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(54) **FERRITIC STAINLESS STEEL HAVING EXCELLENT CORROSION RESISTANCE IN CONDENSED WATER ENVIRONMENT PRODUCED BY EXHAUST GAS FROM HYDROCARBON COMBUSTION**

FERRITISCHER EDELSTAHL MIT HERVORRAGENDER KORROSIONSBESTÄNDIGKEIT IN EINER DURCH ABGAS AUS EINER KOHLENWASSERSTOFFVERBRENNUNG ENTSTANDENEN KONDENSWASSERUMGEBUNG

ACIER INOXYDABLE FERRITIQUE AYANT UNE EXCELLENTE RÉSISTANCE À LA CORROSION DANS UN ENVIRONNEMENT D'EAU DE CONDENSATION PRODUIT PAR LES GAZ D'ÉCHAPPEMENT D'UNE COMBUSTION D'HYDROCARBURES

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Description

TECHNICAL FIELD

[0001] This invention relates to ferritic stainless steel excellent in corrosion resistance for use in the structural members of heat exchangers, namely, secondary heat exchangers said to generate low pH condensed water in water heaters operated with LPG or oil as fuel.

BACKGROUND ART

[0002] Heat exchangers are apparatuses for imparting heat produced by burning any of various fuels to a medium, most often water, and are used in various fields ranging from nuclear power plant steam generators to home water heaters. Among these, the home gas- and oil-fueled water heaters also have built-in heat exchangers for heating water with the combustion heat. In order to increase thermal efficiency, these heat exchangers have conventionally used copper that is easy to process into the fin and other structures and is also excellent in thermal conductivity. However, owing to recent environmental issues, water heaters are being required to reduce CO₂, so that in the interest of further thermal efficiency, a latent heat recovery type water heater was developed that further utilizes the heat of the gas previously exhausted. This water heater has another heat exchanger (secondary heat exchanger) for also utilizing the heat of the exhaust gas from the burned gas or oil after passing through the conventional heat exchanger (primary heat exchanger). The exhaust gas passed through the primary heat exchanger is at about 150 to 200 °C and contains much steam. The secondary heat exchanger improves the total thermal efficiency to 95% or greater by recovering not only the direct heat but also the heat of condensation when the steam becomes water droplets, i.e., the latent heat. An example of the structure of the latent heat recovery type water heater is set out, for example, in Patent Document 1. JP 2006 257 544 discloses a ferritic stainless steel having a good pitting resistance. Here, since the condensed water occurring in the secondary heat exchanger arises from within the exhaust gas produced by burning city gas, LPG, oil or other hydrocarbon fuel, it contains nitrate ions and sulfate ions attributable to the gas components and is known to be a weakly acidic aqueous solution of a pH of around 3 or less. The conventionally used copper (corrodes at pH of 6.5 or less) cannot be used with this solution of low pH. Other ordinary steels (corrode at pH of 7 or less) or aluminum (corrodes at pH of about 3) are also susceptible to corrosion. The materials currently selected for the secondary heat exchanger are therefore stainless steels, which are excellent in corrosion resistance in the weakly acidic region, and among ordinary stainless steels, SUS316L (18 Cr - 10 Ni - 2 Mo) austenitic stainless steel, which is especially excellent in corrosion resistance, is mainly adopted because of the priority on corrosion resistance. But while SUS316L satisfies the corrosion resistance required by the structural members of a secondary heat exchanger applied in a latent heat recovery type water heater, the raw material thereof includes large amounts of Ni and Mo, whose price stability is very unstable. Hopes are that the latent heat recovery type water heater will achieve widespread general adoption as a trump card for reducing CO₂, and additional cost reduction is strongly desired to realize this. The emergence of a low-cost alternative for the SUS316L steel of the secondary heat exchanger is naturally also desired. Further, while no corrosion resistance problem is thought to arise in an ordinary use environment, the possibility cannot be denied that even SUS316L might corrode in coastal and other regions where sea salt particles, which are one cause inhibiting stainless steel corrosion resistance, tend to become airborne. In this case, SUS316L may sustain the stressed corrosion cracking that is one of the shortcomings of austenitic stainless steels.

[0003] In order to resolve such problems occurring when an austenitic stainless steel is applied, attempts have in recent years been made to apply ferritic stainless steels to the secondary heat exchanger components (Patent Documents 1 to 3).

PRIOR ART REFERENCES

Patent Documents

[0004]

Patent Document 1 Unexamined Patent Publication (Kokai) No. 2002-106970
 Patent Document 2 Unexamined Patent Publication (Kokai) No. 2003-328088
 Patent Document 3 Unexamined Patent Publication (Kokai) No. 2009-299182

SUMMARY OF THE INVENTION

Problem to be Solved by the Invention

[0005] By applying the ferritic stainless steels SUS436J1L, SUS436L, and SUS444 to a heat exchanger for latent heat recovery, Patent Document 1 obtains a heat exchanger for latent heat recovery that has pipes and fins excellent in thermal conductivity, corrosion resistance and brazeability, and is also relatively low in cost.

[0006] Further, for a ferritic stainless steel exhibiting durability in the high-temperature steam environment of a heat exchanger environment, Patent Document 2 teaches addition of Cr, Mo, Si and Al content as a function of the estimated use temperature. Moreover, Patent Document 3 prescribes Nb, C and N in a ferritic stainless steel suitable for heat exchanger components subjected to brazing.

[0007] However, Patent Document 1 uses the average corrosion depth as an indicator of corrosion resistance, but local pitting corrosion is what mainly occurs in a stainless steel fundamentally excellent in corrosion resistance, and if the pitting corrosion should penetrate through at any location, the steel becomes unusable. On this point, the conditions set out in Patent Document 1 still require improvement, and a study by the present inventors found that even among the ferritic stainless steels taught by Patent Document 1, some were inferior in corrosion resistance particularly when used in a heat exchanger for latent heat recovery. Patent Document 2 has a problem of the steel becoming extremely hard and brittle owing to heavy Al addition, and the temperature assumed by Patent Document 2 is 300 to 1000 °C, so that it defines a material used in an environment of much higher temperature than the latent heat recovery type water heater under consideration. Further, although Patent Document 3 prescribes Nb as a required element for the purpose of preventing crystal grain enlargement during brazing and during heat treatment, it says nothing about corrosion resistance improvement.

[0008] Thus, the situation in the prior art cannot be said to adequately teach a ferritic stainless steel suitable for secondary heat exchanger components. In the light of these circumstances, the object of the present invention is to provide a ferritic stainless steel of low cost and excellent corrosion resistance that can be suitably used in the structural members of a secondary heat exchanger.

Means for Solving the Problems

[0009] Through an evaluation of the corrosion resistance of various stainless steels in such environments that the inventors conducted toward overcoming the aforesaid problems, it was found that corrosion resistance is especially good when the Cr and Ti contents are high, and particularly when they are concentrated at a passive film surface. It was further learned by an assessment of the corrosion starting points that reduction of Cu and Si improve corrosion resistance in such an environment. The present invention is a ferritic stainless steel excellent in corrosion resistance in a secondary heat exchanger environment that was developed by assiduously studying the corrosion environment in such a secondary heat exchanger.

[0010] Specifically, the present invention which is given in the claims is a ferritic stainless steel characterized as set out below which is excellent in corrosion resistance in a condensed water environment arising from hydrocarbon combustion exhaust gas.

(1) A highly corrosion resistant ferritic stainless steel excellent in corrosion resistance in a condensed water environment arising from a hydrocarbon combustion exhaust gas characterized in comprising, in mass%, C: 0.030% or less, N: 0.030% or less, Si: 0.4% or less, Mn: 0.01 to 0.5%, P: 0.05% or less, S: 0.01% or less, Cr: 16 to 24%, Mo: 0.30 to 3%, Ti: 0.05 to 0.25%, Nb: 0.05 to 0.50%, Al: 0.01 to 0.20%, and Cu: 0.4% or less, one of V: 0.03 to 1.0% and Sb: 0.005 to 1.0%, and optionally further comprising in mass %, one or two or more of Ni: 0.3 to 3%, B: 0.0001 to 0.003% and Sn: 0.005 to 1.0%, the balance being Fe and unavoidable impurities, and satisfying Expression (A): $Cr + Mo + 10Ti \geq 22$ and Expression (B): $Si + Cu < 0.2$,

where Cr, Mo, Ti, Si and Cu in the Expressions represent the contents (mass%) of the respective elements.

(2) A highly corrosion resistant ferritic stainless steel excellent in corrosion resistance in a condensed water environment arising from a hydrocarbon combustion exhaust gas as set out in (1), characterized by further comprising, in mass%, one or two or more among Ni: 0.3 to 3%, B: 0.0001 to 0.003%, and Sn: 0.005 to 1.0%,

(3) A highly corrosion resistant ferritic stainless steel excellent in corrosion resistance in a condensed water environment arising from a hydrocarbon combustion exhaust gas as set out in (1) or (2), characterized in that after conducting 14 cycles of a wet and dry cyclic test of half-immersing a test specimen of the steel set out in (1) or (2) in an aqueous solution of pH 2.5 and containing 100 ppm nitrate ions, 10 ppm sulfate ions and 10 ppm chloride ions and holding it at 80 °C for 24 hours, maximum corrosion depth is 50 μm or less.

EFFECT OF THE INVENTION

[0011] In accordance with the present invention, instead of an austenitic stainless steel added with large amounts of expensive Ni and/or Mo, it is possible to provide a ferritic stainless steel excellent in corrosion resistance in a secondary heat exchanger environment. Further, it becomes possible to exhibit excellent corrosion resistance as a material for equipment, not only water heaters, used in a condensed water environment of combustion gas from LNG, oil or other hydrocarbon used as fuel.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

FIG. 1(a) is a diagram showing the shape of a sample submitted to testing.

FIG. 1(b) is a diagram showing the shape of a sample submitted to testing.

FIG. 2 is a diagram showing the relationship between maximum corrosion depth after testing and constituent elements.

FIG. 3 is a diagram showing the relationship between maximum corrosion depth after testing and constituent elements.

FIG. 4 is a diagram showing the results for examples and comparative examples in terms of relationship between maximum corrosion depth after testing and constituent elements.

MODES FOR CARRYING OUT THE INVENTION

[0013] In order to provide a ferritic stainless steel exhibiting excellent corrosion resistance as a material for the secondary heat exchanger of a latent heat recovery type water heater using LNG, oil or other hydrocarbon fuel, the inventors carried out assiduous development to learn the following as a result.

(i) Among ferritic stainless steels, stainless steels satisfying Expression (A): $\text{Cr} + \text{Mo} + 10\text{Ti} \geq 22$ and Expression (B): $\text{Si} + \text{Cu} \leq 0.2$ exhibited corrosion depth in a wet and dry cyclic test in condensed water from a combustion gas of 50 μm or less.

(ii) In the aforesaid environment, maximum corrosion depth was smaller for a ferritic stainless steel than for an austenitic stainless steel exhibiting the same Expression (A) value.

[0014] A test method simulating the environment concerned is explained first.

[0015] As explained earlier, the condensed water occurring in the combustion gas of ordinary LNG or oil contains nitrate ions and sulfate ions and exhibits acidity of pH = 3 or less. Further, the secondary heat exchanger experiences a cyclic environment of being input with 150 to 200 °C exhaust gas from the primary heat exchanger during use and returning to room temperature when not operating. So for the simulation test, there was prepared from chemicals a test solution of pH = 2.5; nitrate ions, 100 ppm; sulfate ions, 20 ppm; and Cl⁻ ions = 10 ppm. These components are ones simulating the condensed water from LNG combustion exhaust gas, but regarding Cl⁻ ions, instead of the actual several ppm assumed, the concentration was set high at an increasingly fast rate assuming the operating condition in a coastal environment or other high-corrosivity environment. 10 ml of this test solution 3 was placed in a test tube like that shown in FIG. 1(a), and different types of stainless steel samples 2 cut to 1t x 15 x 100 mm and polished entire surfaces thereof using a wet emery paper with a grid of #600 were half-immersed therein so that about 1/2 the longitudinal direction thereof was immersed in the solution (see FIG. 1(b)). The test tube containing the sample was placed in an 80 °C hot bath and held for 24 hours, and the dried out stainless steel sample was then removed and lightly washed with distilled water, whereafter the operation of again placing the test solution in a washed test tube once more in the foregoing manner, again half-immersing the sample, and holding for 24 hours was repeated 14 times (14 cycles). The reason for setting the hold temperature at 80 °C was that, while the temperature of the exhaust gas is 150 to 200 °C, the temperature declines due to the generation of condensed water and the actual temperature of the structural members is thought to become still lower upon being contacted by the generated condensed water, so a temperature lower than 100 °C that is relatively high was targeted to accelerate corrosion.

[0016] The test sample after 14 cycles was descaled and then measured for corrosion depth by the focal depth method using a 200x magnification microscope. The depths of five of the pitting corrosion shaped corrosion holes that occurred here were measured in order of diameter from the largest and the largest depth value was defined as the maximum corrosion depth. This means the same as maximum pitting corrosion depth. Note that the 12 steels indicated in Table 1 were used as the tested materials. When the test result was a maximum corrosion depth exceeding 50 μm , it was judged that hole opening would be reached over the long term, and the assessment was "no corrosion resistance

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present", and when it was 50 μm or less, the assessment was "corrosion resistance present."

[0017] It was discovered that taking a ferritic stainless steel containing Cr as the base, corrosion depth improved in both the case of increasing Cr content and the case of adding Mo and/or Ti. Defining effect per unit increase in Cr content as 1, it was found that effect per unit increase in Mo content was the same as for Cr, and effect exhibited per unit increase in Ti was about 10 fold that for Cr. It was further found that both Si and Cu degraded corrosion depth in a ferritic stainless steel and the Si and Cu contribution rates were judged to be almost equal.

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Table 1

No	Constituent contents (Mass%)														Maximum corrosion depth / μm	
	C	N	Si	Mn	P	S	Cr	Al	Ti	Nb	Mo	Cu	B	(A) Cr+Mo+10+Ti		(B) Si+Cu
1	0.013	0.011	0.25	0.36	0.02	0.002	16.5	0.07	0.15	0.19	0.31	0.19		18.31	0.44	49
2	0.010	0.013	0.16	0.16	0.02	0.002	18.6	0.07	0.19	0.50	0.69	0.30		21.19	0.46	40
3	0.006	0.010	0.10	0.14	0.02	0.001	17.2	0.06	0.09	0.28	0.30	0.10		18.40	0.28	42
4	0.007	0.010	0.10	0.11	0.03	0.006	17.9	0.05	0.20	0.05	1.02	0.00		20.92	0.10	25
5	0.011	0.012	0.12	0.12	0.02	0.004	19.6	0.07	0.17	0.19	1.89	0.02		23.19	0.14	18
6	0.010	0.013	0.08	0.15	0.02	0.003	22.1	0.05	0.13	0.38	1.11	0.04		24.51	0.12	20
21	0.009	0.009	0.18	0.30	0.02	0.001	15.5	0.07	0.13	0.03	0.30	0.45		17.10	0.63	88
22	0.013	0.012	0.14	0.39	0.02	0.004	19.1	0.06	0.10	0.21	0.00	0.47		20.10	0.61	65
23	0.008	0.011	0.15	0.25	0.02	0.005	18.1	0.10	0.05	0.31	0.30	0.85		18.90	1.00	80
24	0.015	0.009	0.42	0.45	0.02	0.002	16.8	0.07	0.01	0.28	0.43	0.05	0.0006	17.33	0.47	63
25	0.010	0.011	0.38	0.25	0.02	0.002	17.1	0.06	0.06	0.20	0.33	0.38		18.03	0.76	65
26	0.011	0.012	0.24	0.19	0.02	0.002	16.1	0.05	0.06	0.21	0.31	0.21		17.01	0.45	74
Steels Nos. 1 to 6 and 21 to 26 in Table 1 are reference examples																

[0018] An evaluation was therefore conducted with respect to how the corrosion depth is affected by two parameters, namely, $\text{Cr} + \text{Mo} + 10\text{Ti}$ and $\text{Si} + \text{Cu}$. The results are indicated in Table 1, FIG. 2 and FIG. 3. As shown in Table 1, FIG. 2 and FIG. 3, the ferritic stainless steels satisfying $\text{Cr} + \text{Mo} + 10\text{Ti}$ of 18 or greater and $\text{Si} + \text{Cu} \leq 0.5$ exhibited maximum corrosion depths of 20 μm or less. Moreover, even when $\text{Cr} + \text{Mo} + 10\text{Ti}$ gave a value of 18 or greater, a maximum corrosion depth exceeding 20 μm resulted if $\text{Si} + \text{Cu} \leq 0.5$ was not satisfied. On the other hand, in the case of an austenitic stainless steel, a maximum corrosion depth exceeding 50 μm resulted even when $\text{Cr} + \text{Mo} + 10\text{Ti}$ gave a value of 18 or greater because $\text{Si} + \text{Cu} \leq 0.5$ is not satisfied in the case of a general-purpose steel. Thus, it became clear that in the case where a wet and dry cyclic environment arises in a solution of low pH in which nitrate ions and sulfate ions are present at a predetermined rate or higher, a ferritic stainless steel satisfying $\text{Cr} + \text{Mo} + 10\text{Ti} \geq 18$ and $\text{Si} + \text{Cu} \leq 0.5$ has excellent corrosion resistance. Cr, Mo, Ti, Si and Cu in the Expressions here represent the contents (mass%) of the respective elements.

[0019] The reason for the maximum corrosion depth becoming small under the present test conditions at $\text{Cr} + \text{Mo} + 10\text{Ti}$ of 18 or greater is thought to be as follows.

[0020] When the passive film of a tested sample of corrosion depth of 20 μm or less in the present test was analyzed by AES, Ti was observed to be concentrated in the surface film in addition to Cr. Further, since the present wet and dry cyclic test is a cyclic corrosive environment of repeating generation of pitting and repassivation by concentrating and drying of a low pH test solution containing nitrate and sulfate ions, the corrosion mechanism of the present test is a corrosion mechanism dominated by pitting corrosion and the concentration of Cr and Ti in the passive film is thought to be effective.

[0021] As shown by the pitting resistance index PI value = $\text{Cr} + 3.3\text{Mo} + 16\text{N}$ known as general indicator of resistance to pitting corrosion, it is known that Mo also contributes to repassivation at the initial stage of pitting occurrence, and its effect was exhibited also in the present test environment, but its contribution ratio was found to be smaller than that of the PI value. Owing to these two mechanisms, it is considered that the maximum corrosion depth in the present test environment comes to be expressed by the index specified as $\text{Cr} + \text{Mo} + 10\text{Ti}$.

[0022] On the other hand, the reason for maximum corrosion depth becoming small at $\text{Si} + \text{Cu}$ of 0.5 or less is thought to be as follows. The causes assumed include that while Cu is an element that ordinarily enhances corrosion resistance by lowering dissolution rate of active state, the Cu in the steel elutes once corrosion occurs, so that particularly in an environment rich in nitrate ions acting as an oxidizer like the present test environment, the eluted Cu ions become Cu^{2+} oxidizer and promote cathodic reaction, thereby increasing the corrosion rate and enlarging corrosion depth.

[0023] As for the effect of Si, when the wet and dry cyclic test was conducted in the aforesaid test solution, precipitation of Si oxide was observed centered on the gas-liquid interface of the Si-containing test specimen, and occurrence of corrosion was observed in the vicinity thereof. From this, corrosion was thought to have been promoted by crevice corrosion occurring between the precipitates and the test specimen, and it was assumed that corrosion was still more accelerated owing to the presence of Cu^{2+} in the environment at that time. Moreover, although the result was that corrosion depth exceeded 20 μm also in austenitic stainless steels even when $\text{Cr} + \text{Mo} + 10\text{Ti}$ was 18 or greater, this was because Si and/or Cu are inevitably high in general-purpose austenitic stainless steels owing to the steelmaking conditions, so that hardly any are thought to achieve $\text{Si} + \text{Cu}$ of 0.5 or less.

[0024] In addition, austenitic stainless steels are higher in MnS and other water-soluble inclusions than ferritic stainless steel, and that is presumed also to be a reason for the high dissolution rate in the present test solution.

[0025] It should be noted that $\text{Cr} + \text{Mo} + 10\text{Ti}$ in the present case is 22 or greater. Further, $\text{Si} + \text{Cu}$ is less than 0.2.

[0026] The detailed designations of the compositional components of the stainless steel of the present invention are explained below.

[0027] Cr is the most important element for ensuring the corrosion resistance of a stainless steel, and at least 16% is necessary for stabilizing the ferrite structure. When Cr is increased, corrosion resistance also improves, but workability and productivity are diminished, so the upper limit is made 24%. It is desirably 18.5 to 23% and more desirably 19.0 to 22.0%.

[0028] Ti is generally a very important element that inhibits intergranular corrosion by fixing C and N and improves workability in the welds of a ferritic stainless steel. In addition, it is an important element from the aspect of corrosion resistance in the corrosion environment under consideration. Although the affinity of Ti for oxygen is very strong, in the present corrosive environment containing nitrate ions, it joins with Cr to form a film on the stainless steel surface, which was found to be very effective for inhibiting occurrence of pitting corrosion. For film-forming and fixing C and N as stabilizing elements, four or more times (C + N) is necessary. However, as excessive addition causes surface defects, its range is made 0.05 to 0.25%. It is more desirably made 0.08 to 0.2%.

[0029] Mo is effective for passive film repair and is a very effective element for improving corrosion resistance that has a pitting resistance improving effect especially when combined with Cr. Therefore, at least 0.30% of Mo must be included. When Mo is increased, corrosion resistance improves, but workability is decreased, while cost rises, so the upper limit is made 3%. It is more desirably 0.50 to 2.00%.

[0030] Cu may be contained as an unavoidable impurity at 0.01% or greater when scrap is used as raw material. In

the environment concerned, however, Cu is undesirable because it promotes corrosion. As pointed out earlier, this is assumed to be because eluted Cu ions promote cathodic reaction once corrosion starts. Therefore, the less Cu, the more desirable, and the range is made 0.4% or less. It is desirably 0.10% or less.

[0031] Si is an element unavoidably entrained from the raw material and is generally effective for both corrosion resistance and oxidation resistance, but in the environment under consideration, not only does it act to promote corrosion advance but excessive addition lowers workability and productivity. The upper limit is therefore made 0.4%. It is more desirably less than 0.2%. Moreover, around 0.05% or greater is usually unavoidably contained because extreme reduction increases cost.

[0032] In addition, the other chemical compositional components designated by the stainless steel of the present invention are explained in detail below.

[0033] C has effects of, inter alia, strength-improving and inhibiting crystal grain enlargement in combination with stabilizing elements but degrades intergranular corrosion resistance at weld zone and workability. As the content thereof must be reduced in a High-Purity Ferritic Stainless Steel, the upper limit is made 0.030%. It is desirably 0.002 to 0.020% because refining cost is made worse when reduced excessively.

[0034] N needs to be reduced in content because, like C, it degrades intergranular corrosion resistance and workability, and the upper limit is therefore made 0.030%. However, since excessive reduction makes refining cost worse, it is desirably 0.002 to 0.020%.

[0035] Mn is an important element as a deoxidation element but when added excessively facilitates generation of MnS that forms corrosion starting points, and also destabilizes the ferrite structure, so the content thereof is made 0.01 to 0.5%. It is more desirably 0.05 to 0.3%.

[0036] P must be held low because it not only lowers weldability and workability but also facilitates intergranular corrosion. Content thereof is therefore made 0.05% or less. It is more desirably 0.001 to 0.04%.

[0037] S forms the aforesaid CaS, MnS and other water-soluble inclusions that form corrosion starting points and therefore needs to be reduced. Content is therefore made 0.01% or less. However, it is more desirably 0.0001 to 0.006% because excessive reduction makes cost worse.

[0038] Al is important as a deoxidation element and also has an effect of refining the structure by controlling the composition of nonmetallic inclusions. However, when added excessively, it causes coarsening of nonmetallic inclusions and is also liable to form starting points for product defects. Therefore, the lower limit value is made 0.01% and the upper limit value 0.20%. It is more desirably 0.03% to 0.10%.

[0039] Nb, like Ti, is a very important element in the inhibition of intergranular corrosion at weld zone and improvement of workability by fixing C and N. Nb must therefore be added at 8 times or greater the sum of C and N (C + N). However, the range thereof is made 0.05 to 0.50% because excessive addition lowers workability. It is more desirably 0.1 to 0.3%.

[0040] One or two or more of Ni, B, and Sn may be added to the stainless steel of the present invention as required in addition to the compositional components set out above, while the presence of one of V and S is mandatory.

[0041] Ni inhibits dissolution rate of active state, and since it is very effective for passivation, is added as necessary at 0.3% or greater. However, the upper limit is made 3% because excessive addition not only lowers workability and destabilizes the ferrite structure but also makes cost worse. It is desirably 0.8 to 1.50%.

[0042] B is a boundary strengthening element effective for improving secondary working embrittlement and can therefore be added as necessary. However, excessive addition solid-solution strengthens the ferrite to become a cause of ductility degradation. Therefore, the lower limit is made 0.0001% and the upper limit 0.003%. It is more desirably 0.0002 to 0.0020%.

[0043] V improves rust resistance and crevice corrosion resistance, and since excellent workability can also be ensured if V is added while holding down use of Cr and Mo, it can be added as necessary. However, since excessive addition of V lowers workability, and further leads to saturation of the corrosion resistance effect, the lower limit of V is made 0.03% and the upper limit 1.0%. It is more desirably 0.05 to 0.50%.

[0044] Sn and Sb can also be added as necessary to ensure outflow rust resistance. These elements are important for inhibiting corrosion rate, but as excessive addition makes productivity and cost worse, the range of each is made 0.005 to 1.0%. It is more desirably 0.05 to 0.5%.

[0045] Moreover, although the steel product of the present invention is a steel that is usable in a heat exchanger and that can be given various forms such as steel sheet, shaped steel, rod, wire, tube and the like, it is produced chiefly as steel sheet. The steel of the composition set out in the aforesaid (1) or (2) is prepared by an ordinary melting-and-refining method using, for example, a converter, electric furnace or the like, conducting vacuum-refining or other secondary refining as required, and casting into a slab by continuous casting or casting into an ingot followed by rolling into a slab. The steel making and casting can be conducted in accordance with ordinary ferritic stainless steel making and casting. After heating, the slab is hot-rolled into a steel product of desired shape. The hot rolling conditions are not particularly restricted and the rolling can be conducted in accordance with the heating and rolling conditions for hot-rolling of an ordinary ferritic stainless steel. Moreover, in the case of a steel sheet, the hot-rolled steel sheet can as necessary further be descaled, annealed and thereafter cold rolled into a cold-rolled steel sheet, and further processed into a desired cold-

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rolled steel sheet by annealing, descaling and the like.

EXAMPLES

[0046] Steels having the chemical compositions shown in Table 2 were produced by an ordinary method of producing High-Purity Ferritic Stainless Steel. Specifically, 40 mm thick ingots were produced following in-vacuo melting and refining and these were rolled to 4 mm thickness by hot rolling. Next, heat treatment at 900 to 1000 °C x 1 min was conducted based on the respective recrystallization behaviors, whereafter scale was removed by grinding and steel sheets of 1.0 mm thickness were produced by cold rolling. As final-annealing, these were heat-treated at 900 to 1000 °C x 1 min based on the respective recrystallization behaviors and subjected to the following test. Note that the heat-treatment temperature was 1100 °C in the case of the austenitic stainless steels.

[0047] The wet and dry cyclic test was the same test as described earlier. The test solution was made nitrate ions NO_3^- : 100 ppm, sulfate ions SO_4^{2-} : 10 ppm, Cl⁻ ions: 10 ppm, and pH = 2.5. 10 ml of this test solution was placed in a test tube like that shown in FIG. 1, and the respective types of stainless steel samples cut to 1t x 15 x 100 mm and polished entire surfaces thereof using a wet emery paper with a grid of #600 were half-immersed therein so that about 1/2 the longitudinal direction thereof was immersed in the solution. The test tube containing the sample was placed in an 80 °C bath, and 24 hours later the dried out stainless steel sample was lightly washed with distilled water, whereafter the operation of again placing the test solution in a washed test tube once more, again half-immersing the sample, and holding at an 80 °C for 24 hours was repeated 14 cycles.

Table 2

No	Constituent contents (Mass%)																	Max. Min. corrosion depth / μm
	C	H	Si	Fe	P	S	Cr	Al	Ti	Mo	Cu	Ni	B	V	Sn	Sb	(A) Cr-Mo-Ni	
1	0.013	0.011	0.25	0.36	0.02	0.0022	16.5	0.07	0.15	0.19	0.31	0.19					10.31	0.44
2	0.010	0.013	0.16	0.16	0.02	0.0015	18.6	0.07	0.19	0.50	0.69	0.30					21.19	0.46
3	0.006	0.010	0.10	0.14	0.02	0.0010	17.2	0.06	0.09	0.28	0.30	0.10					10.40	0.28
4	0.007	0.010	0.10	0.11	0.03	0.0061	17.9	0.05	0.20	0.05	1.02	0.00					20.92	0.10
5	0.011	0.012	0.12	0.12	0.02	0.0035	19.6	0.07	0.17	0.19	1.09	0.02					23.19	0.14
6	0.010	0.013	0.08	0.15	0.02	0.0032	22.1	0.05	0.13	0.30	1.11	0.04					24.51	0.12
7	0.009	0.009	0.19	0.16	0.02	0.0039	22.6	0.07	0.11	0.31	1.15	0.05					24.05	0.24
8	0.006	0.010	0.11	0.12	0.03	0.0015	19.3	0.02	0.18	0.19	1.89	0.02					22.99	0.13
9	0.008	0.011	0.15	0.20	0.02	0.0010	10.5	0.08	0.09	0.25	0.32	0.01					19.72	0.16
10	0.006	0.009	0.11	0.22	0.02	0.0025	19.3	0.09	0.17	0.12	1.05	0.02					22.05	0.13
11	0.009	0.013	0.06	0.16	0.02	0.0033	18.5	0.02	0.12	0.18	0.95	0.01					20.65	0.07
12	0.010	0.008	0.12	0.15	0.02	0.0015	19.2	0.10	0.11	0.32	0.45	0.15	0.0005				20.75	0.27
13	0.008	0.010	0.11	0.14	0.02	0.0030	23.3	0.07	0.15	0.29	0.35	0.01	0.0009				25.15	0.12
14	0.009	0.009	0.16	0.23	0.02	0.0009	18.6	0.09	0.20	0.42	1.50	0.15		0.04			22.10	0.31
15	0.005	0.006	0.06	0.10	0.02	0.0015	19.0	0.04	0.15	0.25	1.10	0.02		0.2			21.60	0.08
16	0.005	0.008	0.15	0.15	0.02	0.0028	22.2	0.08	0.13	0.22	0.56	0.01		0.07			24.06	0.16
17	0.011	0.014	0.13	0.30	0.02	0.0011	19.1	0.04	0.11	0.19	1.10	0.01			0.51		21.30	0.14
18	0.009	0.012	0.22	0.22	0.02	0.0065	22.0	0.05	0.15	0.33	0.95	0.18				0.35	24.45	0.40
19	0.010	0.010	0.11	0.12	0.02	0.0009	18.5	0.09	0.17	0.24	2.01	0.10			0.33		22.21	0.21
20	0.006	0.006	0.14	0.23	0.02	0.0018	19.3	0.06	0.20	0.38	1.59	0.02			0.25	0.31	22.89	0.16
21	0.009	0.004	0.10	0.30	0.02	0.0010	15.5	0.07	0.13	0.03	0.30	0.45					17.10	0.63
22	0.013	0.012	0.14	0.39	0.02	0.0036	19.1	0.06	0.10	0.21	0.00	0.47					20.10	0.61
23	0.008	0.011	0.15	0.25	0.02	0.0045	10.1	0.10	0.05	0.31	0.30	0.95					18.90	1.00
24	0.015	0.009	0.42	0.45	0.02	0.0022	16.0	0.07	0.01	0.28	0.43	0.05	0.0006				17.33	0.47
25	0.010	0.011	0.30	0.25	0.02	0.002	17.1	0.06	0.06	0.20	0.33	0.38					18.02	0.76
26	0.011	0.012	0.24	0.19	0.02	0.002	16.1	0.05	0.06	0.21	0.31	0.21					17.01	0.45
27	0.007	0.011	0.13	0.21	0.02	0.0019	16.2	0.05	0.02	0.22	0.01	0.01					16.41	0.14
28	0.014	0.022	0.53	0.81	0.03	0.0034	18.1	0.01	0.01	0.01	2.01	0.25					20.11	0.70
29	0.059	0.033	0.51	1.00	0.03	0.0064	18.2	0.03	0.01	0.00	0.15	0.29					18.45	0.00

*Underlining indicates not within the range of the present invention.

[0048] In Table 2, Nos. 16 and 20 are invention examples, Nos. 1 to 15 and 17 to 19 are reference examples, and Nos. 21 to 29 are comparative examples. Numerical values outside the ranges of the present invention are underlined. Further, the results of Table 2 are indicated in FIG. 4. As shown in Table 2 and FIG. 4, the result was that the maximum corrosion depth was 50 μm or less with respect to all of the examples which contained components in the ranges of the invention and further satisfied the

[0049] ranges of Expression A) : $\text{Cr} + \text{Mo} + 10\text{Ti} \geq 18$ and Expression B) : $\text{Si} + \text{Cu} \leq 0.5$. It should be noted that the examples that satisfied 20 or greater for Expression A) and less than 0.3 for Expression E) had still smaller maximum corrosion depths, and the invention examples that satisfied 22 or greater for Expression A) and less than 0.2 for Expression B) exhibited outstandingly excellent corrosion resistance results of a maximum corrosion depth of 20 μm or less.

[0050] On the other hand, under conditions that did not satisfy one or both of Expressions (A) and (B), the result was that maximum corrosion depth exceeded 50 μm in all cases. From the foregoing results, it became clear that the present invention makes it possible to provide a ferritic stainless steel excellent in corrosion resistance in an environment of condensed water arising from hydrocarbon combustion exhaust gas equivalent to that of a secondary heat exchanger.

INDUSTRIAL APPLICABILITY

[0051] The present invention can be applied as a material for a heat exchanger, particularly a material for the secondary heat exchanger of a latent heat recovery type water heater. Specifically, it can be applied as a material not only for the case and partitions but also for the heat exchanger pipes and the like. In addition, the present steel can be similarly provided not only for combustion exhaust gas of a hydrocarbon fuel but broadly for any wet and dry cyclic environment where there is exposure to a solution of low pH containing nitrate ions and sulfate ions. Specifically, application is to various types of heat exchangers, outdoor external facing materials for acid rain environments, construction materials, roofing materials, outdoor machinery, water and heated water storage tanks, home appliances, bath tubs, kitchen equipment, and other general outdoor and indoor purposes.

EXPLANATION OF REFERENCE SYMBOLS

[0052]

- 1 Test tube
- 2 Sample
- 3 Test solution

Claims

1. A highly corrosion resistant ferritic stainless steel excellent in corrosion resistance in a condensed water environment arising from a hydrocarbon combustion exhaust gas **characterized in** comprising, in mass%, C: 0.030% or less, N: 0.030% or less, Si: 0.4% or less, Mn: 0.01 to 0.5%, P: 0.05% or less, S: 0.01% or less, Cr: 16 to 24%, Mo: 0.30 to 3%, Ti: 0.05 to 0.25%, Nb: 0.05 to 0.50%, Al: 0.01 to 0.20%, Cu: 0.4% or less, one of V: 0.03 to 1.0% and Sb: 0.005 to 1.0%, and optionally further comprising, in mass%, one or two or more of Ni: 0.3 to 3%, B: 0.0001 to 0.003% and Sn: 0.005 to 1.0% and the balance being Fe and unavoidable impurities, and satisfying Expression (A): $\text{Cr} + \text{Mo} + 10\text{Ti} \geq 22$ and Expression (B): $\text{Si} + \text{Cu} < 0.2$, where Cr, Mo, Ti, Si and Cu in the Expressions represent the contents (mass%) of the respective elements.
2. A highly corrosion resistant ferritic stainless steel excellent in corrosion resistance in a condensed water environment arising from a hydrocarbon combustion exhaust gas as set out in claim 1, **characterized by** further comprising, in mass%, one or two or more among Ni: 0.3 to 3%, B: 0.0001 to 0.003% and Sn: 0.005 to 1.0%.
3. A highly corrosion resistant ferritic stainless steel excellent in corrosion resistance in a condensed water environment arising from a hydrocarbon combustion exhaust gas as set out in claim 1 or 2, **characterized in that** after conducting 14 cycles of a wet and dry cyclic test of half-immersing a test specimen of the steel set out in claim 1 or 2 in an aqueous solution of pH 2.5 and containing 100 ppm nitrate ions, 10 ppm sulfate ions and 10 ppm chloride ions and holding it at 80 °C for 24 hours, maximum corrosion depth is 20 μm or less.

Patentansprüche

1. Ein hochkorrosionsbeständiger ferritischer rostfreier Stahl mit ausgezeichneter Korrosionsbeständigkeit in einer Umgebung mit Kondenswasser, das aus einem Kohlenwasserstoffverbrennungsabgas stammt, **dadurch gekennzeichnet, dass** er in Massen-% umfasst: C: 0,030% oder weniger, N: 0,030% oder weniger, Si: 0,4% oder weniger, Mn: 0,01 bis 0,5%, P: 0,05% oder weniger, S: 0,01% oder weniger, Cr: 16 bis 24%, Mo: 0,30 bis 3%, Ti: 0,05 bis 0,25%, Nb: 0,05 bis 0,50%, Al: 0,01 bis 0,20%, Cu: 0,4% oder weniger, eines von V: 0,03 bis 1,0% und Sb: 0,005 bis 1,0%, und darüber hinaus gegebenenfalls umfassend in Massen-% ein oder zwei oder mehr von Ni: 0,3 bis 3%, B: 0,0001 bis 0,003% und Sn: 0,005 bis 1,0% und wobei der Rest Fe und unvermeidbare Verunreinigungen ist, und der den Ausdruck (A):

$$\text{Cr} + \text{Mo} + 10 \text{ Ti} \geq 22$$

und den Ausdruck (B):

$$\text{Si} + \text{Cu} < 0.2$$

erfüllt, wobei Cr, Mo, Ti, Si und Cu in den Ausdrücken die Gehalte (in Massen-%) der jeweiligen Elemente sind.

2. Ein hochkorrosionsbeständiger ferritischer rostfreier Stahl mit ausgezeichneter Korrosionsbeständigkeit in einer Umgebung mit Kondenswasser, das aus einem Kohlenwasserstoffverbrennungsabgas stammt, gemäß Anspruch 1, **dadurch gekennzeichnet, dass** er darüber hinaus, in Massen-%, eines oder zwei oder mehrere von Ni: 0,3 bis 3%, B: 0,0001 bis 0,003% und Sn: 0,005 bis 1,0% umfasst.
3. Ein hochkorrosionsbeständiger ferritischer rostfreier Stahl mit ausgezeichneter Korrosionsbeständigkeit in einer Umgebung mit Kondenswasser, das aus einem Kohlenwasserstoffverbrennungsabgas stammt, gemäß Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** nach Durchführung von 14 Zyklen eines nassen und trockenen zyklischen Test des zur Hälfte Eintauchens eines Prüfstücks des Stahls gemäß Anspruch 1 oder 2 in eine wässrige Lösung mit pH 2,5, die 100 ppm Nitrat-Ionen, 10 ppm Sulfat-Ionen und 10 ppm Chlorid-Ionen enthält, und des Haltens desselben bei 80 °C für 24 Stunden, die maximale Korrosionstiefe 20 µm oder weniger beträgt.

Revendications

1. Acier inoxydable ferritique résistant fortement à la corrosion d'excellente résistance à la corrosion dans un environnement d'eau condensée provenant d'un gaz d'échappement de combustion d'hydrocarbures **caractérisé en ce qu'il** comprend, en % en masse, C : 0,030 % ou inférieur, N : 0,030 % ou inférieur, Si : 0,4 % ou inférieur, Mn : 0,01 à 0,5 %, P : 0,05 % ou inférieur, S : 0,01 % ou inférieur, Cr : 16 à 24 %, Mo : 0,30 à 3 %, Ti : 0,05 à 0,25 %, Nb : 0,05 à 0,50 %, Al : 0,01 à 0,20 %, Cu : 0,4 % ou inférieur, un parmi V : 0,03 à 1,0 % et Sb : 0,005 à 1,0 %, et comprenant de plus éventuellement, en % en masse, un ou deux ou plusieurs parmi Ni : 0,3 à 3 %, B : 0,0001 à 0,003 % et Sn : 0,005 à 1,0 % et le reste étant Fe et des impuretés inévitables, et satisfaisant l'expression (A) : $\text{Cr} + \text{Mo} + 10 \text{ Ti} \geq 22$ et l'expression (B) : $\text{Si} + \text{Cu} < 0,2$, dans lequel Cr, Mo, Ti, Si et Cu dans les expressions représentent les teneurs (% en masse) des éléments respectifs.
2. Acier inoxydable ferritique résistant fortement à la corrosion d'excellente résistance à la corrosion dans un environnement d'eau condensée provenant d'un gaz d'échappement de combustion d'hydrocarbures selon la revendication 1, **caractérisé en ce qu'il** comprend de plus, en % en masse, un ou deux ou plusieurs parmi Ni : 0,3 à 3 %, B : 0,0001 à 0,003 % et Sn : 0,005 à 1,0 %.
3. Acier inoxydable ferritique fortement résistant à la corrosion d'excellente résistance à la corrosion dans un environnement d'eau condensée provenant d'un gaz d'échappement de combustion d'hydrocarbures selon la revendication 1 ou 2, **caractérisé en ce qu'**après avoir réalisé 14 cycles d'un test cyclique humide et sec de semi-immersion d'un échantillon de test de l'acier selon la revendication 1 ou 2 dans une solution aqueuse de pH 2,5 et contenant 100 ppm d'ions nitrate, 10 ppm d'ions sulfate et 10 ppm d'ions chlorure et de maintien de celui-ci à 80°C pendant 24

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heures, la profondeur maximale de corrosion est de 20 μm ou inférieure.

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Fig.1(a)

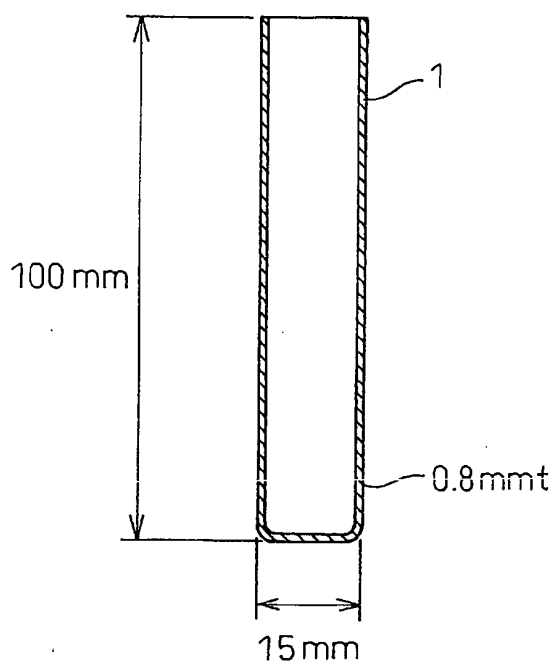


Fig.1(b)

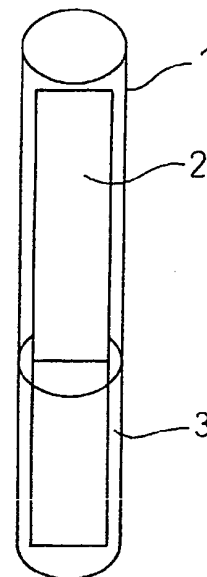


Fig.2

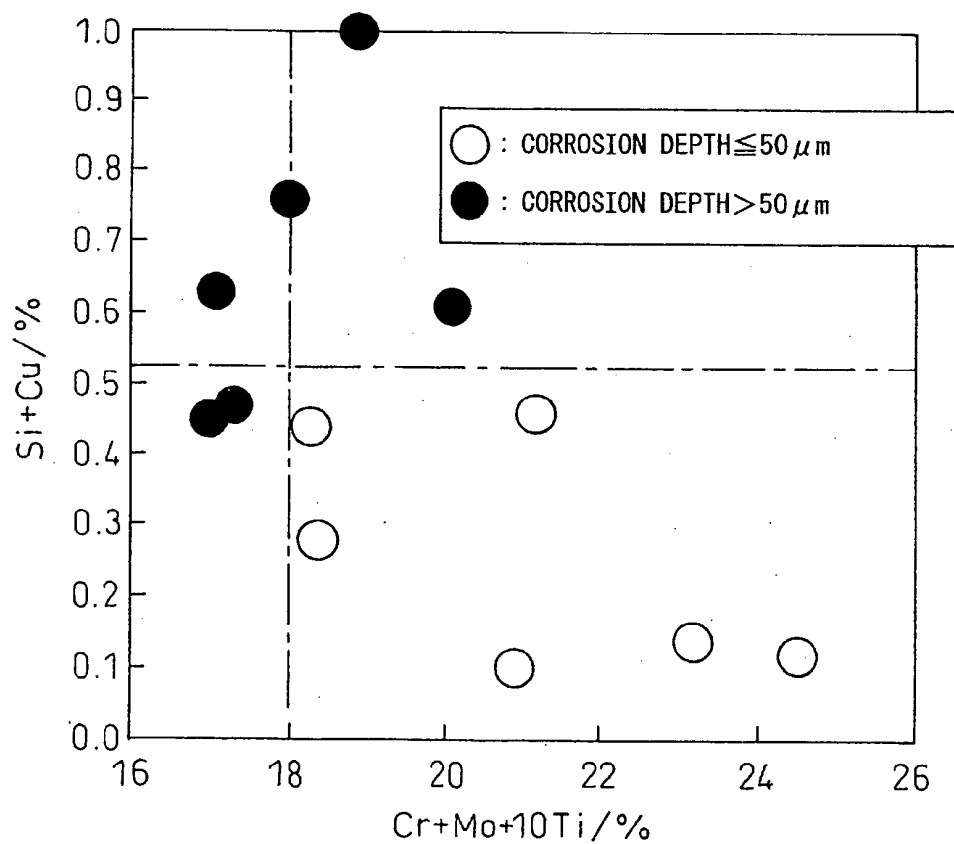


Fig.3

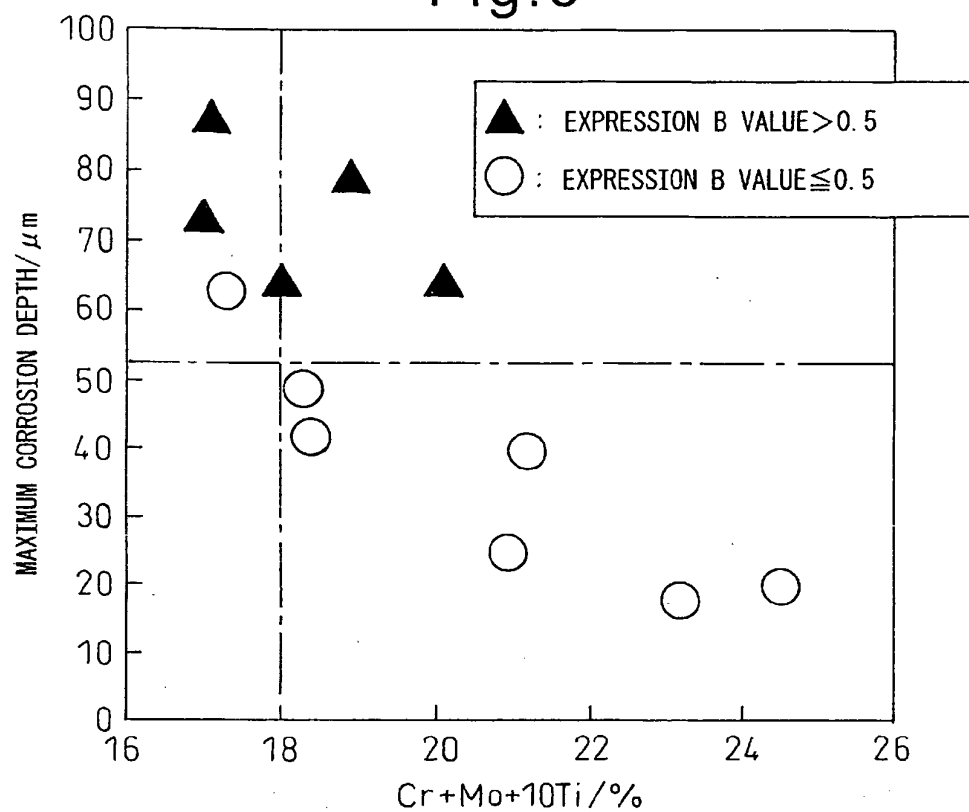
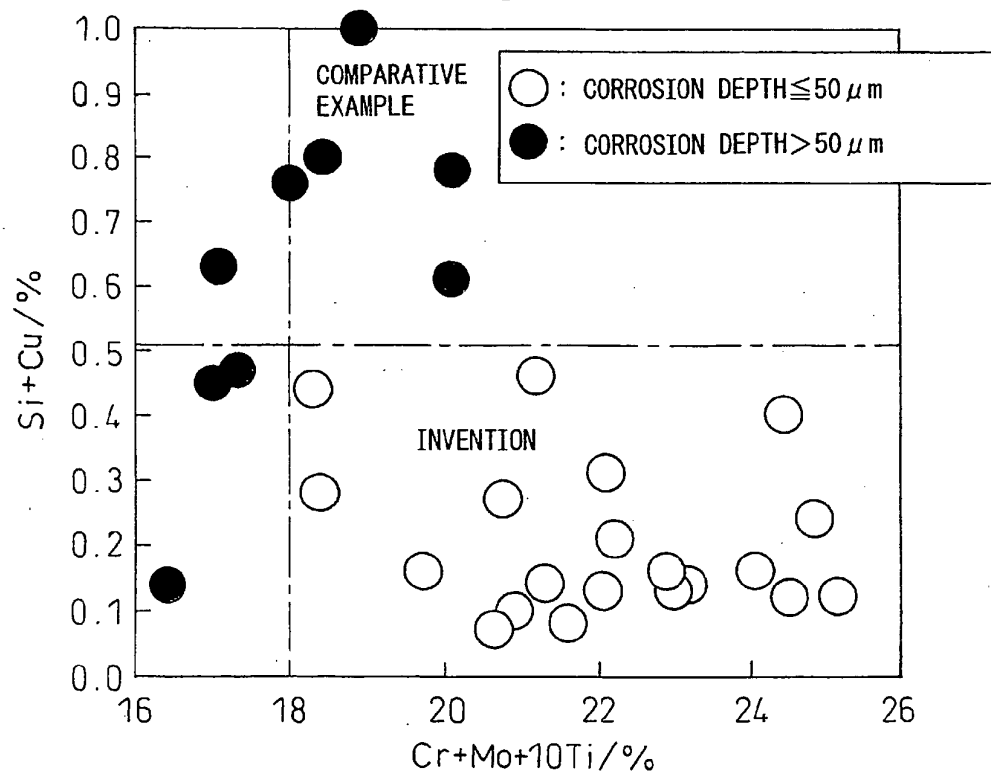


Fig.4



REFERENCES CITED IN THE DESCRIPTION

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