Effects of Melting Condition and Alloying Elements on Localized Corrosion Resistance of High Cr and N Bearing Stainless Steels

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In this study, the characteristics of the experimentally produced high N-high Cr bearing stainless steels are discussed as a part of applications of materials for FGD (Fuel Gas Desulfurization) system of thermal power plants or for power plants using seawater as coolant. Corrosion resistance of developed alloys is especially investigated in detail. Corrosion characteristics of vacuum melted cast are shown to be superior to that of air melted one. From the viewpoint of CPT, It is estimated that the differences of corrosion resistance are 21.8 ℃~24.6 ℃ at PRE 40 and 8 ℃~12.4 ℃ at PRE 50, and the gaps becomes bigger as the PRE values are lower. In the evaluation of corrosion resistance in alloy A2501, Z3101, and A3301 according to Cr concentration, alloy A3301 shows a deviation from the general tendency in chloride solutions. It has relatively high PRE value as 48.6, but it has relatively poor pitting resistance. It is, however, difficult to observe a specific phase except ferrite in microstructure analysis and neither detects special phase such as sigma phase.

Keywords : *stainless steel, chromium, nitrogen, critical pitting temperature, power plant*

1. Introduction

Since the development of stainless steel had started from 12% Cr steel in the early 20th century, the corrosion resistance and mechanical properties of stainless steel have been continuously improved by the enthusiastic research.[1] Type 304 stainless steel is one of the most necessary materials in modern times, and its consumption in Korea has also increased in every year. POSCO (Pohang Steel Corporation, KOREA) recently becomes one of the major suppliers of self-manufactured hot coil. However, Type 304 stainless steels have yet various kinds of corrosion problem s such as pitting and crevice corrosion under corrosive environment that has high concentration of aggressive ion such as chloride ions.[2] Type 316 stainless steel has been developed and widely used and this contains 2~3% Mo to reduce localized corrosion in such environment. However, these types of steels also don't have enough corrosion resistance. Therefore, Allegheny Ludlum Steel Company (USA), for the first time, developed super stainless steel (brand name: Al-6X) composed of 20% Cr-24% Ni-6% Mo and it was commercialized since

1973.[3] After Trent Tube Company became to extremely reduce carbon and nitrogen contents due to the advance of refining technology,[4] it was possible for them to develop high corrosion resistance ferritic stainless steels.[5,6] This steel has a chemical com position of 27.5% Cr-3.5% Mo-1.2% Ni-0.4% Ti, and it has been supplied to the world market with a brand name, 'SEA-CURE' since 1980. Allegheny Ludlum Company immediately developed and commercialized ferritic stainless steel, 'AL 29-4C' composed of 29% Cr-4% Ni-4% Mo-0.5% Ti to keep up with 'SEA-CURE', which was relatively cheaper than 'Al-6X'.[7] In Europe, Nyby-Uddeholm (Sweden) developed ferritic stainless steel composed of 25% Cr-4% Ni-4% Mo-0.5% Ti, and has provided markets with a brand name, 'Monit' since the end of 1970s.[7] It has higher corrosion resistance in comparison with traditional stainless steels. Therefore, they have been widely applied for heat exchangers using seawater as coolant in power plants. However, stainless steels developed in USA and Europe could not totally avoid from pitting or crevice corrosion. Furthermore, these are more sensitive to biological fouling compared with traditional Cu-alloys. Chlorination conducted in order to prevent fouling. High alloy stainless steels have especially insufficient corrosion resistance. Because of bad resistance

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of hydrogen embrittlement in ferritic alloys, such as 'SEACURE', 'AL 29-4C', Monit' etc, the application of cathodic protection system is restricted.[9] It was reported by Eckenorod et.al. in 1977[10] that high alloy stainless steels could have elevated corrosion resistance in the high concentration of chloride environment by the addition of Nitrogen. Because adding Nitrogen to type 304 stainless steel leads to a little improvement of corrosion resistance, it did not take any notice at that time. In the early 1978, the development of stainless steel started, of which cost is cheaper than Ti-alloy and Ni-alloy such as Inconel and Hastelloy, but has corrosion resistance similar to them. This was from the situation that construction of geothermal power plants was urgently needed because of energy crisis due to oil shock at that time. For the construction of them, development of economical super corrosion resistance stainless steels were accelerated, which is endurable in hot brine solution, with the support of the United States Government at the Brookhaven National Lab.[11] At the same time, Avesta Co. (Sweden) set about development of new stainless steel, which has better corrosion resistance than those of traditional stainless steels.[12] SR-50A, 254SMO, AL-6XN, UR B26, etc, for example, that are representatives of commercial alloys, are classified as 6 Mo-bearing austenitic stainless steels of super corrosion resistance. Also, there are many reports for corrosion properties and mechanism of super stainless steels.[13)-17)]

In this study, we have developed high N-high Cr bearing stainless steels and discussed about its characteristics, as a part of development of materials for FGD (Fuel Gas Desulfurization) system of thermal power plants or for power plants using seawater as coolant.

2. Experiments

2.1 Preparation of specimens

Specimens were melted and cast from high frequency induction melting furnace, of which atmosphere was vacuum or air. Shape of cast products was a rectangular, and those were cut following annealing heat treatment and used in the series of experiment as follows. Table 1 shows chemical composition of those alloys.

2.2 Microstructure observation

Specimens for optical microscopic analysis were prepared from cutting to pieces in size of 1.5×1.5 cm. They were fixed in epoxy resin and polished using a SiC paper up to #2000. After that, vibration polisher was used for specimen to have mirror surface. The com position of etching solution for microscopic analysis was 45 ml HCl + 20 ml HNO$_3$ + 20 ml Methanol. Specimens for Scanning Electron Microscopic (SEM) analysis were prepared by exactly same procedures as optical microscopic analysis above. SEM and EDS (Energy Dispersive Spectroscopy) used in this analysis were Model JSM -6300 (JEOL Co.) and ISIS-300 (OXFORD Co.) respectively. For X-ray diffraction analysis (XRD), specimens were polished by using SiC paper up to #600. The model of XRD was D/M AX2000 (RIGAKU Co.), 2θ of X-ray beam was diffracted from $30°$ to $95°$ at the diffraction rate of $4°$/min.

2.3 Hardness test

Specimens were prepared by same procedures as optical microscopic analysis and hardness of them were measured. The type of Hardness meter was Rockwell and B-scale or C-scale was applied.

2.4 Anodic polarization test (APT)

Annealed specimens were cut to pieces in size of 2×2

Table 1. Chemical composition of alloys for experiments (wt%).

Alloys	Cr	Mo	W	Si	Ni	Mn	C	Cu	O	N	P	S	Cr_{eq}/Ni_{eq}	PRE
A - 1	24.9	0.01	-	0.42	13.04	0.50	0.020	-	-	0.362	0.003	0.007	1.12	35.8
A - 2	25.1	1.04	-	0.44	14.10	0.47	0.021	-	0.0305	0.390	0.004	0.004	1.11	40.2
A - 3	25.1	4.52	-	0.44	17.48	0.47	0.029	-	0.0117	0.428	0.003	0.003	1.12	52.9
A - 4	25.2	5.66	-	0.45	18.48	0.46	0.021	-	-	0.439	0.003	0.003	1.14	57.1
A2500	26.35	2.40	1.54	0.77	20.13	0.84	0.023	-	0.0082	0.34	0.006	0.006	1.10	47.0
A2501	24.76	4.57	-	1.08	23.91	0.92	0.023	-	0.0127	0.315	-	-	1.03	49.3
A2502	26.88	4.70	-	0.96	18.76	0.88	0.027	-	0.0115	0.43	0.006	0.006	1.16	55.3
Z3101	32.1	2.6	-	0.98	23.0	3.3	0.06	0.01	-	0.36	-	-	1.07	51.5
A3301	36.23	1.15	-	1.15	27.67	0.77	0.017	0.82	-	0.287	0.009	0.009	1.12	48.6

cm. The covered copper wire was connected to one of specimen's face using soldering and they were set using an epoxy resin. The surfaces of specimens were polished using SiC paper up to #600. After rinsing them, epoxy resin was covered on surfaces with only 0.25 cm^2 of surface area being exposed to test solution. Specimens prepared in this way were kept in the desiccator until test was initiated. The Potentiostat of Model EG&G 273A was used in this experiment, in which the high-density carbon rod was applied as a counter electrode and the saturated calomel electrode as a reference electrode. The test solutions were de-aerated NaCl solution, (HCl + NaCl) mixed solution and H_2SO_4 solution. The scanning rate of potential was 1 mV/sec.

2.5 Critical pitting temperature (CPT) measurement

1 liter volume of glass reactor cells was used in the test, and condensers were installed on the upper part of these cells in order to prevent the evaporation of test solution. Specimens were seated on the insulated wire covered with rubber tube and inserted in the cell at an angle of 45° tilted. Every test time fresh new solutions were applied in the cell. Specimens were plate type sized by 2×2 cm of which surfaces were wet polished with SiC paper up to #120. These were deposited in desiccator until test begins. The corrosion rate of each specimen was obtained from dipping them into 6% $FeCl_3$ solution based on ASTM G48 code or Green Death Solution for 24 hours in each temperature. Critical Pitting Temperature (CPT) was measured in the criterion of the temperature in which weight loss of specimen exceeded 5 mg. With the measurement of weight loss, surface analysis was performed in order to examine pitting creation.

2.6 Acid proof test

The preparation of specimens was same as those of CPT measurement. Specimens were immersed in 80% H_2SO_4 solution at 80 °C and boiling 1.5% HCl solution for 24hours. The weight change was measured and converted to corrosion rate in mpy.

3. Results and discussion

3.1 Effect of melting atmosphere on the properties of alloys

Fig. 1 shows the evaluation results of pitting characteristics in the specimens extracted with variation of distance from the cast surface that were melted in vacuum and air and molded into metallic/sand mold. The purpose of this evaluation is to explain the big differences of corrosion resistance among the positions in even the same
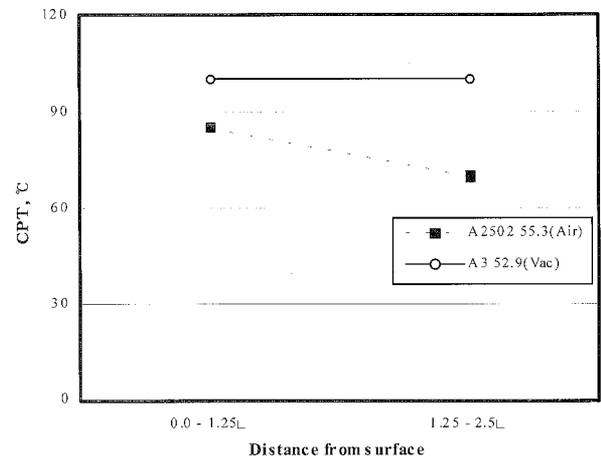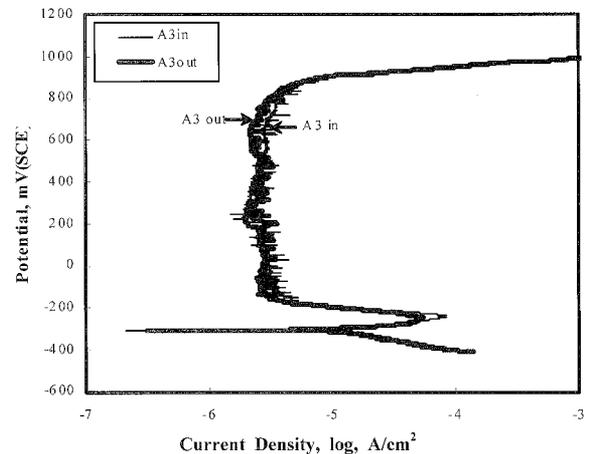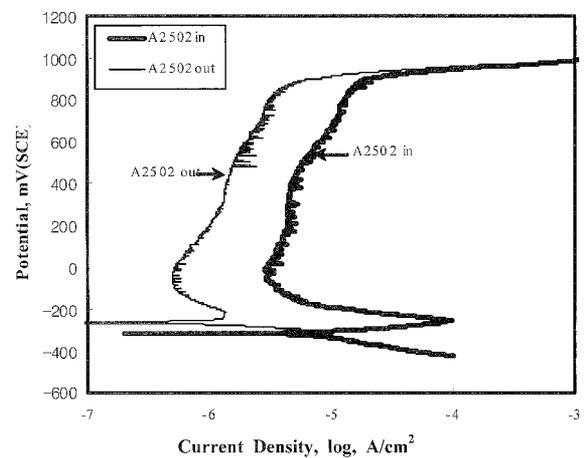

Fig. 1. Critical Pitting Temperatures of cast alloys in Green Death Solution.

(a) A 3

(b) A2502

Fig. 2. Polarization curves of cast specimens with different extracting position in 0.5 N HCl+1 N NaCl solution at 50 °C

cast alloy. As shown in the figure, alloy A3(Vac, PRE 52.9), which is melted in vacuum and cast in metallic

mold, shows a good pitting resistance and similar charac-teristics regardless of the position of extraction. In case of alloy A2502(Air, PRE 55.3) which was air melted and cast in sand mold, however, the corrosion resistance of specimens even extracted from the cast surface is worse than that of cast melted in vacuum. Moreover the corrosion resistance of specimen from the inner cast shows bigger differences. Because of these differences in corrosion resistance with extraction positions of cast alloy, it is judged that extraction positions should be identified espe-cially in cast alloy melted in air and cast in sand mold in order to avoid errors in data.

Fig. 2 shows polarization curves of specimens extracted from different positions in 0.5 N HCl + 1 N NaCl solution at 50 °C. As indicated in this figure, the polarization characteristics of vacuum melted specimens cast in me-tallic mold shows little differences according to extracted positions, but air melted specimens cast in sand mold have highly different passivity according to extracted positions. These are well concordant with results of CPT test.

The results of hardness test of these specimens are shown in Fig. 3. Although inner part specimen of cast alloy shows a little lower hardness, the differences are not so serious, and a little higher hardness of outer speci-men can be presumably explained from the quenching effect of outer surface of cast alloy.

As considered above, there is a quite big difference of corrosion resistance between the cast from air melting/sand mold and that from vacuum melting/metallic mold. This effect is examined in detail in this chapter. Relation of PRE (Pitting Resistance Equivalence) to CPT in 6% $FeCl_3$ solution is summarized in Fig. 4 (Some of data were referred from catalogues of alloy makers). It is clear that these two factors have a linear proportioning relation with each other. This relation can be numerically represented as follows.

$$CPT \text{ (vac. / G48)}, \ °C = 3.1 \times PRE - 67.8 \qquad (1)$$

Fig. 5 shows the relation between pitting resistance index and CPT of vacuum melted A1234 alloy cast in Green Death Solution. Although numbers of data are insufficient, they show the linear relation that has the numerical expression as follows.

$$CPT \text{ (vac. / Green)}, \ °C = 2.9 \times PRE - 59.6 \qquad (2)$$

Fig. 6 represents CPT of air melted casts in 6% $FeCl_3$ related to PRE of alloys. Some of data are a little bit deviated, but the linear relation can be obtained as below.

$$CPT \text{ (air / G48)}, \ °C = 4.3 \times PRE - 137.6 \qquad (3)$$
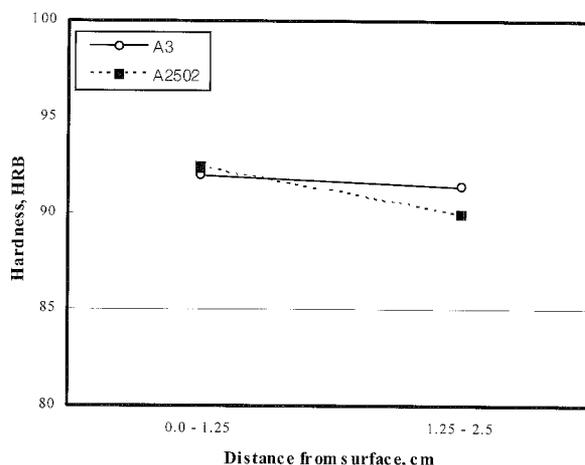

Fig. 3. Hardness variation according to the distance from the cast surface
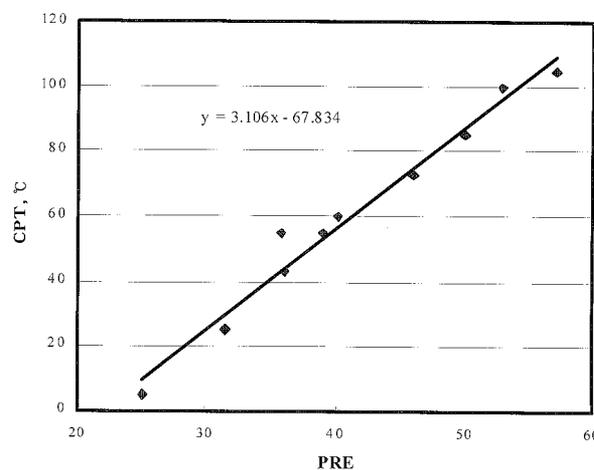

Fig. 4. CPT of vacuum melted casts in 6% $FeCl_3$ solution.
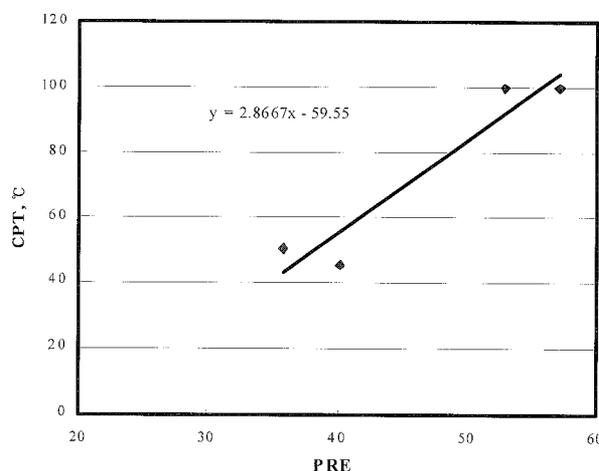

Fig. 5. CPT of vacuum melted casts in Green Death Solution

The CPT of air melted casts Green Death Solution is related to PRE of alloys in Fig. 7. Some of data are a
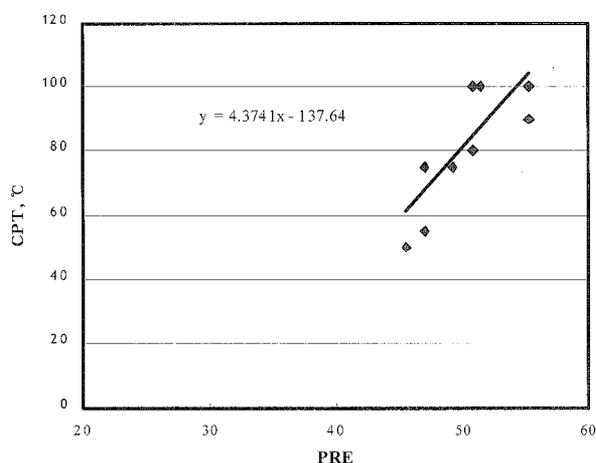
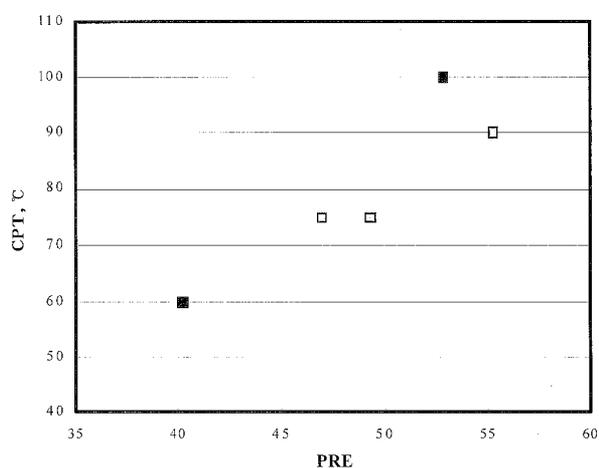Fig. 6. CPT of air melted casts in 6% FeCl₃ solution

Fig. 8. CPT and PRE of representative air/vacuum melted cast alloys
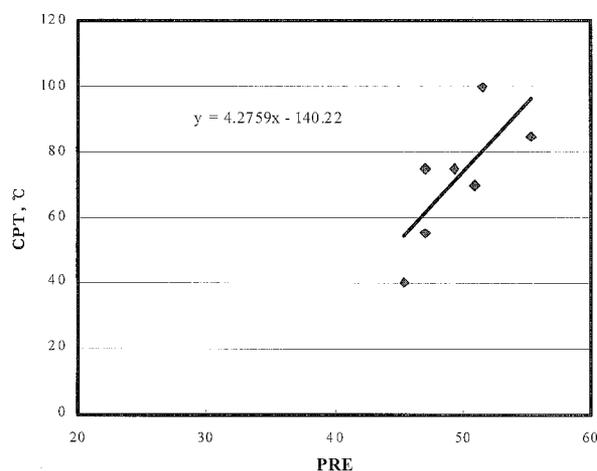

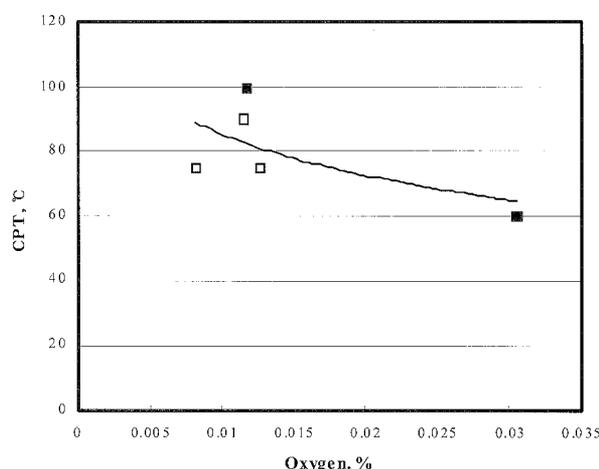Fig. 7. CPT of air melted casts in Green Death Solution.

Fig. 9. The relation of CPT and oxygen concentration in alloys

little bit deviated, but the linear relation can be also obtained as follows.

$$\text{CPT (air / Green), }^\circ C = 4.3 \times PRE - 140.2 \qquad (4)$$

4 numerical relations obtained above are arranged in Table 2. From Table 2 and figures above, it is difficult

to find out big differences of results among CPT test method, but there are some distinctive differences of relation formula as to melting conditions, i.e. air melting and vacuum melting. 21.8 °C ~ 24.6 °C of corrosion resistance can be estimated from above relations in that CPT in PRE 40 is 56.2-56.4 °C (vacuum) and 34.4-31.8 °C (air). On the other hand, there are minimum 8 °C to maximum

Table 2. Effects of PRE vs CPT relations experimentally obtained according to melting conditions.

Melting method	Test solution	relations	CPT estimation of PRE 40	CPT estimation of PRE 50
Air melting	G 48	CPT (vac/G48), °C = 3.1*PRE − 67.8	56.2	87.2
	Green Death Solution	CPT (vac/Green), °C = 2.9*PRE − 59.6	56.4	85.4
Vacuum melting	G 48	CPT (atr/G48), °C = 4.3*PRE − 137.6	34.4	77.4
	Green Death Solution	CPT (atr/Green), °C = 4.3*PRE − 140.2	31.8	74.8

12.4 °C of corrosion resistance in case of PRE 50 from the estimation of CPT that show 87.2-85.4 °C (vacuum) and 77.4-74.8 °C (air). It means that corrosion resistance of vacuum melted casts is higher than that of air melted ones and the differences are more distinctive when PRE is lower. It should be considered, how ever, that this estimation may have errors due to substitution 100 °C to above 100 °C data because of temperature limitation in experimental solutions.

Fig. 8 indicates the relations between PRE and pitting resistance of representative vacuum melted (■)/air melted (□) cast alloys. As mentioned above, this figures also shows the fact that vacuum melted casts have superior corrosion resistance to air melted ones.

Fig. 9 shows the variation of critical pitting temperature with oxygen concentration in alloys. As shown in this figure, the corrosion resistance has the tendency to be lowered, as oxygen concentration becomes higher. However, this kind of approach could lead to an error because, in some cases, the oxygen concentration of vacuum melted alloys is higher than that of air melted alloys. Therefore, it is more reasonable to convert corrosion resistance with oxygen concentration to CPT/PRE of alloys considering (only) PRE. Fig. 10 is the results in this point of view, and it seems that the analysis of vacuum melted alloys has no problem. However, in case of air melted alloys, there are some what difficulties in analyzing corrosion resistance of air melted alloys from oxygen concentration.

3.2 Effect of Cr concentration on corrosion resistance

Alloy A3301 has the highest Cr concentration as 36% but PRE of it is a little lower as 48.6 due to other composition effects. The next rank in respect of Cr concentration is A2501 of which PRE is lesser than that of alloy Z3101 (51.5), but the difference of it is only 2.8 compared with A3301. Fig. 11 shows hardness of alloys according to Cr concentration. The hardness of alloy A2501 of which Cr concentration is about 25% is the lowest, the next higher one is A3301 of which Cr concentration is about 36%, and the highest one is alloy Z3101 which has about 32% of Cr in it.

Critical pitting temperatures of above alloys in 6% FeCl₃ are represented in Fig. 12 with reference to PRE of alloys. It shows no linear relations between PRE and CPT, while a specific alloy has very low CPT (alloy A3301 (○)).

Fig. 13 shows corrosion resistance of three representative alloys. From the figure, it is known that corrosion resistance does not increase as PRE of alloys increases, but that of alloy A3301 is the lowest.

Fig. 14 indicates CPT in Green Death Solution according to PRE of alloys. It shows no linear relations between
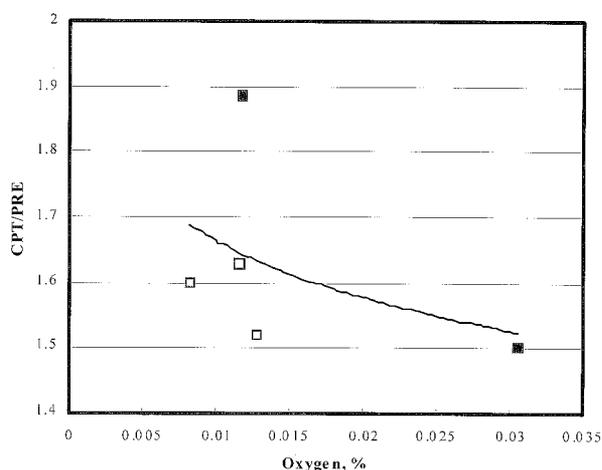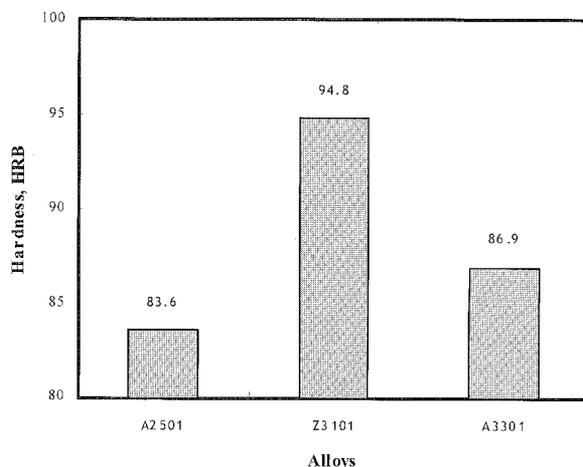

Fig. 10. CPT/PRE and oxygen concentration in alloys.

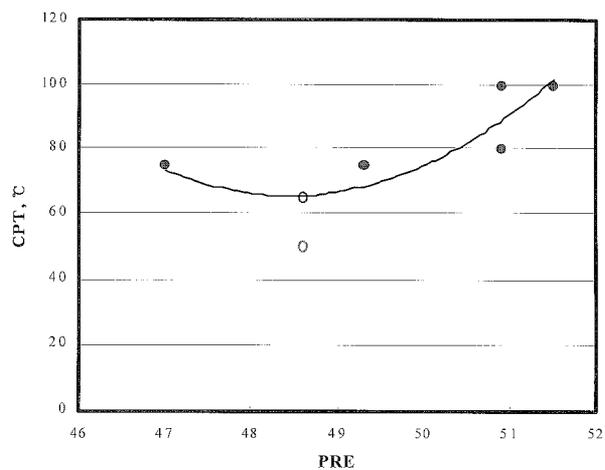**Fig. 11.** Hardness variation according to Cr concentration in alloys

Fig. 12. Non-linear relation between PRE and CPT (6% FeCl₃) of alloys
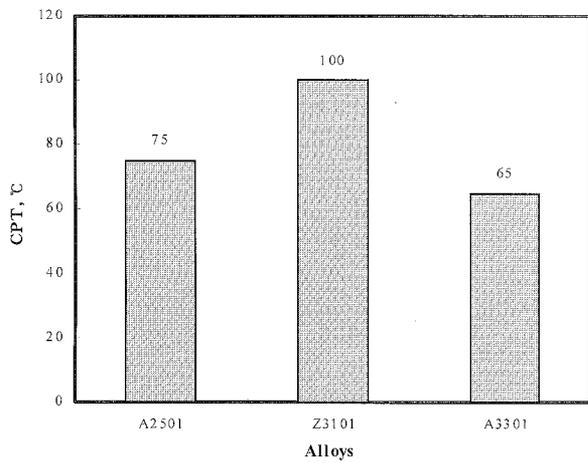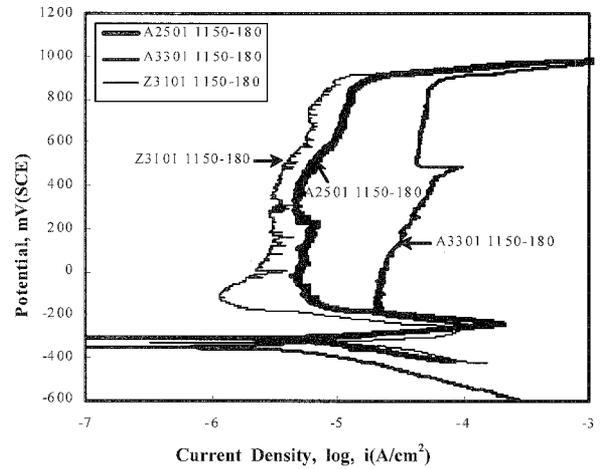
Fig. 13. CPT of alloys in 6% FeCl₃ solution

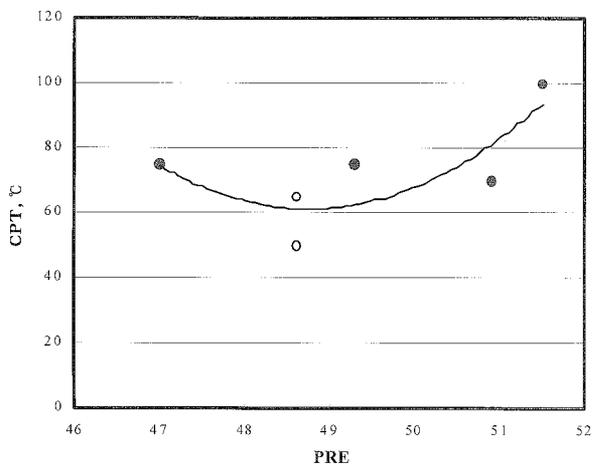Fig. 16. APT curves of three alloys in 0.5 N HCl+1 N NaCl solution at 50 °C.

Fig. 14. Non-linear relation between PRE and CPT (Green Death Solution) of alloys
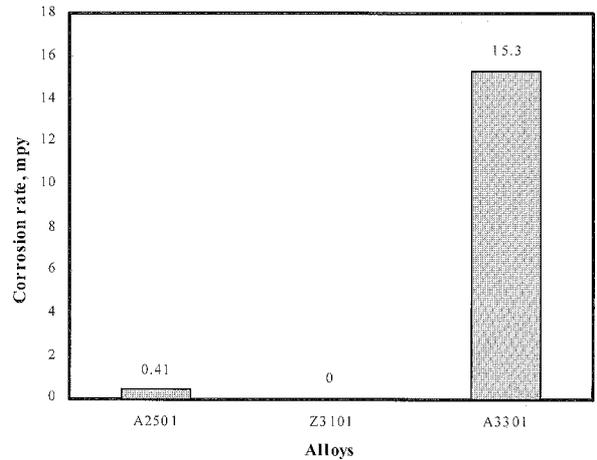

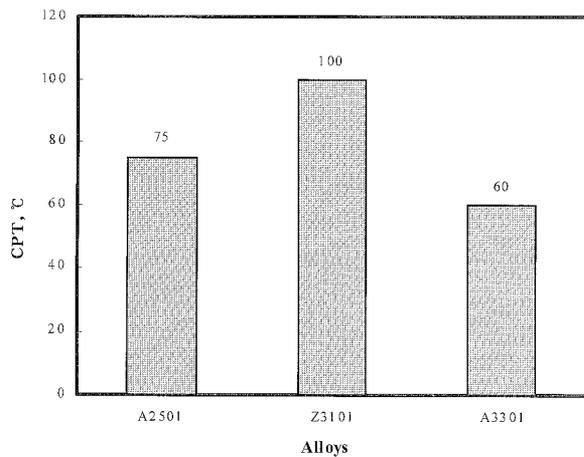Fig. 17. Corrosion rates of alloys obtained from 1.5% HCl solution.
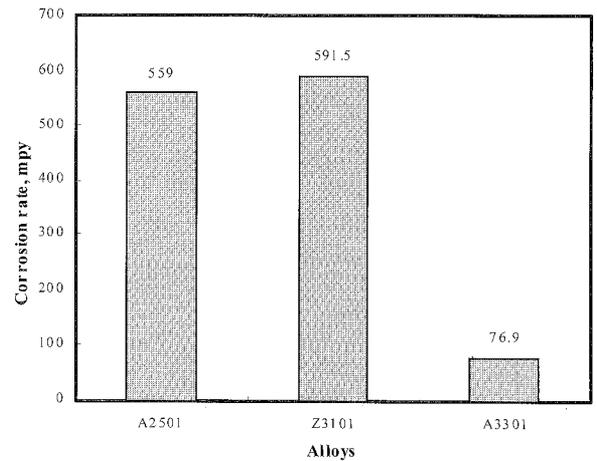

Fig. 15. CPTs of three alloys in Green Death Solution

Fig. 18. Corrosion rates of alloys in 80 °C 80% H_2SO_4 solution.

PRE and CPT, while a specific alloy has very low CPT (alloy A3301 (○)).

Fig. 15 shows corrosion resistance of typical three alloys. As shown in this figure, it is known that corrosion resistance does not increase as PRE of alloys increases, but that of alloy A3301 is the lowest.

The APT data in 0.5 N HCl + 1 N NaCl solution at 50 °C are displayed in Fig. 16. Alloy Z3101 shows the least current density of passivity and the passive current density of alloy A2501 is a little higher but it shows a stable passivity. However, the passive current density of alloy A3301 is relatively higher than those of the other two alloys. These results well correspond to pitting corrosion tests above.

Fig. 17 shows corrosion rates of these alloys obtained from boiling 1.5% HCl solution. Alloy A2501 and alloy Z3101 have very low corrosion rate but alloy A3301 has relatively higher one. On the other hand, Fig. 18 indicates corrosion rates obtained from 80 °C 80% H_2SO_4 solution in which alloy A2501 and alloy Z3101 shows very high corrosion rates but alloy A3301 shows relatively lower one. It seems to be caused by 0.82% Cu addition to A3301.As already mentioned above, alloys produced in this study don't have Cu element which made them selves show poor corrosion resistance in sulfuric acid. In case of A3301, how ever, it has only 1/8 of corrosion rate as a result of 0.82% Cu addition though it shows poor pitting conditions in other various solutions.

It is noteworthy that alloy A3301 deviates from the general tendency of corrosion resistance in chloride solutions as well as in sulfuric acid. Its PRE value is relatively as high as 48.6 but it shows poor pitting resistance. This alloy doesn't show other specific phases except ferrite in microscopic observation, and neither detects specific phase such as sigma phase in XRD analysis. Therefore, a further study is to be needed on the corrosion resistance loss of alloy A3301.

4. Conclusions

1) The corrosion characteristics of vacuum melted cast were shown to be superior to that of air melted one. From the viewpoint of CPT, it was estimated that the differences of corrosion resistance were 21.8 °C~24.6 °C at PRE 40 and 8 °C~12.4 °C at PRE 50, and the gaps became bigger as the PRE values are lower. It seemed that oxygen contents would affect corrosion resistance of alloys.

2) The relationships between CPT and PRE value were

obtained in highly chloride solutions. However, it should be noted that relation formulae obtained in this study had some limitations on classification of corrosion resistance coming from the restriction of solutions that possibly leads to an error.

3) In the evaluation of corrosion resistance in alloy A2501, Z3101, and A3301 according to Cr concentration, alloy A3301 showed a deviation from the general tendency in chloride solutions(of course, it shows superior corrosion resistance in sulfuric acid). It had relatively high PRE value as 48.6, but it had relatively poor pitting resistance.

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