Journal of the Korean Society of Marine Engineers, Vol.28, No.2, pp.217~227, 2004(ISSN 1226-9549)

# The Effect of Solution Heat Treatments on the Microstructure and Corrosion Behaviour for a Duplex Stainless Steel

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(Manuscript : Received DEC 02, 2003 ; Revised JAN 05, 2004)

**Abstract :** The bowl in a ship purifier suffers from high stress and high temperature in a detrimental heavy fuel oil environment. Duplex stainless steel(DSS) is a primary material to withstand this harsh condition. Newly-manufactured STS 329 grade DSS has been evaluated by various mechanical and electrochemical test methods. Eight heat treatment(HT) conditions with different temperature and time were applied to the DSS samples to improve corrosion resistance. Microstructure and polarization test results concluded the optimum HT condition was 1,090℃-60 minutes. Confirmation experiments for applying to a real bowl including stress corrosion cracking test exhibited the reproducibility of the optimum HT condition.

**Key words :** Ship purifier, Bowl, Duplex stainless steel(DSS), Heat Treatment(HT), Corrosion Resistance, Polarization, Microstructure

## 1. Introduction

### 1.1 Ship purifier

Purifiers are the cleaning machinery for engine fuel and lubricating oil, and it becomes one of the inevitable auxiliary machinery in a ship. The purification principal is a separation of deteriorated materials(sludge) from dirty oil by means of centrifuging force which is generated by rotation of the center part of a purifier, so-called a bowl. In general, the rotation speed of ship purifiers ranges between 6,000 - 12,000 rpm. In such a high rpm, a considerable force is affecting to the bowl in operation.

During the past three decades, the quality of fuel oil has been getting worse and worse. The viscosity of low grade fuel oil presently supplying to ships is considerable high(nearly 1=water),

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therefore, it should be heated up to 120℃ before using in engine. In addition the fuel oil contains a considerable amount of impurities including sulphur and carbon residue, consequently, it can not be used without purification.

The operational conditions of bowl in a ship purifier are very severe, i.e. high stress by rapid rotation, high temperature for heating to reduce its viscosity, and high corrosivity due to detrimental elements in low grade oil. From these reasons, stress-corrosion-cracking(SCC) resistance metals are required as a bowl material. Duplex stainless steel has been widely accepted as one of bowl candidates.

### 1.2 Duplex stainless steel

Duplex stainless steel(DSS) is developed as a stainless steel which has both high mechanical strength and excellent corrosion resistance. Two-phased microstructure of ferrite(a) and austenite(g) is designated as Duplex (combination of ferritic and austenitic structures)[1]. High content of chromium and molybdenum is responsible for the excellent corrosion resistance of ferritic structure as well as the favorable mechanical properties of austenitic one.[2,3] When the DSS has an equal amount of ferrite and austenite, it has better toughness and strength than any single phase.

The development of 0.02C-0.5Si-5.5Ni-22Cr-3Mo-0.16N, initially designated as Z3 CND 22-5 Az(UR 45N)[4], confirmed the principal duplex grades with chemical balance of a 50% ferritic/50% austenitic structure after solution treatment at 1,050℃. It has the low carbon level and nitrogen content between 0.10 and 0.15%.

Numerous structural modifications have been developed in DSS by heat treatments. The majority of them concern the ferrite, since diffusion rates are much higher in ferrite(body-centered-cubic, BCC) structure than in austenite(faced-centered-cubic, FCC)[4]. The ferrite phase is enriched in chromium and molybdenum, which have a strong tendency to promote the formation of intermetallic compounds.

Microstructure of DSS can be changed by heat treatment(HT). The austenite forms on cooling by the solid state transformation from aferrite to g-austenite[5]. The control of ferrite content with alloy composition was attempted by heat treatment in the temperature range of 1,050℃ and 1,150℃[6]. It revealed that the microstructure change followed by mechanical and electrochemical variations with/without compositional change could be achieved by means of appropriate heat treatment.

### 1.3 Content of study

The purpose of this study is an attempt to improve the corrosion resistance of STS 329 grade duplex stainless steel which was made as a candidate material for a ship purifier bowl. The original sample was manufactured by one of the special steel companies in Korea. After mechanical and electrochemical tests for the first sample, heat treatment was applied at 8 different conditions. The test items to check mechanical properties and corrosion resistance are as follows: (1)

chemical composition, (2) tensile test, (3) hardness test, (4) microstructure inspection, (5) polarization(corrosion) test, and (6) stress corrosion cracking test.

## 2. Experimental procedures

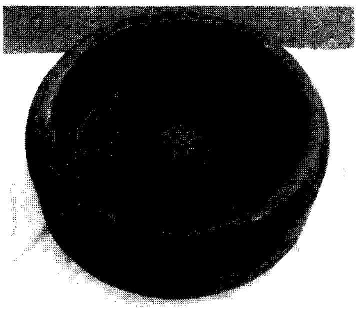
### 2.1 Materials and mechanical properties

The test material was the STS 329 grade duplex stainless steel(DSS) which was manufactured by one of Korean special steel companies. Through a series of DSS manufacturing processes, a bowl sample was casted and it was shaped by final forging with a simultaneous heat treatment. Photographs in Fig. 1 show bowl (a) just after forging, and (b) after machining. Table 1 is the chemical composition of sample with the specification of STS 329(=ASTM 329=SUS 329=EN 1.4460)[7] grade DSS. The composition of this experiment sample was satisfied with the specification for the STS 329 material.

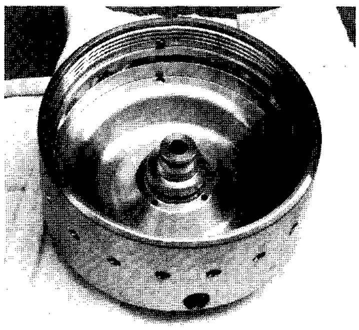
The specimens for basic mechanical and electrochemical tests were sectioned from a forged bowl. For a tensile test a sub-size specimen was adopted because of the small size of bowl containing various windings. The diameter and gauge length of a round-type tensile specimen were 12.5 mm and 62.5 mm[8], respectively, and all the other procedures were followed to both KS and ASTM standards. For a comparison purpose some specimens were prepared from the 329 grade DSS which was imported from a foreign country. Hardness was measured by Brinell tester in three directions, X, Y and Z, and average.

### 2.2 Polarization(Corrosion) test

The polarization tests were carried out for comparing corrosion resistance of each



(a) Just after forging



(b) After final machining

**Fig. 1 Photographs of purifier bowl for a ship**

**Table 1 Chemical composition of bowl material and the specification of STS 329 grade DSS**

| Element | C | Si | Mn | P | S | Cr | Ni | Mo | Cu | N |
|---|---|---|---|---|---|---|---|---|---|---|
| Specification (STS 329) | Max. 0.03 | Max. 1.00 | Max. 1.00 | Max. 0.04 | Max. 0.03 | 24.5 26.0 | 4.50 5.50 | 1.00 2.00 | 0.50 1.00 | 0.08 0.15 |
| Bowl Sample | 0.02 | 0.48 | 0.58 | 0.022 | 0.003 | 24.5 | 5.11 | 1.73 | 0.68 | 0.15 |

sample. The exposed area of a specimen was 1 $cm^2$, and the other area including connection with a lead wire was insulated by epoxy resin. Saturated calomel electrode(SCE) was used as a reference, and high density graphite rod as a counter electrode. The potential range for polarization experiment was selected between -1.2 and 1.2 V/SCE according to the preliminary test results, and scanned from lowest cathodic to highest anodic potential direction. Natural seawater was decided as a primary test solution because of common and the most corrosive media in marine environment, and for a comparison purpose 2N HCl solution was used in some final stage of experiments according to the ASTM standard[9]. The initial scan rate was 10mV/min. recommended by ASTM standard, however, it was increased to 300mV/min. to reduce the testing time since there was little different in the polarization results between the two. The initial stabilization time in test solution was 20 minutes. The polarization test system as shown in Fig. 2, including a potentiostat and the related software, was manufactured by Gamry co.(US).

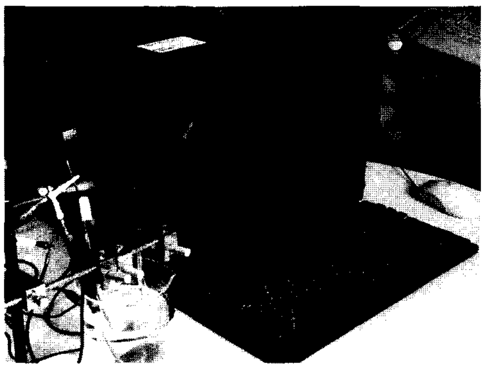


**Fig. 2 Corrosion(polarization) test equipment**

### 2.3 Microstructure examination

For a microstructure examination the domestic bowl and imported samples were sectioned in three dimensional directions, X, Y and Z. The test sample was sectioned from the center position of bowl thickness where cooling and heating rate was lowest. The surface was polished with up to 5$\mu$m by polishing compound, and followed by etching. The etchant was Glyceregia(glycerol:HCl:$HNO_3$=3:3:1)[10], and microstructure photographs were taken by a stereo microscope.

### 2.4 Stress corrosion cracking test

Stress Corrosion Cracking(SCC) test was carried out to the real bowl to study the optimum HT condition. The samples were sectioned from cylinder and hood parts of bowl, and U-bend type of specimens were fabricated as shown in Fig. 3[11].

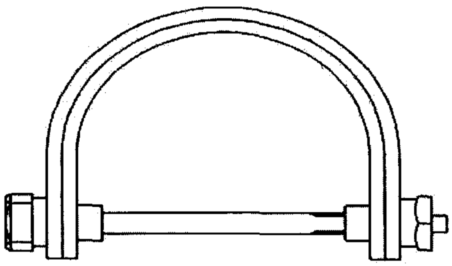


**Fig. 3 U-bend type SCC test specimen**

The SCC test solutions were 1% $FeCl_3$ and mixed solution of $CuSO_4$-$H_2SO_4$ indicated in the JIS standard which the foreign DSS was tested. The ratio of the solution was $CuSO_4$:$H_2SO_4$:water=1:1:8 as regulated in the JIS standard[12]. The test temperature in the $FeCl_3$ solution was 99℃ instead of boiling temperature to reduce the evaporation of solution during a test, and the mixed solution 95℃. The duration of test time was 16 hours for the $FeCl_3$ and 240 hours for the mixed, respectively. Specimens were degreased by acetone, and the test solution was filled in a beaker of 1,000ml up to 800ml. Each beaker was covered by plastic sheet to minimize the evaporation of solution during a test. Temperature controlling container was maintained the target temperature within ±1℃ of error, and the top of container was covered by aluminium foil to minimize the evaporation of water from the container.

## 3. Results and discussion

### 3.1 Physical properties for the DSS bowl material

Table 2 is the mechanical properties for four different sizes of bowl. The diameter of bowls was 100-150 mm. The tensile strength(TS) was 705-735 $N/mm^2$ and the yield strength(YS) 588-617 $N/mm^2$. Those strengths satisfied the specification of STS 329 grade, which was minimum 617 $N/mm^2$ in TS and 441 $N/mm^2$ in YS. Elongation was far improved compared to the specification of minimum 20%, and hardness was also higher than that for the same grade of foreign-made DSS (HB=226). Consequently, all mechanical properties were satisfied with either the specifications of the target grade(STS 329) or the test results of same grade foreign DSS.

**Table 2 Mechanical properties for the DSS bowl material**

| Diameter of Bowl | Tensile Strength ($N/mm^2$) | Yield Strength ($N/mm^2$) | Elongation (%) | Hardness (HB) |
|---|---|---|---|---|
| ϕ100mm | 705 | 588 | 40 | 235 |
| ϕ120mm | 735 | 617 | 38 | 229 |
| ϕ140mm | 725 | 598 | 39 | 232 |
| ϕ150mm | 725 | 598 | 40 | 232 |

Fig. 5 is the comparison of microstructures between the imported(foreign) and the domestic(Korean) DSS in three directions, i.e. X, Y and Z. Those microstructures showed little directional difference, however, there was an apparent distinction between the two materials. The foreign DSS which was imported from foreign country showed a typical pattern of duplex stainless steel, i.e. a base ferrite structure with an island-like austenite pattern which was formed during a solid solution treatment. The island-like austenite structure was quite uniformly distributed all over the sample. On the other hand, the domestic DSS sample showed a number of small particles which concentrated area by area with some acicular shape. This indicated that the austenite structures have not developed sufficiently up to the island-like adequate structure, and also its distribution was not uniform. At this point two possible reasons could be arisen to explain it, i.e. a compositional problem and/or an insufficient heat treatment(HT). As previously indicated in Table 1, the composition was satisfied with the STS 329 grade in all elements, therefore, the second question, i.e. HT, was doubted.

In order to investigate the effect of microstructure difference which affecting to corrosion resistance, polarization tests were carried out for the same samples in Fig. 4. Fig. 5 represents the results of three directional specimens for the two materials. As the experimental details described in Section 2.2, the test solution was natural seawater; and the scan rate and the potential range were 10mV/min. and -0.5~-1.0 V/SCE, respectively. The present data designated as Korea showed considerably high current density(CD), which implied that the corrosion resistance was poor, compared to the imported specimen designated Foreign. There was some difference of directional polarization behaviour, however, the CD difference between the two DSSs was more significant than that between directions. The high CD trend for the domestic DSS compared to the imported was in not only anodic polarization curve but also cathodic one. Consequently, the corrosion resistance of presently-manufactured DSS was much lower than that of the foreign, which was consistent with the result of previous microstructure examination. From these results, the difference of microstructure and corrosion resistance for the domestic-made DSS was due to the lack of heat treatment

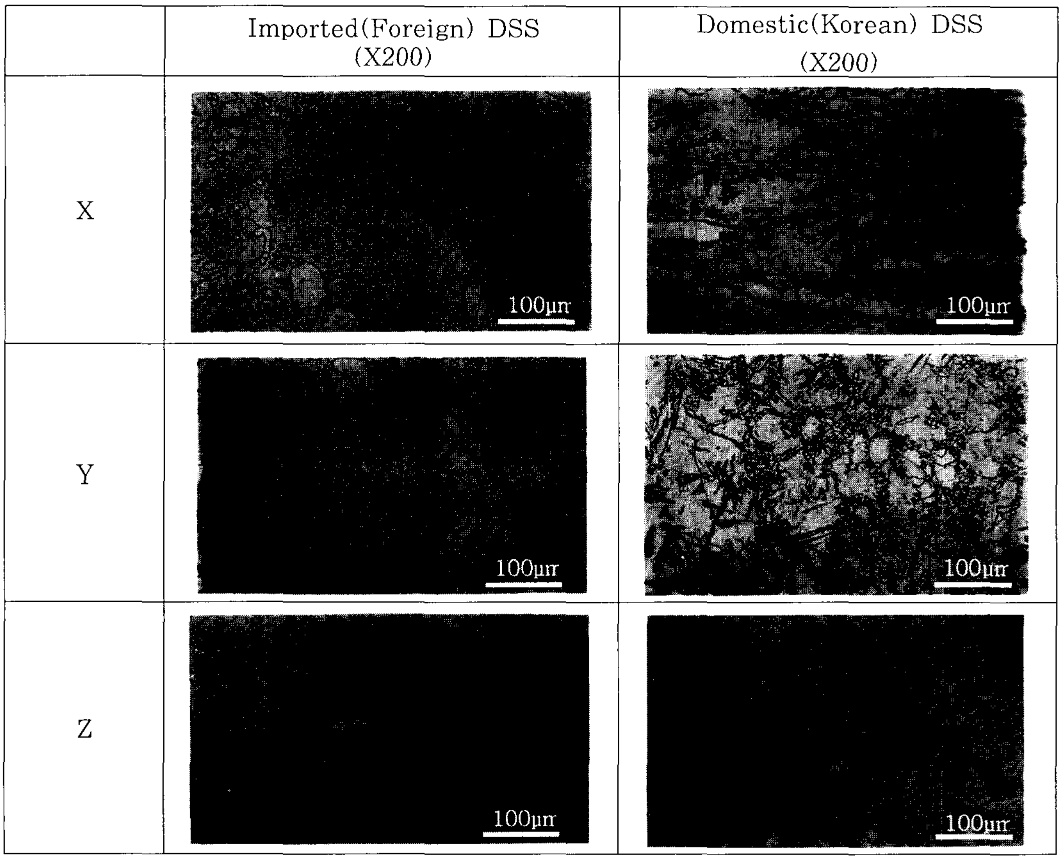


**Fig. 4 Microstructures of the foreign-made DSS sample and the domestic one**

instead of compositional distinction.

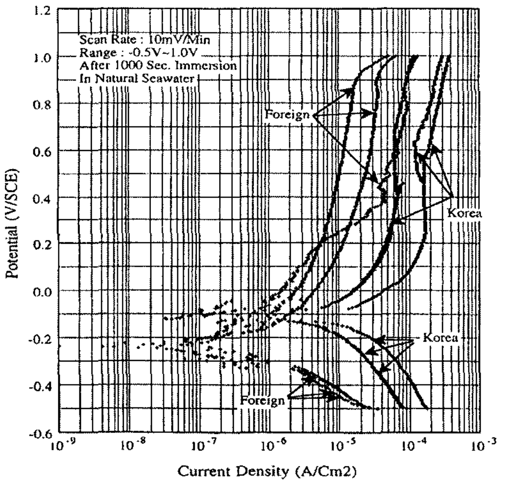



**Fig. 5 Comparison of polarization curves between the domestic DSS(Korea) and the foreign one**

### 3.2 Determination of the optimum heat-treatment condition

In order to investigate the optimum heat-treatment(HT) for improving microstructure and corrosion resistance of domestic-made DSS, various HT conditions have been considered according to the literature[6]. Table 3 lists the selected HT conditions with different temperature and duration(time). Four different kinds of temperature between 1,050 ~ 1,150℃, and two durations of HT, i.e. 30 min. and 60 min. were chosen.

The samples for HT were sectioned by the size of 5cm×5cm×thickness of bowl from an initially forged bowl disk before machining. Annealing with solution treatment at the conditions in Table 3 was carried out in an electric furnace followed by rapid cooling in fresh water. The samples were machined again to the size for microstructure examination and polarization test after the HT. The other experimental procedures were the same as in Section 2.

**Table 3 Conditions of heat treatment**

| Type of HT | Temperature | Duration |
|---|---|---|
| # 1 | 1,050℃ | 30 min. |
| # 2 | 1,150℃ | 60 min. |
| # 3 | 1,090℃ | 30 min. |
| # 4 | 1,090℃ | 60 min. |
| # 5 | 1,120℃ | 30 min. |
| # 6 | 1,120℃ | 60 min. |
| # 7 | 1,150℃ | 30 min. |
| # 8 | 1,150℃ | 60 min. |

Fig. 6 shows the microstructures of the re-heat treated samples at different HT conditions. It was difficult to distinguish an apparent difference between specimens, however, the size of grain became larger with increasing heating temperature and time. They could be divided by two groups according to the size of grain. The first group was #1~#3 samples(1,050℃ 30/60min. and 1,090℃ 30min.) which had a small size of grains. The second group of #4~#8 showed a relatively large size of grain. It seems that the grain size of the second group was thought to be reasonable, however, the other physical and electrochemical properties should be tested for checking out the optimum HT condition.

Fig. 7 shows the polarization test results for the different heat-treated samples at above eight conditions. The great difference of polarization behaviour was appeared in the anodic polarization curve. The data at 1,150℃-30min. was the highest current density in most of

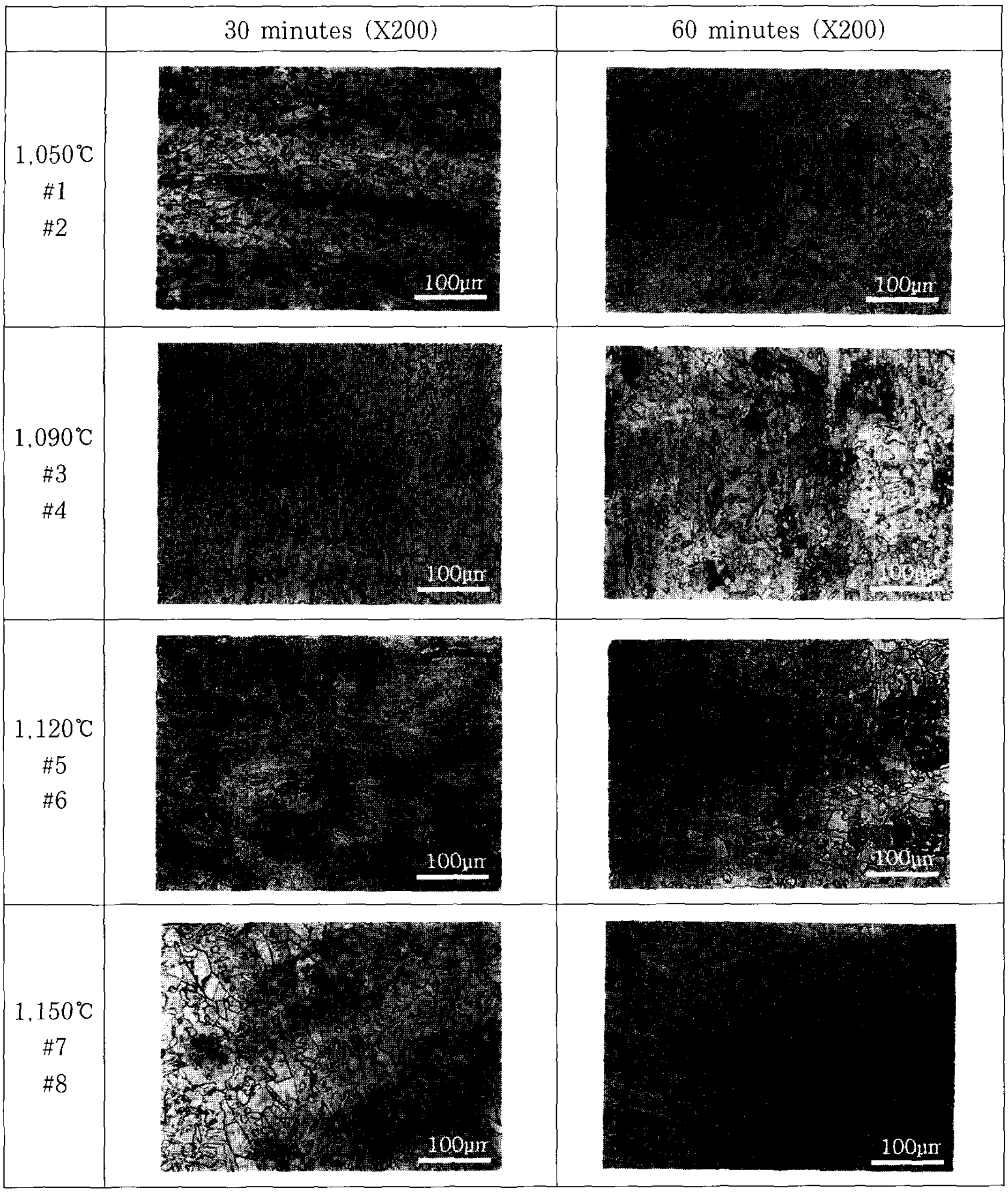



**Fig. 6 Microstructures of the heat-treated specimens at 8 different conditions**

anodic polarization curve, and 1,050℃-60min. was the second. The other data were comparatively samll difference of CD in anodic region except 1,090℃-60min., which showed the lowest current density.

According to the test results of microstructure and polarization, the sample heat-treated at 1,090℃-60min was revealed the best properties. Consequently, this temperature-time combination was selected as an optimum HT condition in this study.

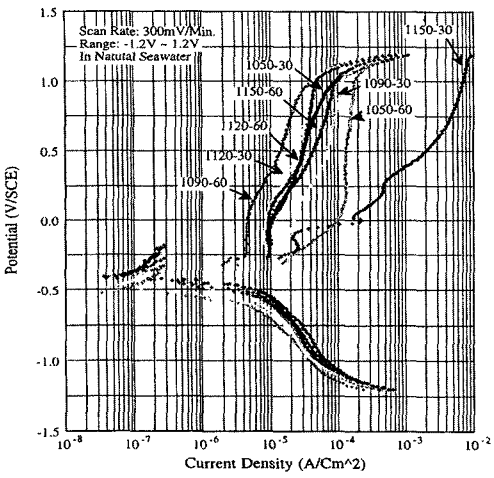
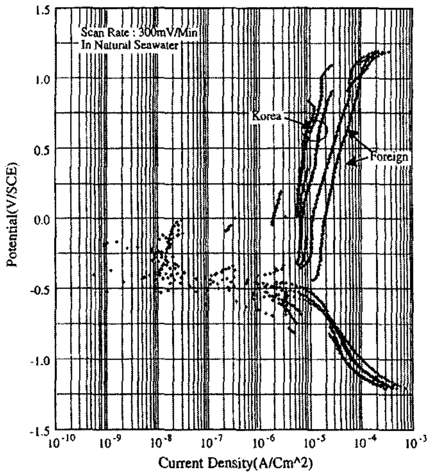



**Fig. 7 Comparison of polarization curves for the domestic DSS samples at eight different HT conditions**

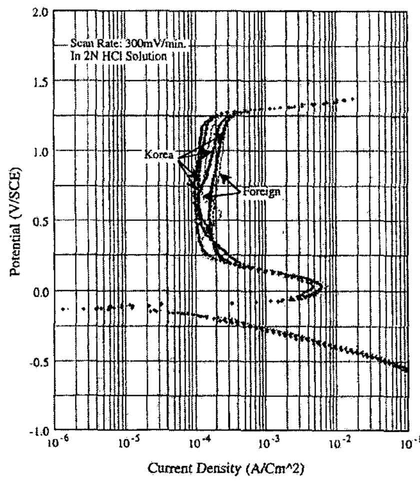
3.3 Performance test results for applying the optimum HT condition

The final experiment was carried out to the real bowl at the optimum HT condition, 1,090℃-60min. The optimum HT was applied to a bowl in a large commercial furnace which was in a HT specialized company in Busan, Korea. After the HT, the specimens for microstructure examinations and polarization tests were conducted for the checkout of optimum HT condition.

The same duplex microstructure was revealed again(not shown in this paper) in these inspections, which was similar to that for Foreign sample in Fig. 4. The polarization behaviours were compared with those of Foreign as well. Fig. 8 illustrated the comparison results between the two samples in natural seawater and in 2N HCl solution. In both figures the current density for the domestic bowl(Korea) was less than that for the foreign, which revealed that the corrosion resistance for the newly HT material was improved by the HT condition of 1,090℃-60min.




(a) In natural seawater




(b) In 2N HCl

**Fig. 8 Comparison of polarization curves between the 2nd HT bowl and the control DSS in both natural seawater and 2N HCl solution**

3.4 Stress corrosion cracking test results

The same bowl DSS, which was utilized in Section 3.3 for the microstructure examination and the polarization test, was used for the stress corrosion cracking(SCC) tests. U-bend type specimens were immersed in the test solution which was one specimen each beaker with about 800ml as mentioned in Section 2.4, and a group of beakers were heated simultaneously in a temperature controlling equipment. The specimens were sectioned from a bowl, and made four specimens from cylinder part and six specimens from hood.

Table 4 is the summary of SCC test results. Among 10 test conditions, only one specimen in 1% FeCl3-95℃-240hrs for the hood of bowl(H4) displayed small pitting, and no cracks were found. It is considered that the HT condition of 1,090℃-60min. is reasonable to improve the SCC resistance property for a DSS bowl material.

**Table 4 The results of stress corrosion cracking experiments for a real bowl material**

| Specimen ID | | Solution | Temp. | Time | Result |
|---|---|---|---|---|---|
| Cylinder | C1 | $H_2SO_4$-$CuSO_4$ | 99℃ | 20 hrs | No crack |
| | C2 | $H_2SO_4$-$CuSO_4$ | 99℃ | 20 hrs | No crack |
| | C3 | 1%$FeCl_3$ | 99℃ | 20 hrs | No crack |
| | C4 | 1%$FeCl_3$ | 99℃ | 20 hrs | No crack |
| | C5 | 1%$FeCl_3$ | 95℃ | 240 hrs | No crack |
| Hood | H1 | $H_2SO_4$-$CuSO_4$ | 99℃ | 20 hrs | No crack |
| | H2 | $H_2HO_4$-$CuSO_4$ | 99℃ | 20 hrs | No crack |
| | H3 | 1%$FeCl_3$ | 95℃ | 240 hrs | No crack |
| | H4 | 1%$FeCl_3$ | 95℃ | 240 hrs | Pitting |
| | H5 | 1%$FeCl_3$ | 95℃ | 240 hrs | No crack |

## 4. Conclusions

Through a series of mechanical and electrochemical experiments for a newly-attempted STS 329 grade duplex stainless steel(DSS) which was a candidate material of bowl for a ship purifier, the following conclusions were obtained.

1. The microstructure of DSS in this study, which had the inferior ferrite-austenite combination after a forging, was improved by solution heat-treatment.

2. Corrosion resistance of the DSS was increased with improving its microstructure.

3. From various mechanical and electrochemical experiments, the optimum heat-treatment condition was 1,090℃-60min.

4. The SCC quality of the final DSS was good enough to that of the imported (foreign) one.

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