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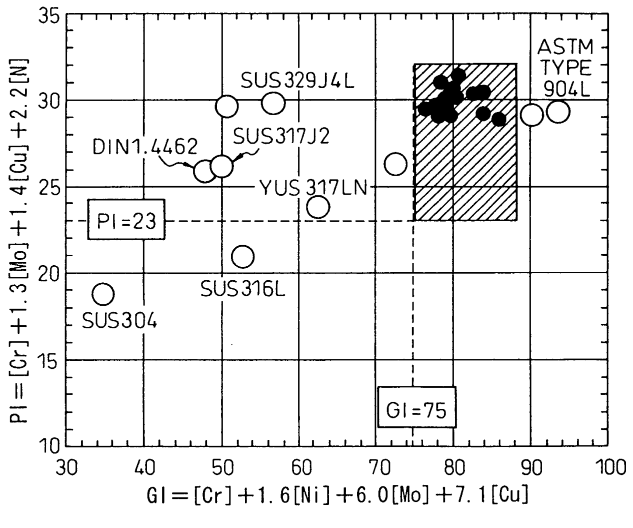
(54) Steel for chemical tank, excellent in sulfuric acid corrosion resistance and pitting corrosion resistance

(57) The present invention provides a steel for a chemical tank, the steel suppressing the generation of corrosion damage by sulfuric acid and pitting corrosion by salt water, and is a steel for a chemical tank, the steel being excellent in sulfuric acid corrosion resistance and pitting corrosion resistance, characterized in that: the steel contains, by mass, C: 0.003 to 0.05%, Si: not more than 5%, Mn: not more than 2%, P: not more than 0.03%, S: not more than 0.010%, O: not more than 0.0050%, Cr: 18 to 25%, Ni: 10 to 20%, Mo: 1.0 to 4.5%, Cu: 1.0 to 3.0%, and N: 0.05 to 0.3%, with the balance consisting of Fe and unavoidable impurities; the GI value defined by the expression GI = [Cr] + 1.6 x [Ni] + 6.0 x [Mo] + 7.1 x [Cu] is in the range from 75 to 88, wherein the relevant components are expressed in terms of a mass percent; and the PI value defined by the expression PI = [Cr] + 1.3 x [Mo] + 1.4 x [Cu] + 2.2 x [N] is in the range from 23 to 32, wherein the relevant components are expressed in terms of mass percent.

Fig.5



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Description

[0001] The present invention, with respect to a tank used for storage and transportation of crude sulfuric acid, provides a steel for the tank capable of preventing corrosion caused by crude sulfuric acid that remains stuck to the wall of the tank when crude sulfuric acid is discharged from the tank and preventing, to the utmost, pitting corrosion caused by salt water, such as natural seawater, that is used for cleaning the tank.

[0002] A carbon steel, a low alloy steel, a stainless steel, an Ni-base alloy and the like have so far been properly selected and used for a tank or a similar container that is used for storage and transportation of crude sulfuric acid, depending on the concentration and/or temperature of sulfuric acid. In particular, with respect to a chemical tanker that is loaded with various kinds of raw materials for chemicals, raw materials for food, oils and fats, organic solvents, etc., a stainless steel such as an SUS 304 steel or an SUS 316L steel, which has generally been regarded as a material having good corrosion resistance, has been widely used as a material for a tank because of the broad variety of the cargoes.

[0003] However, the corrosion damages that a tank material incurs are mostly caused by general corrosion by crude sulfuric acid and the incident of corrosion by other chemicals are few. Salt water such as seawater is generally employed for cleaning the interior of a tank after a cargo is discharged. In that case, when a water rinse and drying in the subsequent processes are incomplete, local corrosion such as pitting corrosion occurs caused by the residue of seawater components (chloride ions) occurs on the surface of a tank material and much time and labor are required for the repair. This constitutes a problem.

[0004] An austenitic stainless steel having sulfuric acid corrosion resistance is disclosed in

[0005] JP-A- 10-18004 and JP-A-11-189848, for example. However, the stainless steel is a material that is applied to a boiler in a thermal power plant, a flue or a stack. Further, an austenitic stainless steel capable of suppressing corrosion by chlorine ions is disclosed in

[0006] JP-A-62-247049, for example. However, the stainless steel is a corrosion resistant material used in a wet-type phosphoric acid manufacturing process. The technologies disclosed in the above documents cannot solve the aforementioned problems that plauge a material for a chemical tanker.

[0007] The present invention provides a stainless steel material capable of avoiding general corrosion (weight loss corrosion) by crude sulfuric acid and pitting corrosion by residual chloride ions, and relates to a stainless steel for a chemical tank, capable of securing the safety of the relevant tank for a long period of time and minimizing the maintenance of the tank.

[0008] Firstly, the present inventors, from the above viewpoint, applied exposure tests to various kinds of stainless steels in crude sulfuric acid and in salt water, namely in the environments wherein the materials were exposed. That is, each of the stainless steels was once dipped in crude sulfuric acid and in salt water and then exposed in the upper space (hereinafter referred to as a vapor phase space), and the state of corrosion was observed. As a separate test, the general corrosion rates of each of the stainless steels in sulfuric acid solutions having various concentrations were measured and also the pitting corrosion potential (conforming to JIS G0577) of each of the stainless steels in salt water was measured.

[0009] As a result of the above intensive studies, the present inventors came to specify the alloying components of a stainless steel capable of suppressing, to the utmost, both the general corrosion by sulfuric acid contained in a tank for storage and transportation and the pitting corrosion by salt water, both corrosions having been the problems in the past, and established the present invention.
The object of the present invention can be achieved by the features specified in the claims.

[0010] The gist of the present invention is as follows:

(1) A steel for a chemical tank, the steel being excellent in sulfuric acid corrosion resistance and pitting corrosion resistance, characterized in that:

the steel contains, by mass,

C: 0.003 to 0.05%,
Si: not more than 5%,
Mn: not more than 2%,
P: not more than 0.03%,
S: not more than 0.010%,
O: not more than 0.0050%,
Cr: 18 to 25%,
Ni: 10 to 20%,
Mo: 1.0 to 4.5%,

Cu: 1.0 to 3.0%, and
N: 0.05 to 0.3%,

with the balance consisting of Fe and unavoidable impurities;

the GI value (General Corrosion Resistance Index) defined by the following expression is in the range from 75 to 88,
GI = [Cr] + 1.6 x [Ni] + 6.0 x [Mo] + 7.1 x [Cu], wherein the relevant components are expressed in terms of a mass percent; and
the PI value (Pitting Corrosion Resistance Index) defined by the following expression is in the range from 23 to 32,

PI = [Cr] + 1.3 x [Mo] + 1.4 x [Cu] + 2.2 x [N], wherein the relevant components are expressed in terms of a mass percent.

(2) A steel for a chemical tank, the steel being excellent in sulfuric acid corrosion resistance and pitting corrosion resistance, according to the item (1), characterized in that the steel further contains, in mass, one or more of

W: not more than 3%,
V: not more than 4%,
Co: not more than 2%, and
Ti: not more than 1%.

(3) A steel for a chemical tank, the steel being excellent in sulfuric acid corrosion resistance and pitting corrosion resistance, according to the item (1) or (2), characterized in that:

the steel further contains either or both of Ca and Ce at 0.001 to 0.03% in mass;
the δcal value defined by the following expression is in the range from -20 to 16,
δcal = 3 x ([Cr] + 1.5 x [Si] + [Mo]) - 2.8 ([Ni] + 0.5 x [Mn] + 30 x [C] + 30 x [N] + 0.5 x [Cu]) - 19.8, wherein the relevant components are expressed in terms of a mass percent; and
the value of the expression [S] + [O] - 0.8 x [Ca] - 0.3 x [Ce] is not more than 40, wherein the relevant components are expressed in terms of a mass ppm (1 mass ppm = 0.0001 mass percent).

[0011] The feature of the present invention is to regulate a GI value and a PI value on the bases of the combined addition of the five components, Cr, Ni, Mo, Cu and N, for securing corrosion resistance in the environments of sulfuric acid and salt water (satisfying both the sulfuric acid corrosion resistance and the pitting corrosion resistance).
The invention is described in more detail in connection with the drawings.

[0012] Fig. 1 is a graph showing the relation between the sulfuric acid concentrations and the times during which the sulfuric acid is left in the air as it is, the sulfuric acid concentrations being calculated by measuring the change of the weight increase with the passage of time when crude sulfuric acid having a sulfuric acid concentration of 95% is taken out in the glass petri dishes by the precise volume of 0.1, 1 and 10 ml respectively and the dishes are left in the air as they are. The sulfuric acid concentrations drastically drop as the volumes of sulfuric acid decrease.

[0013] Fig. 2 is a graph showing the relation between the instantaneous corrosion rates of the SUS 316L stainless steel and the times during which the stainless steel is left in the air, as it is, when crude sulfuric acid having a sulfuric acid concentration of 95% is dripped on the surface of the SUS 316L stainless steel at the volume of 0.1 ml and the stainless steel is left in the air, as it is. The maximum corrosion rate appears at the time when about 30 minutes have passed after the stainless steel is left in the air. It is understood that the sulfuric acid concentration at the time is about 50% by referring to Fig. 1.

[0014] Fig. 3 is a graph showing the relation between the general corrosion rates and the GI values when the comparative steels are immersed in the sulfuric acid aqueous solution of 50% concentration at 40°C. The figure shows that a corrosion rate of not more than 1 mm/y., at which a steel can sufficiently stand actual use, is obtained so long as a GI value is not less than 75.

[0015] Fig. 4 is a graph showing the relation between the pitting corrosion potentials and the PI values, the pitting corrosion potential being measured in a 3.5%-NaCl solution at 40°C by using a method conforming to the method specified in JIS G0577. In any stainless steel having the PI value not less than 23, pitting corrosion is not generated and an oxygen evolution potential caused by the electrolysis of water is observed.

[0016] Fig. 5 is a graph showing the relation between the GI values and the PI values of the invention steels and the comparative steels. The area that conforms to the present invention is shaded with oblique lines. The invention steels and the comparative steels in Table 1 are shown by the symbols ● and ○ respectively.

[0017] The present inventors studied in detail the corrosion phenomena of stainless steels which corrosion phenomena occurred in the environments of crude sulfuric acid and salt water. That is, each of the stainless steels was once immersed in crude sulfuric acid or in salt water, thereafter pulled out from the solution into the open air, and left as it was for some time, and then the corrosion state of the stainless steel surface was investigated. As a result, it was found that the color of the surface of any stainless steel treated in crude sulfuric acid changed from gray to black and the corrosion proceeded under the discolored surface. Afterward, it was suggested that the phenomenon was based on self-dilution of sulfuric acid (refer to H. Bablik "Iron Age", 123, 879 (1929)).

[0018] Thereafter, the present inventors, with intent to clarify the self-dilution of sulfuric acid, investigated the influence of the time during which crude sulfuric acid was left in the air as it was on the sulfuric acid concentration when prescribed volumes of crude sulfuric acid having a sulfuric acid concentration of 95% were taken out in glass petri dishes and the dishes were left in the air as they were. As a result, it was found that, as shown in Fig. 1, the crude sulfuric acid absorbed water in the air (moisture) and was diluted with the passage of time, and that, in particular, the concentration lowered in a short time as the initial volume of sulfuric acid decreased.

[0019] Another experiment was carried out wherein 0.1 ml of crude sulfuric acid having a sulfuric acid concentration of 95% was dripped on the surface of the SUS 316L stainless steel and the stainless steel was left in the air as it was. As a result, as shown in Fig. 2, it was found that the corrosion rate of the SUS 316L stainless steel increased at a time when about 30 minutes to one hour had passed after the steel sheet was left in the air.

[0020] Consequently, the present inventors acquired the knowledge that sulfuric acid in crude sulfuric acid was diluted by absorbing moisture in the air and a stainless steel was corroded by the diluted sulfuric acid. Then, the present inventors found that the sulfuric acid concentration that created the most violent corrosion of a stainless steel was 50% and, on the basis of the finding, carried out the corrosion loss measurement test in a sulfuric acid solution of 50% concentration at 40°C.

[0021] Concretely, stainless steels were experimentally produced by using steels containing 18% Cr, 12% Ni, 3% Mo, 1% Cu and 0.1% N as the base steels and by varying the amounts of Cr, Ni, Mo, Cu and N, the dependence of the corrosion rates on the amounts of those alloying elements was clarified by statistically applying the multiple regression analysis to those alloying elements, and, by so doing, the General Corrosion Resistance Index (GI) was established.

[0022] The General Corrosion Resistance Index obtained is as follows:

$$\text{GI (General Corrosion Resistance Index)} = [\text{Cr}] + 1.6 \times [\text{Ni}] + 6.0 \times [\text{Mo}] + 7.1 \times [\text{Cu}].$$

[0023] It was clarified from the GI that the combined addition of Ni, Mo and Cu was extremely effective for the improvement of general corrosion resistance but the addition of N had no influence on general corrosion resistance. The relation between the GI values obtained and the corrosion rates of the various kinds of actually used stainless steels is shown in Fig. 3.

[0024] In actual applications, a stainless steel can stand actual use with no problems as long as a corrosion rate is not more than 1 mm/y. On the basis of the fact, the threshold GI value beyond which a corrosion rate was not more than 1 mm/y. was examined from Fig. 3. As a result, it was clarified that general corrosion resistance could sufficiently be secured when a GI value was not less than 75.

[0025] Next, with respect to salt water, considering the fact that salt condensed by the evaporation of water after a stainless steel was pulled up from salt water into a vapor phase space and that red rust appeared in the vicinity of the portions where salt condensed and led to pitting corrosion, pitting corrosion potentials were measured electrochemically in a 3.5%-NaCl solution at 40°C in a manner conforming to the method specified in JIS G0577 (except for the temperature being 40°C).

[0026] Concretely, stainless steels were experimentally produced by using steels containing 18% Cr, 12% Ni, 3% Mo, 1% Cu and 0.1% N as the base steels and by varying the amounts of Cr, Ni, Mo, Cu and N, the dependence of the pitting corrosion potentials (Vc', 100) on the amounts of those alloying elements was clarified by statistically applying the multiple regression analysis to those alloying elements, and, by so doing, the Pitting Corrosion Resistance Index (PI) was established.

[0027] The Pitting Corrosion Resistance Index obtained is as follows:

$$\text{PI (Pitting Corrosion Resistance Index)} = [\text{Cr}] + 1.3 \times [\text{Mo}] + 1.4 \times [\text{Cu}] + 2.2 \times [\text{N}].$$

[0028] It was clarified from PI that the combined addition of Mo, Cu and N was extremely effective for the improvement of pitting corrosion resistance but the addition of Ni had a little influence on pitting corrosion resistance. The relation between the PI values obtained and the pitting corrosion potentials of the various kinds of actually used stainless steels is shown in Fig. 4. From the relationships, it was clarified that, when a PI value was not less than 23, pitting corrosion did not occur at all but the electrolysis of water occurred on the surface of a stainless steel, eliminating the dependence of a pitting corrosion potential on the amounts of alloying elements, and that the pitting corrosion resistance could sufficiently be secured when a PI value was not less than 23.

[0029] The present inventors, aiming to clarify the components of a stainless steel material appropriate for suppressing the corrosion of the stainless steel to the utmost, studied the influence of the kinds and amounts of alloying components on the general corrosion of a stainless steel in sulfuric acid and a pitting corrosion potential in salt water. As a result of the intensive study, the present inventors specified the appropriate kinds and amounts of alloying components and thus established the present invention.

[0030] The reasons for limiting the requirements constituting the present invention are described hereunder. The contents of the components are expressed in terms of a mass percent.

[0031] C is required to be contained to some extent from the viewpoint of securing strength, though it is detrimental to the corrosion resistance of a stainless steel. The production cost increases with an ultra-low C amount of less than 0.003%. On the other hand, when a C amount exceeds 0.05%, pitting corrosion resistance markedly deteriorates. Therefore, the C content was determined to be in the range from 0.003 to 0.05%.

[0032] Si improves corrosion resistance of a stainless steel in a sulfuric acid environment and is also an element effective for securing oxidation resistance. However, when an Si amount exceeds 5%, hot workability deteriorates considersbly. Therefore, the Si amount was set at not more than 5.0%.

[0033] Mn is an element able to stabilize austenite and can be added as a substitute for expensive Ni. However, a Mn amount exceeding 2.0% has no effect on corrosion resistance in salt water, which is one of the subjects of the present invention. Therefore, the Mn amount was set at not more than 2.0% as the upper limit not causing a bad influence on pitting corrosion resistance.

[0034] It is preferred that as little P as possible is added from the viewpoints of pitting corrosion resistance and hot workability. When a P amount exceeds 0.03%, hot workability deteriorates extremely. Therefore, the P amount was set at not more than 0.03%.

[0035] S is an element that substantially influences not only corrosion resistance but also hot workability, and the smaller the amount, the better. Therefore, the S amount was set at not more than 0.010%.

[0036] O, like S, is an element that substantially influences hot workability, and the smaller the amount, the better. Therefore, the O amount was limited to not more than 0.0050% that was the amount obtainable in an ordinary steelmaking method of a stainless steel.

[0037] Cr is a basic component in the present invention and is added in the form of coexistence with Ni, Mo, Cu and N. Cr is required to be added at not less than 18% for securing a good corrosion resistance in sulfuric acid and in salt water even if Mo, N, V and W coexist with Cr. Though corrosion resistance improves as a Cr amount increases, if it exceeds 25%, then the production of a stainless steel becomes somewhat difficult and the cost thereof becomes rather expensive. Therefore, the Cr amount was limited in the range from 18 to 25%.

[0038] Ni, similarly to Cr, Mo, Cu and N, is a basic component in a stainless steel according to the present invention and is necessary for securing corrosion resistance in sulfuric acid. In addition, it is necessary to make a metallographic structure an austenite phase in order to facilitate the production of a stainless steel plate, and, in that sense, an addition of Ni is inevitable. The minimum Ni amount required for securing an austenite phase in a stainless steel according to the present invention is 10%. When an Ni amount is excessive, not only the cost of a stainless steel increases but also the production thereof becomes difficult. Therefore, the upper limit of the Ni amount was determined to be 20% as the largest amount required to maintain an austenite phase at a low cost.

[0039] Mo, similarly to Cr, Ni, Cu and N, is a basic component in a stainless steel according to the present invention and is an element indispensable for securing high corrosion resistance in a sulfuric acid environment and in a salt-water environment. The effect appears when an addition amount of Mo is in the range from 1.0 to 4.5% and Mo coexists with Cr and N. When an Mo amount is less than 1.0%, corrosion resistance is insufficient. However, if an Mo amount exceeds 4.5%, the corrosion resistance improvement effect is saturated and the cost increases.

[0040] Cu is an element indispensable for obtaining a high corrosion resistance in a sulfuric acid environment and in a salt-water environment while coexisting with Cr, Ni, Mo and N. The effect of the coexistence of Cu with those elements becomes conspicuous when Cu is added by not less than 1.0%. On the other hand, when a Cu amount exceeds 3.0%, corrosion resistance is saturated and hot workability is deteriorated. Therefore, the Cu amount was limited in the range from 1.0 to 3.0%.

[0041] N is added as a basic component in the form of coexistence with Cr, Ni, Mo and Cu. N is a strong austenite forming element and, at the same time, is also an element that hinders the progress of pitting corrosion occurring on a stainless steel. An N amount of not less than 0.05% is necessary for obtaining pitting corrosion resistance stably. However, it is very difficult to add N at more than 0.3% from the viewpoint of steelmaking and moreover such an N amount decreases the hot workability of a stainless steel. Therefore, the N amount was limited in the range from 0.05

to 0.3%.

[0042] W makes a passivation film further stable when it is added in the form of coexistence with Cr, Mo, N and V, and also improves pitting corrosion resistance of a stainless steel in salt water. W is added at not more than 3% according to the specific use in the environment. Further, a W addition of more than 3% deteriorates hot workability remarkably.

[0043] V makes a passivation film further stable when it is added in the form of coexistence with Cr, Mo, N and W, and also improves pitting corrosion resistance in salt water. V is added at not more than 4% according to the specific use in the environment. The larger the V amount is, the more the corrosion resistance improves. However, when V is added in excess of 4%, the hot workability of a stainless steel deteriorates considerably, it becomes difficult to produce the stainless steel, and the cost increases. Therefore, the upper limit of the V amount was set at 4%.

[0044] Co further improves general corrosion resistance in sulfuric acid when it is added in the form of coexistence with Cr, Ni, Mo and Cu. Co is added by not more than 2% according to the specific use in the environment. The larger the Co amount is, the more the sulfuric acid corrosion resistance improves. However, when Co is added in excess of 2%, it becomes difficult to produce a stainless steel and, at the same time, the cost increases. Therefore, the upper limit of the Co amount was set at 2%.

[0045] Ti fixes C and improves corrosion resistance. In addition, Ti fixes O by coexisting with Ca, thus suppresses the formation of the oxides of Si and Mn, and, by so doing, improves hot workability and corrosion resistance. Further, Ti is added by not more than 1% according to the specific use in the environment. When a Ti amount exceeds 1%, hot workability deteriorates.

[0046] Ca or Ce is added usually in the range from 0.001 to 0.03% as a deoxidizing agent or a desulfurizing agent in molten steel. Even though Ca or Ce is added in excess of 0.03%, the deoxidizing effect and the desulfurizing effect are saturated. Furthermore, in relation to S and O, by adding Ca and Ce in combination so that the following expression may be satisfied, O in a low sulfur steel is fixed, the generation of MnS is prevented, and thus hot workability improves remarkably:

$$[S + O - (0.8 \times Ca\ (ppm)) - (0.3 \times Ce\ (ppm))] \leqq 40\ ppm.$$

[0047] In addition, a δcal value is defined by the following expression:

$$\delta cal = 3 \times ([Cr] + 1.5 \times [Si] + [Mo]) - 2.8 ([Ni] + 0.5 \times [Mn] + 30 \times [C] + 30 \times [N] + 0.5 \times [Cu]) - 19.8,$$

wherein the relevant elements are expressed in terms of a mass percent.

[0048] This value represents the percentage of a δ-ferrite amount in a solidification structure. When δ-ferrite appears, it mitigates the segregation of S and O at the portions where intergranular corrosion occurs. When a δ-ferrite amount (in volume percent) is in the range from larger than -20% to smaller than 16%, the synergetic effect with the function of the regulation $[S + O - (0.8 \times Ca\ (ppm)) - (0.3 \times Ce\ (ppm))] \leqq 40$ ppm is effectuated and hot workability is improved remarkably. Therefore, the δcal value was limited in the range from -20 to 16.

[0049] When a GI value of a stainless steel, the GI value being defined by the expression $GI = [Cr] + 1.6 \times [Ni] + 6.0 \times [Mo] + 7.1 \times [Cu]$, is not less than 75, the corrosion rate of the stainless steel is not more than 1 mm/y., at which corrosion rate the stainless steel can stand actual use with no problems. However, when a GI value exceeds 88, the alloy addition effect decreases and, at the same time, the cost in the production of a stainless steel increases substantially and, thus, the stainless steel cannot stand actual use. For that reason, the GI value was limited in the range from 75 to 88.

[0050] When a PI value of a stainless steel, the PI value being calculated by the expression $PI = [Cr] + 1.3 \times [Mo] + 1.4 \times [Cu] + 2.2 \times [N]$, is not less than 23, the stainless steel does not generate pitting corrosion substantially. On the other hand, when a PI value exceeds 32, the cost in the production of a stainless steel increases considerably and there arises a problem in wide applications of a stainless steel. For that reason, the PI value was limited in the range from 23 to 32.

Example 1

[0051] The present invention is hereunder explained on the basis of examples.

[0052] Table 1 shows the comparison between the invention steels and the comparative steels with regard to the chemical compositions, general corrosion resistance and pitting corrosion resistance. Those steels were melted and refined by the electric furnace-AOD method and the electric furnace-VAC method. The resulting molten steels were cast into continuously produced slabs under normal conditions. Thereafter, the slabs were subjected to a soaking treatment in the temperature range from 1,150°C to 1,250°C for a half to one hour. After being subjected to surface conditioning, the slabs were hot rolled into the thickness of 6 mm, heated at a temperature of 1,100°C for a half hour, and thereafter subjected to a solution heat treatment by water quenching. Then the specimens for the sulfuric acid corrosion test and the specimens for the pitting corrosion potential measurement in salt water were cut out from the steel products and the specimens were subjected to the test and the measurement.

[0053] Fig. 5 shows the result of the relation between the GI values and the PI values with respect to the invention steels and the comparative steels. The area that conforms to the present invention is shaded with oblique lines and the invention steels in Table 1 are shown by the symbols ● (the comparative steels by the symbols ○).

[0054] With regard to the corrosion test in sulfuric acid, the corrosion test specimens 25 x 25 mm in size and 4 mm in thickness were cut out from the product sheets, the whole surfaces thereof were polished up to the roughness of #400 with wet emery paper, thereafter the specimens were subjected to ultrasonic cleaning in acetone and then dried, the weights of the specimens before subjected to the test treatments were measured precisely using a chemical balance, and after that the specimens were immersed in a solution having a sulfuric acid concentration of 50% for six hours at 40°C. After the elapse of a prescribed time, the specimens were pulled up quickly from the sulfuric acid solution, subjected to water rinse, cleaned of corrosion products, subjected to ultrasonic cleaning in acetone, and dried. Thereafter the weights of the specimens after being subjected to the test treatments were measured, and the corrosion rates were calculated from the weight differences between before and after the test treatments.

[0055] With regard to the measurement of the pitting corrosion potential, the measurement was carried out basically by a method conforming to the method described in JIS G0577 except the temperature that was changed to 40°C.

[0056] The synthetic evaluation was carried out by directly calculating the GI values and the PI values. That is, the specimens satisfying both the expressions $75 \leqq GI \leqq 88$ and $23 \leqq PI \leqq 32$ simultaneously were represented by the mark ○, and the specimens that do not satisfy either or both of the expressions by the mark X.

[0057] From the results shown in Table 1, it was understood that any stainless steel according to the present invention was extremely excellent in both the sulfuric acid corrosion resistance and the pitting corrosion resistance with the cost being comparatively low, and was suitable as a steel for a chemical tank.

[Table 1]

		Chemical components (mass %)														Hot work-ability index1) δ_{CAL}	Gl2)	Pl3)	Corrosion test result		6)Evaluation	Name of steel
		C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N	W	V	Co	Others				①4)	②5)		
Invention steel	1	0.015	0.51	0.98	0.010	0.005	22.31	13.87	3.14	1.99	0.145	-	-	-	-	2.41	77.47	29.50	0.32	1099	○	
	2	0.016	0.50	0.97	0.011	0.005	23.98	14.01	2.99	1.98	0.151	-	-	-	-	5.97	78.39	30.97	0.28	1111	○	
	3	0.014	0.49	1.01	0.009	0.005	22.03	15.99	3.21	1.81	0.145	-	-	-	-	-3.95	79.73	29.06	0.19	1098	○	
	4	0.015	0.47	0.98	0.009	0.005	21.95	17.96	3.03	2.12	0.148	-	-	-	-	-11.07	83.92	29.18	0.09	1097	○	
	5	0.014	0.50	1.20	0.009	0.006	21.88	19.98	2.99	1.99	0.149	1.01	-	-	-	-17.04	85.92	28.88	0.07	1101	○	
	6	0.015	0.48	1.31	0.010	0.008	21.99	14.03	3.98	2.02	0.148	-	1.03	-	-	2.63	82.66	30.32	0.13	1105	○	
	7	0.015	0.49	1.20	0.011	0.004	22.03	14.13	3.02	2.99	0.140	-	-	1.05	-	-0.90	83.99	30.45	0.09	1125	○	
	8	0.016	0.50	1.38	0.010	0.005	21.97	14.03	3.12	2.10	0.049	-	-	-	Ti:0.20	8.10	78.05	29.07	0.29	1106	○	
	9	0.015	0.51	1.33	0.009	0.005	21.88	13.98	2.99	2.31	0.253	-	-	-	-	-9.65	78.59	29.56	0.27	1095	○	
	10	0.017	0.49	1.39	0.009	0.006	23.03	12.03	3.43	2.52	0.151	-	-	-	Ce:0.01	8.52	80.75	31.35	0.17	1085	○	
	11	0.018	0.55	1.41	0.009	0.005	23.03	12.04	3.49	1.99	0.048	-	-	-	Ca:0.01	15.22	76.36	29.46	0.39	1102	○	
	12	0.020	0.61	1.38	0.010	0.006	21.98	11.99	3.49	2.49	0.052	-	-	-	-	14.32	79.78	30.12	0.22	1106	○	
	13	0.021	0.60	1.38	0.013	0.005	21.93	12.03	3.32	2.49	0.148	-	-	-	-	5.35	78.78	30.06	0.24	1112	○	
	14	0.020	0.61	1.35	0.015	0.005	22.03	11.71	3.59	2.51	0.147	-	-	-	-	7.59	80.13	30.53	0.19	1121	○	
	15	0.022	0.60	1.38	0.016	0.005	21.83	11.95	3.58	2.54	0.049	-	-	-	-	14.22	80.46	30.15	0.18	1105	○	
Comparative Steel	1	0.067	0.48	0.86	0.028	0.006	18.12	8.72	0.17	0.25	0.033	-	-	-	-		34.87	18.78	1223.4	318	X	SUS 304
	2	0.014	0.69	0.99	0.024	0.002	17.40	12.06	2.31	0.28	0.021	-	-	-	-		52.54	20.84	70.15	367	X	SUS 316L
	3	0.018	0.46	1.77	0.025	0.001	21.73	5.35	2.88	0.04	0.132	-	-	-	-		47.83	25.82	50.31	1098	X	DIN 1.4462
	4	0.019	0.51	1.47	0.016	0.001	26.76	7.17	2.07	0.01	0.114	-	-	-	-		50.69	29.71	32.43	1110	X	
	5	0.013	0.56	0.85	0.017	0.001	25.30	7.01	3.18	0.14	0.136	-	-	-	-		56.59	29.93	55.22	1101	X	SUS 329 J4L
	6	0.026	0.51	1.26	0.024	0.001	18.55	13.12	3.50	0.28	0.135	-	-	-	-		62.53	23.79	3.81	1085	X	YUS 317 LN
	7	0.024	0.86	1.54	0.017	0.003	24.41	12.71	0.85	0.03	0.313	-	-	-	-		50.03	26.24	244.82	1089	X	SUS 317 J2
	8	0.015	0.51	0.55	0.016	0.001	19.97	15.01	2.99	1.49	0.146	-	-	-	-		72.51	26.26	0.35	1102	X	
	9	0.010	0.41	0.58	0.011	0.001	22.17	23.90	4.22	1.11	0.028	-	-	-	-		93.61	29.27	0.07	1095	X	ASTM TYPE 904L
	10	0.012	0.54	0.53	0.013	0.001	19.80	18.18	6.12	0.67	0.196	-	-	-	-		90.37	29.13	0.14	1100	X	

1) δ_{CAL} = 3 x ([Cr] + 1.5 x [Si] + [Mo]) - 2.8 x ([Ni] + 0.5 x [Mn] + 30 x [C] + 30 x [N] + 0.5 x [Cu]) - 19.8

2) Gl = [Cr] + 1.6 x [Ni] + 6.0 x [Mo] + 7.1 x [Cu]

3) Pl = [Cr] + 1.3 x [Mo] + 1.4 x [Cu] + 2.2 x [N]

4) **Corrosion test result ①: general corrosion rate (mm/y.) after a specimen is immersed in a 50%-H_2SO_4 solution for six hours at 40°C.**

5) **Corrosion test result ②: 3.5%-NaCl solution, 40°C, Ar deaeration, conforming to JIS G0577. $V'_{c.100}$ mV vs. Ag/Agcl$_{(KCl\ 2st)}$**

6) **Evaluation ○: steels satisfying both the expressions 75 ≦ GI ≦ 88 and 23 ≦ PI ≦ 32 simultaneously.**

X: steels not satisfying either or both of the above expressions with regard to the GI value and the PI value.

Claims

1. A steel for a chemical tank, the steel being excellent in sulfuric acid corrosion resistance and pitting corrosion resistance, **characterized in that**:

   the steel contains, by mass,

   C: 0.003 to 0.05%,
   Si: not more than 5%,
   Mn: not more than 2%,
   P: not more than 0.03%,
   S: not more than 0.010%,
   O: not more than 0.0050%,
   Cr: 18 to 25%,
   Ni: 10 to 20%,
   Mo: 1.0 to 4.5%,
   Cu: 1.0 to 3.0%, and
   N: 0.05 to 0.3%,

   with the balance consisting of Fe and unavoidable impurities;
   the GI value (General Corrosion Resistance Index) defined by the following expression is in the range from 75 to 88,

   $$GI = [Cr] + 1.6 \times [Ni] + 6.0 \times [Mo] + 7.1 \times [Cu],$$

   wherein the relevant components are expressed in terms of a mass percent; and
   the PI value (Pitting Corrosion Resistance Index) defined by the following expression is in the range from 23 to 32,

   $$PI = [Cr] + 1.3 \times [Mo] + 1.4 \times [Cu] + 2.2 \times [N],$$

   wherein the relevant components are expressed in terms of a mass percent.

2. A steel for a chemical tank, the steel being excellent in sulfuric acid corrosion resistance and pitting corrosion resistance, according to claim 1, **characterized in that** the steel further contains, by mass, one or more of

   W: not more than 3%,
   V: not more than 4%,
   Co: not more than 2%, and
   Ti: not more than 1%.

3. A steel for a chemical tank, the steel being excellent in sulfuric acid corrosion resistance and pitting corrosion resistance, according to claim 1 or 2, **characterized in that**:

   the steel further contains either or both of Ca and Ce at 0.001 to 0.03% by mass;
   the δcal value defined by the following expression is in the range from -20 to 16,

   $$\delta cal = 3 \times ([Cr] + 1.5 \times [Si] + [Mo]) - 2.8 ([Ni] + 0.5 \times [Mn] + 30 \times [C] + 30 \times [N] + 0.5 \times [Cu]) - 19.8,$$

   wherein the relevant components are expressed in terms of a mass percent; and
   the value of the expression [S] + [O] - 0.8 x [Ca] - 0.3 x [Ce] is not more than 40, wherein the relevant components are expressed in terms of a mass ppm (1 mass ppm = 0.0001 mass percent).

Fig. 1

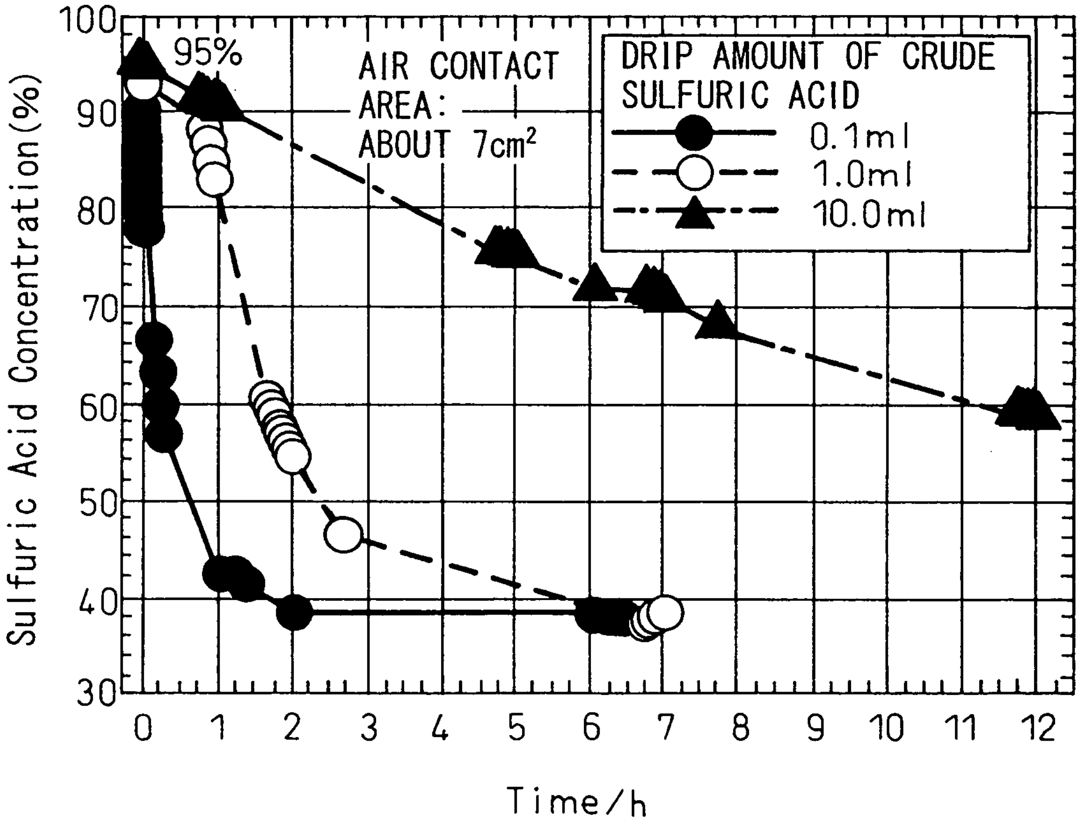

Sulfuric Acid Concentration(%)
100
90
80
70
60
50
40
30
95%
AIR CONTACT AREA: ABOUT 7cm^2
DRIP AMOUNT OF CRUDE SULFURIC ACID
● 0.1ml
○ 1.0ml
▲ 10.0ml
0
1
2
3
4
5
6
7
8
9
10
11
12
Time/h

Fig. 2

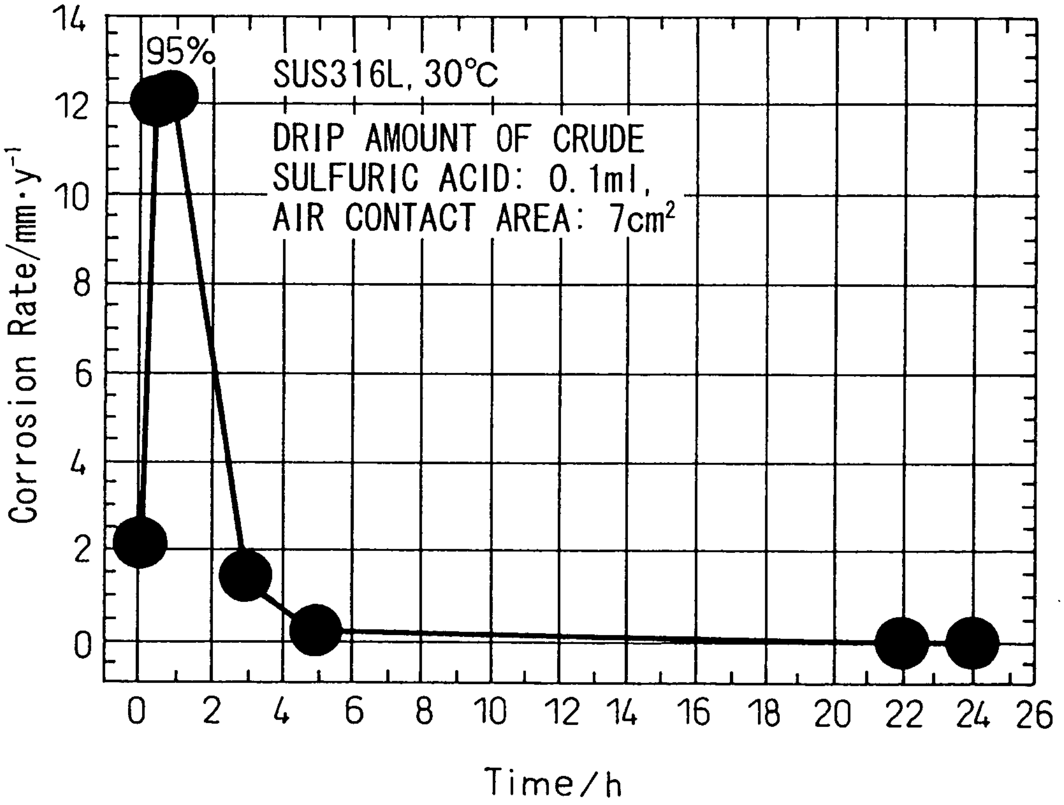

95%
SUS316L, 30°C
DRIP AMOUNT OF CRUDE SULFURIC ACID: 0.1ml, AIR CONTACT AREA: 7cm²
Corrosion Rate/mm·y⁻¹
14
12
10
8
6
4
2
0
0
2
4
6
8
10
12
14
16
18
20
22
24
26
Time/h

Fig.3

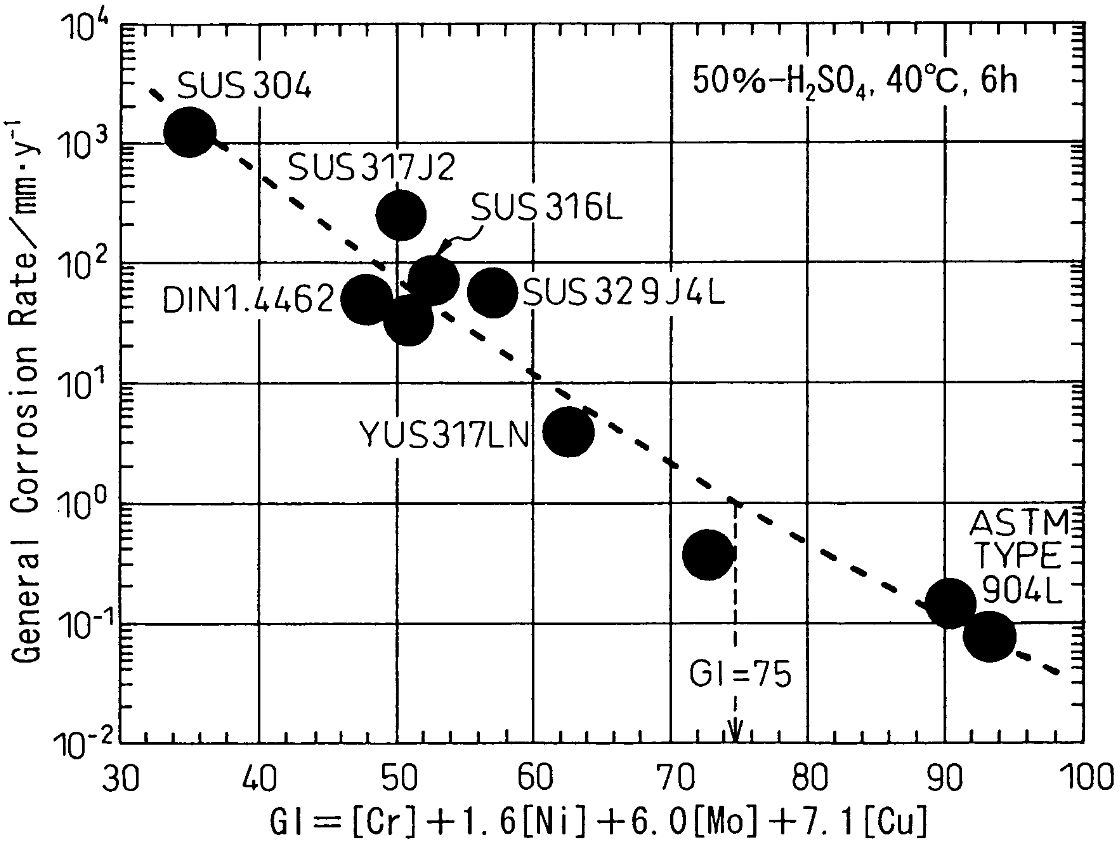

10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
General Corrosion Rate／mm·y^{-1}
30
40
50
60
70
80
90
100
GI = [Cr] + 1.6[Ni] + 6.0[Mo] + 7.1[Cu]
50%-H_2SO_4, 40°C, 6h
SUS304
SUS317J2
SUS316L
DIN1.4462
SUS329J4L
YUS317LN
ASTM TYPE 904L
GI=75

Fig.4

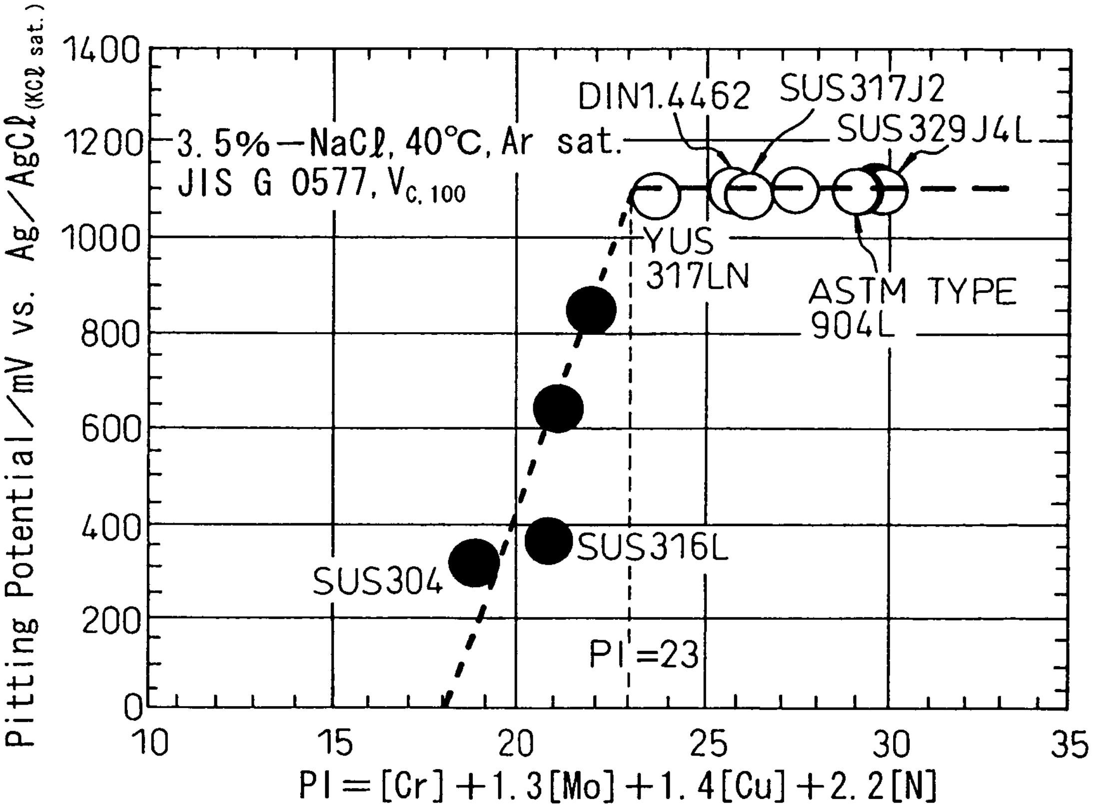
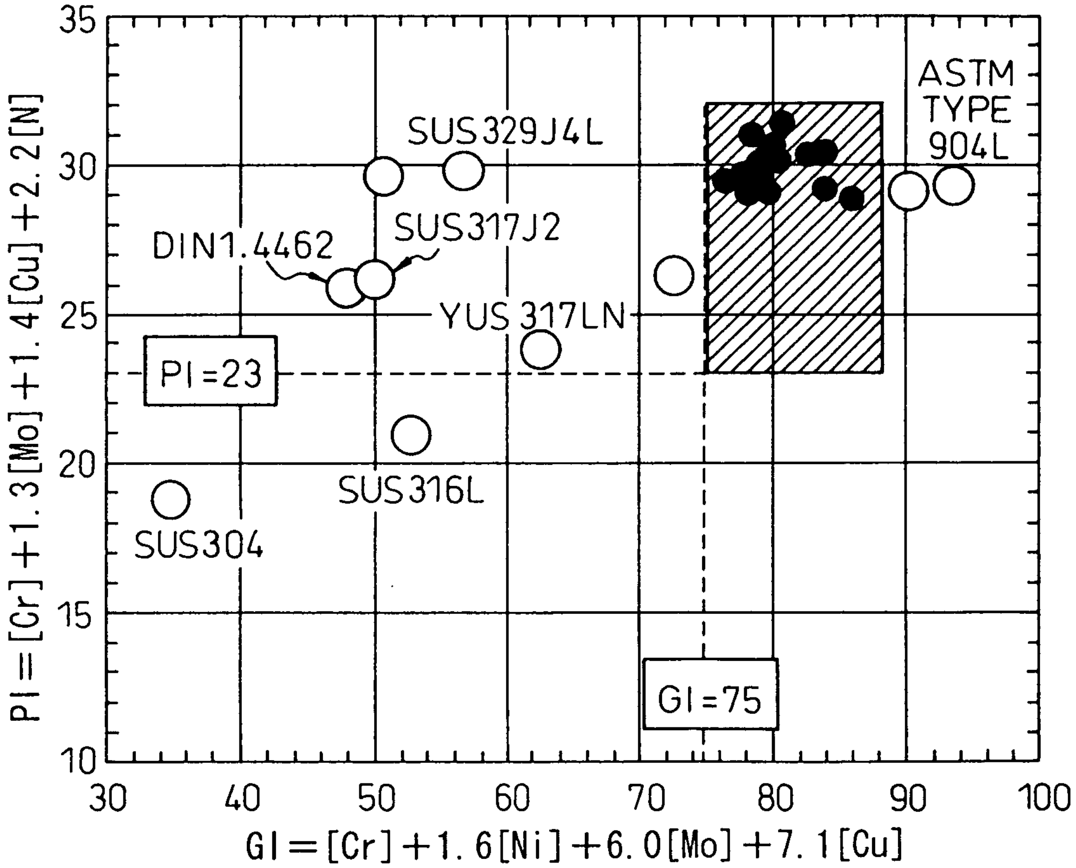

Pitting Potential／mV vs. Ag／AgCℓ(KCℓ sat.)
1400
1200
1000
800
600
400
200
0
10
15
20
25
30
35
PI＝[Cr]＋1.3[Mo]＋1.4[Cu]＋2.2[N]
3.5%－NaCℓ, 40°C, Ar sat.
JIS G 0577, V_{C,100}
DIN1.4462
SUS317J2
SUS329J4L
YUS 317LN
ASTM TYPE 904L
SUS316L
SUS304
PI＝23

Fig.5


35
30
25
20
15
10
30
40
50
60
70
80
90
100
PI = [Cr] + 1.3[Mo] + 1.4[Cu] + 2.2[N]
GI = [Cr] + 1.6[Ni] + 6.0[Mo] + 7.1[Cu]
SUS329J4L
ASTM
TYPE
904L
DIN1.4462
SUS317J2
YUS 317LN
PI=23
SUS316L
SUS304
GI=75

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 01 0309

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 439 (C-0761), 19 September 1990 (1990-09-19) -& JP 02 170946 A (NIPPON STEEL CORP;OTHERS: 01), 2 July 1990 (1990-07-02) * abstract; figures 2,3; table 1 * * page 272, left-hand column, line 6-13 * ---	1-3	C22C38/00 C22C38/40 C22C38/42 C22C38/44
X	PATENT ABSTRACTS OF JAPAN vol. 003, no. 037 (C-041), 29 March 1979 (1979-03-29) -& JP 54 013412 A (NIPPON STEEL CORP), 31 January 1979 (1979-01-31) * abstract; table 1 * ---	1-3	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	4 August 2003	Catana, C

CATEGORY OF CITED DOCUMENTS

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EPO FORM 1503 03.82 (P04C01)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 01 0309

DOCUMENTS CONSIDERED TO BE RELEVANT			
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			TECHNICAL FIELDS SEARCHED (Int.Cl.7)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	4 August 2003	Catana, C

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D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

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04-08-2003

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