002	18.0	0.04	0.19	0.0014	0.014	
28	0.012	0.28	0.23	0.018	0.003	23.5	0.10	0.21	0.0019	0.012	1.56

TABLE 1-continued

No.	Nb	Ni	Cu	B	V	Zr	Fe and unvoidable impurities	
1							Balance	inventive
2							Balance	inventive
3	0.20						Balance	inventive
4	0.31					0.05	Balance	inventive
5	0.28						Balance	inventive
6	0.18						Balance	inventive
7	0.22						Balance	inventive
8	0.23	0.12	0.20		0.10		Balance	inventive
9	0.25	0.15	0.15		0.08		Balance	inventive
10	0.45	0.28	0.44				Balance	inventive
11	0.25			0.0007			Balance	inventive
12	0.21	1.02			0.06		Balance	inventive
13	0.51					0.12	Balance	inventive
14	0.17	0.40	0.50	0.0004	0.12		Balance	inventive
15	0.55						Balance	inventive
16							Balance	inventive
17		0.25	0.39				Balance	inventive
18							Balance	inventive
19	0.21						Balance	inventive
20	0.38						Balance	inventive
21	0.19			0.0008		0.09	Balance	inventive
22	0.22						Balance	comparative
23	0.41	0.25	0.39				Balance	comparative
24					0.11		Balance	comparative
25				0.0010			Balance	comparative
26							Balance	comparative
27	0.36						Balance	comparative
28	0.18					0.08	Balance	comparative

[0080] The thus obtained test pieces of Nos. 1 to 28 were subjected to TIG welding under the following welding conditions, and formation length ratio of black spot was measured in accordance with the following manner. In addition, corrosion experiment was performed for the test piece of Nos. 1 to 28.

[0081] Welding Conditions

[0082] Pieces of the same steel were butted and subjected to TIG welding with feed rate of 50 cm/min, and heat input of 550 to 650 J/cm^2. Argon was used both in shielding of torch side and shielding of back side.

[0083] Ratio of Formation Length of Black Spot

[0084] The formation length ratio of black spots was determined as a standard for showing the amount of generated black spots after the TIG welding. The formation length ratio of black spots was obtained by integrating length of each black spot along the welding direction, and dividing the integrated value by the total welding length. Practically, photograph of a 10 cm length weld zone was taken by a digital camera, length of each black spot was measured, and ratio of the integrated length of black spots to the welding length was calculated using image processing.

[0085] Corrosion Test

[0086] TIG weld zones of test pieces were subjected to bulging and were used as test pieces for corrosion test. Erichsen test conditions in accordance with JIS2247 were used as the bulging conditions. The penetration side was used as the surface, and a punch of 20 mm ϕ was used in the bulging. The working of each test piece was paused so as to adjust the working conditions with respect to the height of the bulge. The paused height (height of bulge) was standardized to 6 mm and 7 mm Each test piece was subjected to continuous spray test of 5% NaCl in accordance with JIS Z 2371, and corrosion was evaluated by presence or absence of outflow rust in the test piece at 48 hours after the spray test. Where the outflow rust was not observed in the bulged test piece with bulging height of 6 mm after the continuous spray test of 5% NaCl, the result was evaluated as "GOOD". Where the outflow rust was not observed in the bulged test piece with bulging height of 7 mm after the same spray test, the result was evaluated as "EXCELLENT". Where the outflow rust occurred after the continuous spray test, the result was evaluated as BAD.

[0087] BI values determined from the chemical component in Table 1, formation length ratio of black spots, and the results of corrosion test are shown in Table 2.

TABLE 2

No.	BI	Formation length ratio of black spots (%)	Results of corrosion test	
1	0.40	10	EXCELLENT	inventive
2	0.40	7	EXCELLENT	inventive
3	0.35	3	EXCELLENT	inventive
4	0.30	0	EXCELLENT	inventive
5	0.39	9	EXCELLENT	inventive
6	0.38	7	EXCELLENT	inventive
7	0.39	9	EXCELLENT	inventive
8	0.39	10	EXCELLENT	inventive
9	0.40	8	EXCELLENT	inventive
10	0.40	9	EXCELLENT	inventive
11	0.24	0	EXCELLENT	inventive
12	0.40	9	EXCELLENT	inventive
13	0.32	7	EXCELLENT	inventive
14	0.53	22	GOOD	inventive
15	0.44	15	GOOD	inventive
16	0.65	41	GOOD	inventive
17	0.68	49	GOOD	inventive
18	0.45	19	GOOD	inventive
19	0.49	20	GOOD	inventive
20	0.64	39	GOOD	inventive

TABLE 2-continued

No.	BI	Formation length ratio of black spots (%)	Results of corrosion test	
21	0.70	45	GOOD	inventive
22	1.07	78	BAD	comparative
23	0.70	45	BAD	comparative
24	0.91	86	BAD	comparative
25	0.79	60	BAD	comparative
26	0.92	89	BAD	comparative
27	1.10	83	BAD	comparative
28	1.03	88	BAD	comparative

[0088] As shown in Table 2, formation length ratios of black spots were small, that is, amounts of generated black spots after the TIG welding were small in the test pieces Nos. 1 to 21 that had chemical component (composition) within the range of the present invention and BI value of 0.8 or less.

[0089] Generation of black spots was suppressed in the test pieces No. 1 to 15, 18, and 19 having a BI value of 0.6 or less. Further, generation of black spots was mostly suppressed in Nos. 1 to 13 having a BI value of 0.4 or less such that the ratio of formation length of black spots was 10% or less. In test pieces No. 1 to 21 which were worked to have a bulge height of 6 mm using an Erichsen test machine, rust from the weld zone was not observed after the continuous spray test of 5% NaCl. In test pieces No. 1 to 21 which were more severely worked to have a bulge height of 7 mm, rust was not observed in test pieces having BI value of 0.4 or less, and rust was observed in test pieces having BI value exceeding 0.4.

[0090] On the other hand, the test pieces Nos. 22, 24, 26 to 28 having BI value exceeding 0.8 showed large formation length ratio of black spots after the TIG welding and rust from the weld zone was observed in each specimen in the corrosion test. Magnified images of rust portions of test pieces Nos. 22, 24, 26 to 28 were observed using a magnifying glass. As a result, exfoliation was observed in the boundary between the black spots and the weld bead portion. Rust was generated in corrosion test of Nos. 22, 26, 27, and 28 in which concentrations of Al, Ti, Si, and Ca exceeded the regulated values.

[0091] Occurrence of rust was observed in the corrosion test of the test piece No. 25 in which component ratio of Cr was less than 16% and the test piece No. 23 in which component ratio of Ti was less than 0.05%.

Experimental Example 1

[0092] Test materials were produced in accordance with the same manner as test piece No.1 except for that steel plates of 1 mm thick were produced by cold-rolling of ferritic stainless steels having the below described chemical components (compositions). Test piece A and test piece B were obtained using the test materials.

[0093] Chemical Component (Composition)

[0094] Test Piece A

[0095] C: 0.007%, N: 0.011%, Si: 0.12%, Mn: 0.18%, P: 0.22%, S: 0.001%, Cr: 19.4%, Al: 0.06%, Ti: 0.15%, Ca: 0.0005%, balance: iron and unavoidable impurities.

[0096] Test Piece B

[0097] C: 0.009%, N: 0.010%, Si: 0.25%, Mn: 0.15%, P: 0.21%, S: 0.001%, Cr: 20.2%, Al: 0.15%, Ti: 0.19%, Ca: 0.0015%, balance: iron and unavoidable impurities.

[0098] The thus obtained test piece A and test piece B were subjected to TIG welding under the similar welding conditions as the test piece No. 1, and appearance of black spots generated in the back side during TIG welding was observed.

[0099] The results are shown in FIG. **1**A and FIG. **1**B.

[0100] FIG. **1**A is a photograph that shows an appearance of black spots generated in back side during TIG welding. FIG. **1**B is a schematic drawing that shows an appearance of black spots generated in back side during TIG welding and that corresponds to FIG. **1**A.

[0101] In FIG. **1**A and FIG. **1**B, the left-side figures show a photograph and a drawing of test piece A in which BI value is 0.49, and the right-side figures show a photograph and a drawing of test piece B in which BI value is 1.07.

[0102] As shown by the arrows in FIG. **1**A and FIG. **1**B, spot-like black spots are observed dispersingly both in the test piece A with BI value of 0.49 and test piece B with BI value of 1.07. However, it is recognized that the black spots are generated in larger amount in test piece B (right-side photograph) having a larger BI value.

[0103] Two portions selected from the weld bead portion and the black spot portion of the test piece B with a BI value of 1.07 were subjected to auger electron spectroscopy (AES). The results are shown in FIG. **2**A and FIG. **2**B.

[0104] A FE (Field Emission) Auger Electron Spectroscopy was used in the AES analysis, and the analysis was performed until intensity of oxygen spectrum was almost not detected under conditions of an acceleration voltage of 10 keV, a spot diameter of 40 nm, and a sputtering rate of 15 nm/min. Although a position dependent error may occur due to small spot of AES measurement, the results were applied as values showing approximate thickness.

[0105] FIG. **2**A and FIG. **2**B are graphs that show depth profile of elements (concentration distribution of elements in depth direction) in the black spot and the weld bead portion on the back side of the test piece as a result of AES analysis. FIG. **2**A is a result of weld bead portion, and FIG. **2**B is a result of a black spot.

[0106] As shown in FIG. **2**A, the weld bead portion was an oxide having a thickness of several hundred A that mainly contained Ti, and also contained Al and Si. On the other hand, as shown in FIG. **2**B, the black spot was a thick oxide having a thickness of several thousand A that mainly contained Al, and also contained Ti, Si, and Ca. From the graph of black spot shown in FIG. **2**B, it was confirmed that Al was contained in the black spot at the highest concentration and Ca was contained in the black spot at high concentration irrespective of its small amount in the steel.

Experimental Example 2

[0107] Test materials of ferritic stainless steel having various component ratios (compositions) were produced in accordance with the production method similar to that of test piece A, where each steel had a basic composition of C: 0.002 to 0.015%, N: 0.02 to 0.015%, Cr: 16.5 to 23%, Ni: 0 to 1.5%, Mo: 0 to 2.5%, and also contained main components of black spots such as Al, Ti, Si, and Ca in different amount. Using the test materials, a plurality of test pieces was obtained.

[0108] The thus obtained plurality of test pieces were subjected to TIG welding under similar welding conditions as the test piece No. 1, and ratios of formation length of black spots were calculated in accordance with the same manner as the test piece No. 1.

[0109] As a result, the formation length ratio of black spots tended to increase in accordance with the increasing amounts of Al, Ti, Si, and Ca. Those elements are elements having specifically strong affinity with oxygen. It was found that Al had the highest effect, and Ca had a strong influence on black spots irrespective of its small amount in the steel. It was also confirmed that Ti and Si also contributed to the generation of black spots.

[0110] Based on the results, it was found that there was a strong possibility of generation of black spots even under shielding conditions where large amounts of Al, Ti, Si, and Ca were added, and that Al and Ti had strong influence on generation of black spots.

[0111] BI value shown by the below described formula 1 was calculated for the plurality of test pieces, and the relationship between the BI value and the ratio of formation length of black spots was examined.

$$BI=3Al+Ti+0.5Si+200Ca \leqq 0.8 \quad (1)$$

[0112] where Al, Ti, Si, and Ca in the formula 1 respectively denotes an amount of each element in mass % of the steel.

[0113] The results are shown in FIG. **3**. FIG. **3** is a graph showing the relationship between the BI value and the ratio of formation length of black spots. As shown in FIG. **3**, it is recognized that the ratio of formation length of black spots increases with an increasing BI value.

[0114] Each of the plurality of test pieces was subjected to corrosion test in accordance with the same manner as the test piece No. 1. The results are shown in FIG. **4**. FIG. **4** is a graph that shows a relationship between the BI values and the results of corrosion resistance evaluation after the spray test after working. In the figure, double circles (◎) show excellent results, circles (○) show good results, and crosses (x) show bad results. As shown in FIG. **4**, corrosion did not occur in the specimen with bulge height of 6 mm where BI value was 0.8 or less. Especially, where BI value was 0.4 or less, specifically good results were achieved such that corrosion was not observed in the specimen with bulge height of 7 mm.

INDUSTRIAL APPLICABILITY

[0115] The ferritic stainless steel of the present invention can be appropriately used in members requiring corrosion resistance in a structure of, for example, exterior materials, building materials, water or hot water containers, consumer electronics, kitchen equipment, drain water collectors and heat exchanger of gas condensing boiler, various welded pipes or the like that are formed by TIG welding and used in general indoor or outdoor environment. Specifically, the ferritic stainless steel of the present invention is appropriately used in a member that is subjected to working after the welding. Since the ferritic stainless steel of the present invention is excellent not only in corrosion resistance but also in workability of TIG weld zone, the steel can be widely used in the usage suffering severe working conditions.

1. A ferritic stainless steel containing, in mass %, 0.020% or less of C, 0.025% or less of N, 1.0% or less of Si, 1.0% or less of Mn, 0.035% or less of P, 0.01% or less of S, 16.0 to 25.0% of Cr, 0.12% or less of Al, 0.05 to 0.35% of Ti, 0.05 to 0.6% of Nb and 0.0002 to 0.0015% of Ca, and the balance consisting of Fe and unavoidable impurities, wherein the following formula 1 is satisfied.

$$BI=3Al+Ti+0.5Si+200Ca \leqq 0.8 \quad (1)$$

where Al, Ti, Si, and Ca in the formula 1 each denotes an amount of each element in mass % of the steel.

2. (canceled)

3. A ferritic stainless steel according to claim **1**, further containing, in mass %, 3.0% or less of Mo.

4. (canceled)

5. A ferritic stainless steel according to claim **1** or **3**, further containing, in mass %, one or two selected from 2.0% or less of Cu and 2.0% or less of Ni.

6. A ferritic stainless steel according to claim **1** or **3**, further containing, in mass %, one or two selected from 0.2% or less of V and 0.2% or less of Zr.

7. A ferritic stainless steel according to claim **5**, further containing, in mass %, one or two selected from 0.2% or less of V and 0.2% or less of Zr.

8. A ferritic stainless steel according to claim **1** or **3**, further containing, in mass %, 0.005% or less of B.

9. A ferritic stainless steel according to claim **5**, further containing, in mass %, 0.005% or less of B.

10. A ferritic stainless steel according to claim **6**, further containing, in mass %, 0.005% or less of B.

11. A ferritic stainless steel according to claim **7**, further containing, in mass %, 0.005% or less of B.

* * * * *