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Electrochemical Properties and Corrosion Protection of Stainless Steel for Hot Water Tank

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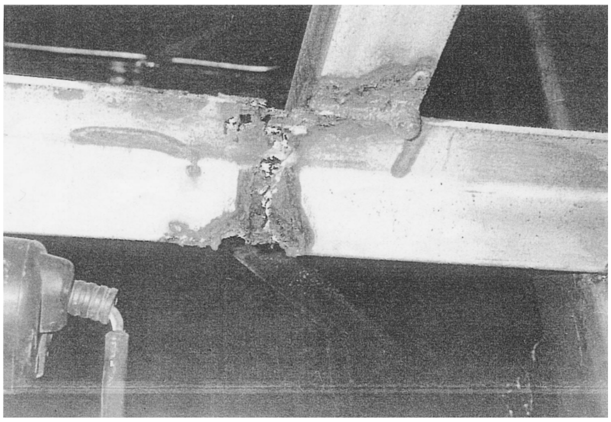
Abstract−The state in which a stainless steel (STS) exhibits a very low corrosion rate is known as passivity, which is self-healing in a wide variety of environments. However, for those STS the corrosion includes pitting, crevice corrosion, galvanic corrosion, hydrogen embrittlement and stress corrosion cracking etc. And the corrosion resistance of STS is affected by area ratio, solution temperature and solution condition etc. Corrosion characteristics of STS 304, welding parts STS 316, STS 329 and STS 444 were investigated with parameters such as corrosion potential, galvanic current measurements, cathodic and anodic polarization behaviors as a function of area ratio and solution temperature in solution for hot water tank. It was found that galvanic current is affected by the area ratio, temperature and a kind of STS for hot water tank. Corrosion potential of welding part STS 316 was lower than that of STS 304, STS 329, STS 444 in solution for #1, #2 hot water tank. Therefore, it is suggested that the welding part STS 316 acts as anode for the other STSs. The amplitude of galvanic current between welding parts STS 316 and STS 304, STS 329, STS 444 in #1 solution is smaller than that in #2 solution. This is the reason that chloride ion quantity in #2 solution is more than that for #1 solution. And then welding part STS 316 corrodes easily by acting as anode compared to the other STS.

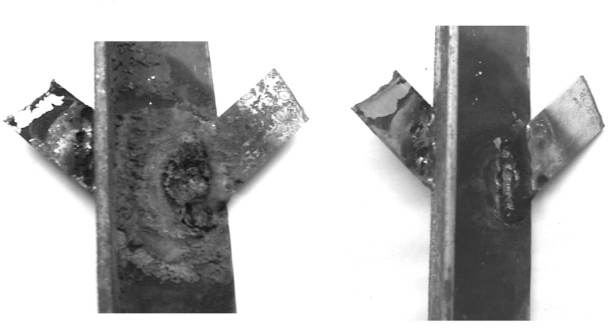
Key words: Electrochemical Property, Passivity, Hydrogen Embrittlement, Corrosion Characteristics, Polarization Behaviors

INTRODUCTION

In general, stainless steels (STSs) are widely used under many circumstances such as in the chemical industry, food industry, machinery industry and building industry due to its excellent corrosion resistance. However, those STSs have the possibility of fracture at an early stage by pitting, crevice corrosion, galvanic corrosion, stress corrosion cracking, and hydrogen embrittlement [Mansfield, 1973, 1977; Fontana et al., 1978; Mansfield et al., 1974, 1977]. Furthermore, because of the structure is being welded continuously, the variation of hardness and microstructure due to rapid heating and cooling by welding process resulting in galvanic cell by potential difference of each welding part; subsequently it can be attributed to enhancing the galvanic corrosion of welding parts. Particularly, austenite STS has also the possibility of weld decay, knife line attack and several defects [Fontana et al., 1996; Jones, 1992]. According to Lauer et al. [Sedriks, 1996], the welding of two alloys with small difference in E_{corr} values (e.g., type 316 L base metal with type 308 L filler metal) can lead to increased corrosion of the more active material [Guidelines for selection of Ni stainless steel for marine environment, 1987, Nickel development institute, 1989]. In an attempt to provide an indication of which metal or alloy combinations are likely to cause galvanic corrosion in sea water, the International Nickel Company has developed a chart of E_{corr} values of various metals and alloy in sea water [Laque, 1975]. Other guidelines have also been published related to galvanic corrosion on STSs [Pryor, 1976]. Studies using natural sea water [Wallen et al., 1986] and chlorinated sea water [Shone et al., 1988] have shown that no galvanic corrosion occurs when the supergrades of STSs are coupled to titanium or a high-molybdenum nickel-chromium alloy such



(a) Inner side of corroded hot water tank



(b) Before removing rust (c) After removing rust

Photo 1. Photographs of corroded stainless steel for hot water tank.

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as alloy 625 alloy C-276 [Francistish, 1994].

In this study, STSs for a hot water tank were made of walls with STS 444; reinforced material with STS 304 and filler metal with STS 316. The inner side of the tank was corroded at the welding parts. Photo 1 shows the present condition of inner side corrosion of a certain hot water tank. Once, we thought of possibility of galvanic corrosion being due to the big ratio of cathodic to anodic area. So the reasons and countermeasures were investigated with parameters such as corrosion potential measurement, galvanic corrosion experiment, cathodic and anodic polarization trend as a function of area ratio, temperature (room temperature, 50 °C) and two kinds of hot waters.

TEST SPECIMEN AND TEST METHOD

1. Test Specimen and Test Solution

The test specimens were welded STS 304 and STS 304, STS 329 and STS 329, STS 444 and STS 444 with 316 filler metal, respectively. And test specimens of STS 304, STS 329 and STS 444 were selected as unaffected parts by welding heat. Chemical composition and mechanical properties of various STSs are shown in Table 1. The exposed areas of each test specimen are 1, 5, 10 cm^2, connected lead line, and other parts were also insulated with masking tape, while welding part, STS 316, was cut only at the welding part. And Table 2 shows analysis results of #1, #2 solutions. It is suggested that the major components affecting corrosion among components of Table 2 are S, Cl^- and HCO_3^-. The largest component difference among S, Cl^- and HCO_3^- out of #1, #2 solutions is Cl^-. Therefore it is estimated that corrosion possibility in #1 solution is smaller than that in #2 solution.

2. Test Method

STS 304, welding parts STS 316, STS 329 and STS 444 (Exposed area: 1 cm^2) were used to carry out corrosion potential measurement experiments during 180 minutes in #1, #2 solutions (Capacity: 500 CC). Galvanic test [Lauer et al., 1970; Weisstuch et al., 1972] was executed between STS 316 (welding part, exposed area: 1 cm^2) and STS 304, STS 329, STS 444 (base metal part, exposed area: 1, 5, 10 cm^2) with zero resistance ammeters as a function of temperature and #1, 2 solutions. Distance between galvanic test specimens was maintained at 2 cm by using an acryl spacer of 4 mm thickness. Polarization test was measured with scan rate 1 mV/sec by using SSCE as reference electrode and Pt as counter electrode in #1, #2 solutions. Exposed area of all specimens is 1 cm^2. And anodic polarization and cathodic polarization trends were measured from open circuit potential to noble and active directions.

Table 2. Analysis results of #1, #2 solution

	S (mg/L)	F^- (mg/L)	Na^+ (mg/L)	Cl^- (mg/L)	HCO_3^- (ppm)	pH
#1 Water	0.2	23	570	260	1491.4	8.4
#2 Water	0.1	32	780	390	1466.8	8.3

RESULTS AND DISCUSSION

1. Microstructures Observation

Photo 2 shows a schematic diagram and microstructures welded with 316 filler metal between STS 304 and STS 304. Microstructure (a) of STS 304, base metal, shows typical austenite microstructures. Microstructure (b) shows the welding part, heat affected zone and base metal. And it appears that microstructure (c) is dendrite microstructures by welding heat.

2. Corrosion Potential Measurement Experimental

Fig. 1 shows variation of corrosion potential of STS 304, welding parts STS 316, STS 329 and STS 444 in #1 solution. As shown in Fig. 1, corrosion potential at 50 °C is more active compared to room temperature. STS 329 is the highest noble potential compared to welding part STS 316, STS 304 and STS 444 without regard to temperature. On the other hand, welding part STS 316 is the most active potential compared to the others STS. So welding part STS 316 acts as an anode for the other STS. It is suggested, therefore, that galvanic corrosion possibility of welding part STS 316 is the highest over the other STSs.

In #2 solution, general trends of corrosion potential are similar with Fig. 1. Welding part STS 316 is the most active potential compared to the other STSs. So welding part STS 316 must be given consideration as to possibility of galvanic corrosion by large cathode - small anode. And corrosion potential shifts to noble potential with the lapse of time by formation of passivity film in solutions for hot water tanks. According to Yamamoto et al. [1986] and Taka-

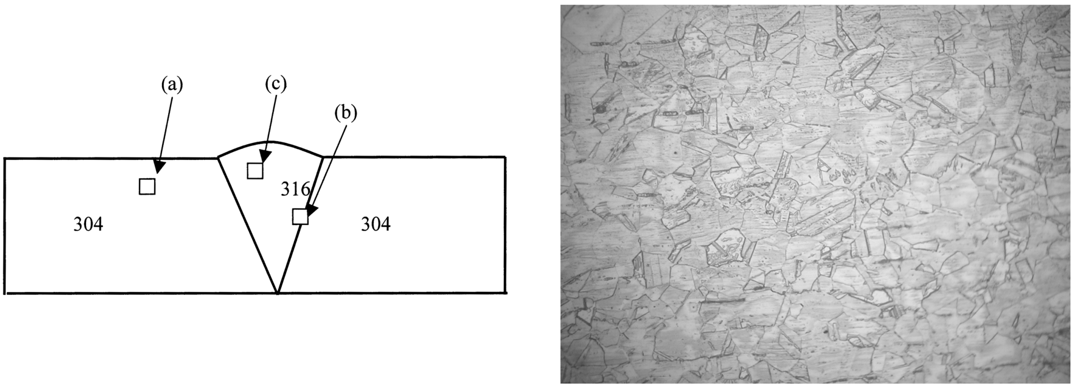
Table 1. Chemical composition and mechanical properties of various STSs

(a) Chemical composition

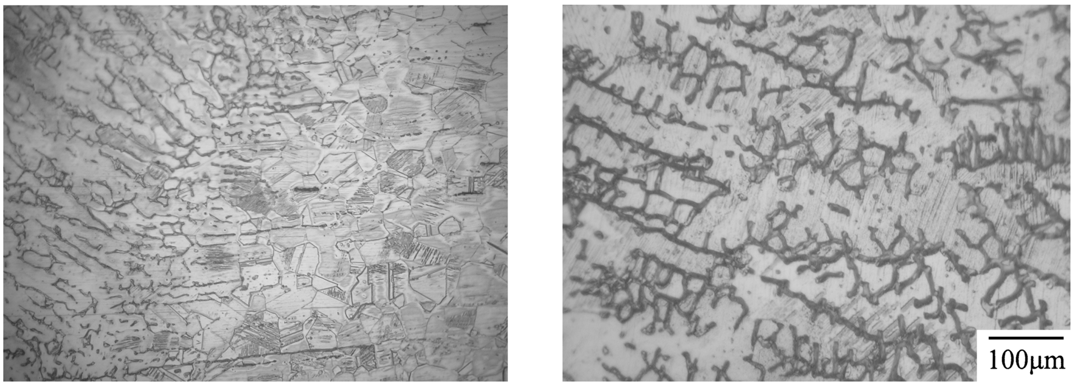
	Cr	Ni	C	Mn	Si	P	S
STS 304	18	8	0.08	2.0	1.0	0.045	0.030
STS 316	16	10	0.08	2.0	1.0	0.045	0.030
STS 329	27	5	0.20	1.0	0.75	0.040	0.030
STS 444	19.5	1.0	0.025	1.0	1.0	0.040	0.030

(b) Mechanical properties

	Tensile strength (MPa)	Yield strength (MPa)	Elongation (%)	Rockwell hardness
STS 304	580	292	55	81
STS 316	581	293	51	79
STS 329	726	557	26	98
STS 444	485	279	32	85



(a) Base metal



(b)Welding Metal, Heat Affected Zone and Base Metal

(c) Welding metal

Photo 2. Microstructures of STS 304 welded with 316 filler metal.

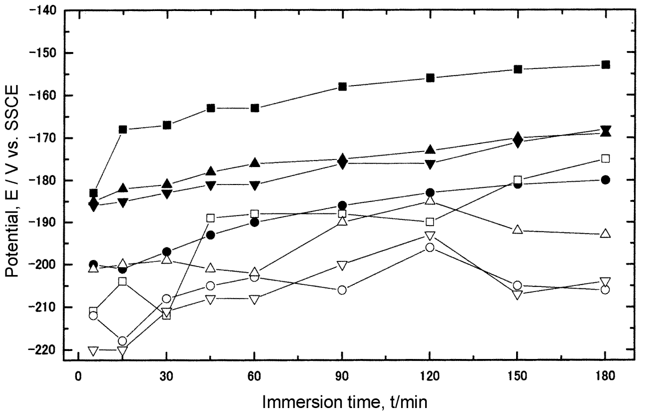


Fig. 1. Variation of corrosion potential of STS 304, welding part STS 316, STS 329 and STS 444 in #1 water [Room Temperature; STS 329 (■), STS 316 (●), STS 444 (▲) STS 304 (▼), At 50 °C; STS 329 (□), STS 316 (○), STS 444 (△), STS 304 (▽)].

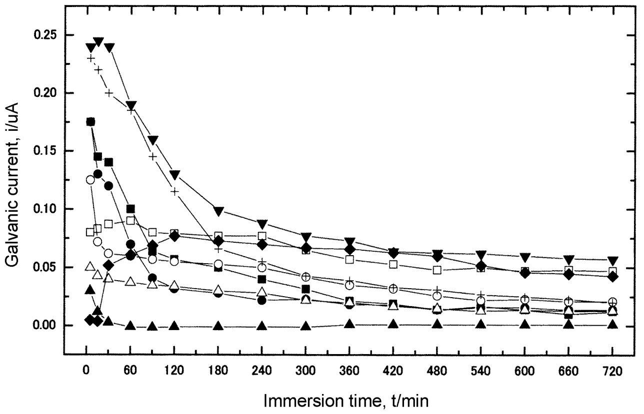


Fig. 2. Galvanic current between welding part STS 316 and STS 304, STS 329, STS 444 in #1 water at 50 °C [Area Ratio (1 : 1); STS 329 (■), STS 444 (●), STS 304 (▲), Area Ratio (1 : 5); STS 329 (□), STS 444 (○), STS 304 (△), Area Ratio (1 : 10); STS 329 (▼), STS 444 (◆), STS 304 (+)].

mura et al. [Akira et al., 1969], corrosion potential of STS 316 L with the lapse of time is shifted about 20 mV to noble direction during 120 minutes in H_2SO_4 solution. In addition, it is reported that the potential direction is different with the sort that contained a very small amount element. And corrosion potential at 50 °C is more active than that at room temperature regardless of #1, #2 solutions. It is suggested that ion is dissolved, easily, like residual chloride in higher temperature solutions. It is reported that temperature affects corrosion occurrence, corrosion type and corrosion rate [Wakahiro et al., 1998].

3. Galvanic Corrosion Test

Fig. 2 shows current flowing between welding part STS 316 and STS 304, STS 329, STS 444 at 50 °C in #1 solution. Welding part STS 316 is connected with the black terminal of the zero resistance ammeter, while STS 304, STS 329 and STS 444 are connected with red terminals. So it means that welding part STS 316 is corroded in the case of plus value (anode). As shown in Fig. 2, the galvanic current is increased with increasing area ratio. Galvanic currents were stabilized at approximately 180 min after immersion for all specimens. And potential difference between welding part STS 316 and STS 329 was the largest value; so current flowing between them is the largest value. Whereas, the potential difference between welding parts STS 316 and STS 304 is the smallest one, so flowing current is the smallest value. Accordingly, welding part STS 316, which became anode, is corroded because all current flowing became plus values. Galvanic current between welding parts STS 316 and STS 304, STS 329, STS 444 in room temperature of #1 solutions, in 50 °C and room temperature of #2 solution appeared to have almost similar trend as Fig. 2.

Galvanic current value after galvanic test 720 minutes at 50 °C in #1, 2 solutions is shown in Fig. 3. Generally, flowing current of STS 329 is the largest value, and than STS 444, STS 304. The galvanic current is increased with increasing area ratio. And potential difference between welding part STS 316 and STS 329 is the largest one, so galvanic current between them is the largest. On the other hand, potential difference between welding part STS 316 and STS 304 is the smallest, so galvanic current is the smallest.

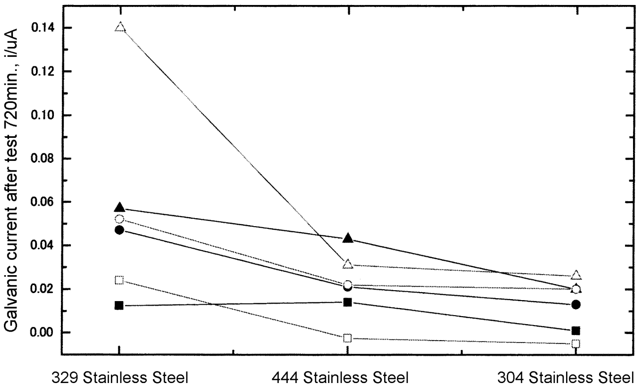


Fig. 3. Galvanic current after galvanic test 720 minutes at 50 °C as a function of water [#1 water, 50 °C; 1 : 1 (■), 1 : 5 (●), 1 : 10 (▲), #2 water, 50 °C; 1 : 1 (□), 1 : 5 (○), 1 : 10 (△)].

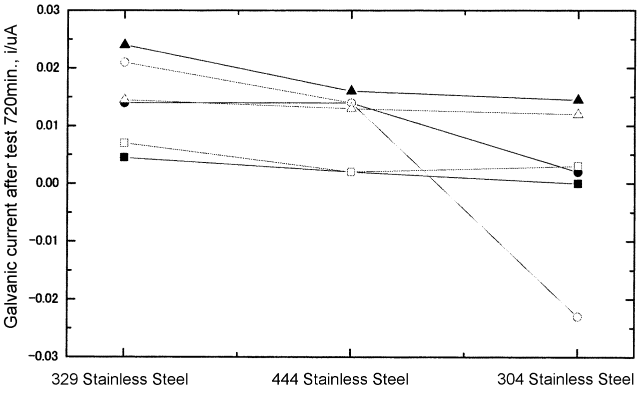


Fig. 4. Galvanic current after galvanic test 720 minutes at room temperature as a function of water [(#1 water, Room Temperature; 1 : 1 (■), 1 : 5 (●), 1 : 10 (▲), #2 water, Room Temperature; 1 : 1 (□), 1 : 5 (○), 1 : 10 (△)].

Fig. 4 shows galvanic current after galvanic test 720 minutes at room temperature in #1, #2 solutions. Galvanic current of Fig. 4 is by far smaller than that of 50 °C condition. It means that the possibility of galvanic corrosion at room temperature is by far smaller than 50 °C condition [Bellucci, 1991].

4. Anodic Polarization Test

Anodic polarization test of STS under corrosion environment can decide pitting potential and anodic protection potential region.

Anodic polarization curves of STS 304, welding parts STS 316, STS 329 and STS 444 in #1 solution are shown in Fig. 5. As shown there, all anodic polarization curves reveal passivity properties for all specimens. Passivity property of STS 329 is most excellent and then STS 444, welding parts STS 316, STS 304. Properties of welding parts STS 316, STS 329 and STS 444 are similar, while for STS 304 there appears large current density. And pitting potential of STS 329 is the highest value while that of STS 304 is the smallest one.

Fig. 6 shows anodic polarization curves of STS 304, welding parts STS 316, STS 329 and STS 444 in #2 solution. All anodic polarization curves in #2 solution also show passivity properties as like

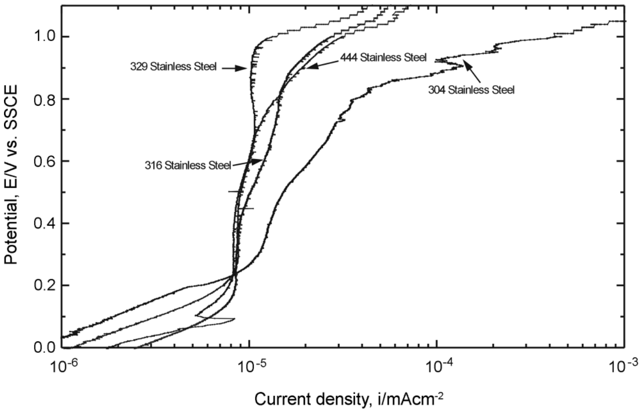


Fig. 5. Anodic polarization curves of STS 304, welding part STS 316, STS 329 and STS 444 in #1 water.

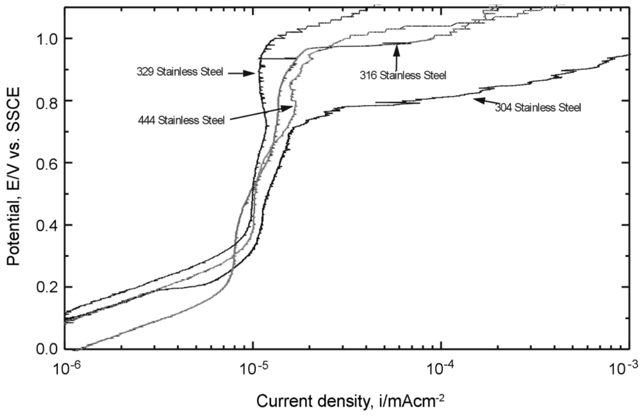


Fig. 6. Anodic polarization curves of STS 304, welding part STS 316, STS 329 and STS 444 in #2 water.

Table 3. Region of passivity potential in #1, #2 solutions

	STS 304	STS 316	STS 329	STS 444
#1 Water	0.27-0.85	0.16-1.01	0.1-1.0	0.23-1.01
#2 Water	0.315-0.78	0.215-0.97	0.36-1.0	0.35-0.94

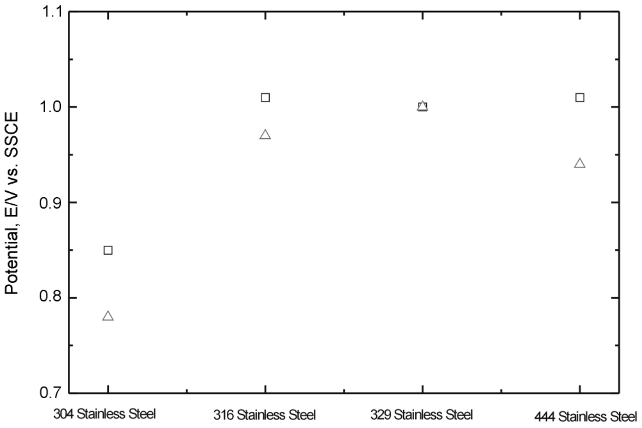


Fig. 7. Pitting potential of STS 304, welding part STS 316, STS 329 and STS 444 in #1, #2 waters (#1 water; □, #2 water; △).

#1 solution. Current density at passivity range in #2 solution is large compared to that in # 1 solution. Passivity property of STS 329 shows the most excellent property, while that of STS 304 appears the worst.

Next, Table 3 shows the region of passivity potential in #1, #2 solutions. Generally, passivity potential range can be practically defined as the range between active-passive transition and pitting potential. Therefore, this means that passivity formation potential is anodic protection region.

Fig. 7 is rearranged pitting potential through Fig. 5 and Fig. 6. Pitting potential of STS 304 is the lowest without regard to #1, #2 solutions. The low pitting potential means larger possibilities for pitting to occur. It is suggested that passive film of STS 304 is easier to destroy by chloride ion more than that of the other STS. In general, the greater the quantity of Cr and Ni, the more pitting potential shifts to noble potential direction. Whereas, it is reported that pitting potentials in chloride-containing solutions shift more than active potentials and current density is larger than no chloride solutions [Sedriks, 1996]. Therefore, the reason suggested is that passive film was destroyed by chloride ion. Pitting limiting potential should not be exceeded during anodic protection.

5. Cathodic Polarization Test

Cathodic polarization curves of STS under corrosion environment showed concentration polarization due to oxygen reduction reaction ($O_2+2H_2O+4e \rightarrow 4OH^-$) and activation polarization due to hydrogen gas generation ($2H^++2e \rightarrow H_2$, $2H_2O+2e \rightarrow H_2+2OH^-$). Cathodic protection limit potential is the boundary between concentration polarization and activation polarization. Therefore, under cathodic protection the limit potential has a risk of hydrogen embrittlement when over-protected.

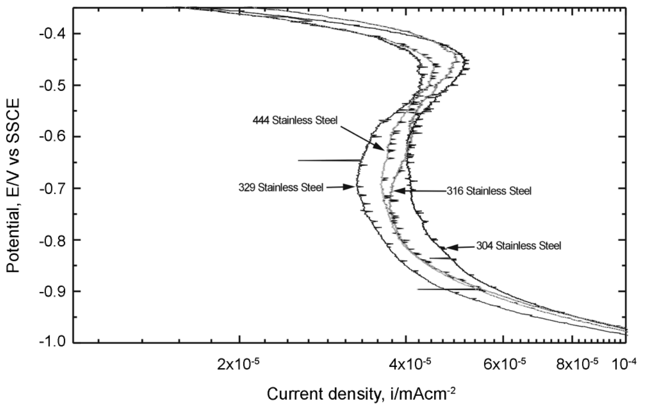


Fig. 8. Cathodic polarization curves of STS 304, welding part STS 316, STS 329 and STS 444 in #1 water.

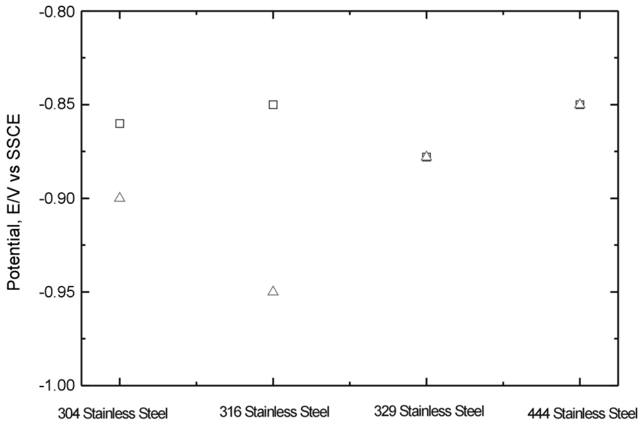


Fig. 9. Limiting potential of hydrogen embrittlement in #1, #2 waters (#1 water; □, #2 water; △).

Fig. 8 shows cathodic polarization curves of STS 304, welding parts STS 316, STS 329 and STS 444 in # 1, #2 solutions. As shown in Fig. 8, all polarization curves show concentration polarization and activation polarization. On the whole, current density of STS 329 is smallest. However, current densities of passivity range at anodic polarization curves are smaller than that of dissolved oxygen reduction reaction range at cathodic polarization curves. It means that anodic protection is beneficial compared to cathodic protection from an economic viewpoint. And corrosion current densities of #2 solution were larger than those of #1 solution.

Potential range showing dissolved oxygen reduction reaction in #1, #2 solutions is in Table 4. Fig. 9 shows limiting potential of hydrogen embrittlement in #1, #2 solutions. Limit potential of concentration polarization due to oxygen reduction reaction is approximately −850 mV~−950 mV (SSCE). However, this is hydrogen em-

Table 4. Potential range showing of dissolved oxygen reduction reaction in #1, #2 solutions

	STS 304	STS 316	STS 329	STS 444
#1 solution	−0.435~−0.86	−0.41~−0.85	−0.42~−0.878	−0.45~−0.85
#2 solution	−0.435~−0.90	−0.533~−0.95	−0.4~−0.878	−0.411~−0.85

brittlement due to molecular hydrogen, which can be seen with the naked eye, while it is reported that hydrogen embrittlement potential by atomic hydrogen ($H^+ + e \rightarrow H$) is likely to be more somewhat noble potential [France et al., 1999; Kazinczy, 1954; Galofalo et al., 1960]. Till now, electrochemical properties of specimens immersed in #2 solution are inferior to that in #1 solution through corrosion potential measurement, galvanic test and polarization test. It is the reason that Cl^- quantity in #2 solution is more than that in #1 solution [Lu et al., 1990].

6. Comparison Experiment of Standard STS 316 and Welded STS 316

Up to now, it has been suggested that the most direct reason is galvanic corrosion due to corrosion potential difference between welding parts STS 316 and STS 304, STS 329, STS 444. Therefore, filler metal should be used of the same material with base metal in order to make the hot water tank structure. And welding of dissimilar metals causes variation of steel composition; welding microstructures accompany intergranular corrosion and welding crack since corrosion and mechanical properties change. However, it is unknown whether welding part STS 316 has this property originally. Therefore, we investigated the reason through cathodic and anodic polarization test by using welding part STS 316 and standard STS 316 specimens.

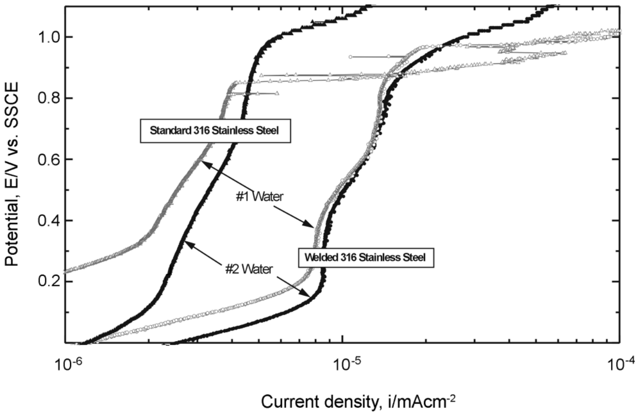


Fig. 10. Anodic polarization curves of welded STS 316 and standard STS 316 in #1, 2 water.

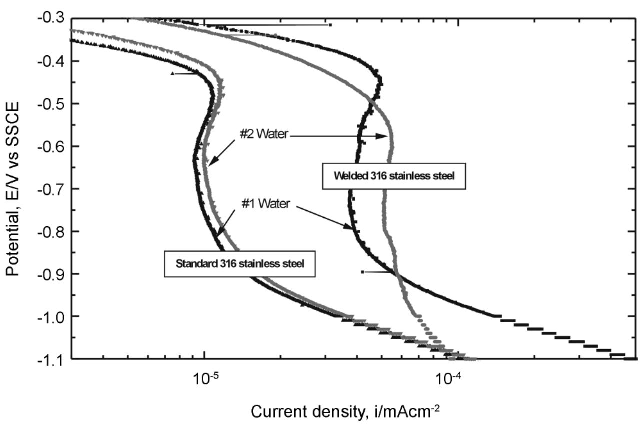


Fig. 11. Cathodic polarization curves of welded STS 316 and standard STS 316 in #1, 2 water.

Fig. 10 shows anodic polarization curves of welding part STS 316 and standard STS 316 in #1, #2 solutions. Current density at passivity region in welding part STS 316 is larger than that in standard STS 316 without regard to in #1, #2 solutions.

The cathodic polarization curves of welding part STS 316 and standard STS 316 in #1, #2 solutions are shown in Fig. 11. Current density at concentration polarization by dissolved oxygen reduction reaction in welding part STS 316 is about four times larger than that in standard STS 316 regardless of #1, #2 solutions. As shown in Fig. 10 and Fig. 11, electrochemical properties of standard STS 316 are better than those of welding part STS 316 in #1, #2 solutions. It was suggested that variation of hardness and microstructure due to rapid heating and cooling by welding process were resulting in galvanic cell by potential difference of each welding part; subsequently, it can be attributed to enhancing the galvanic corrosion of welding parts. In addition, it was reported that corrosion problems probably might be caused by both physical parameters such as welding methods, welding design condition and residual stress as well as metallurgical parameters such as chemical composition, segregation, inclusion and impurity [Nishiyi, 1964].

From now, we are investigating in relation to STS corrosion of a hot water tank. Adequate countermeasures are anodic and cathodic protection methods. Anodic protection method must maintain passivation formation potential in the range of Table 3. And cathodic protection method must maintain potential, which occurred, dissolved oxygen reduction reaction above hydrogen embrittlement generation potential like the range of Table 4. It is suggested that to maintain cathodic protection potential of STS for hot water tank carried out sacrificial anode protection method by Al alloy etc. and impressed current method by Pt electrode etc. Besides, galvanic corrosion is prevented by executing post-weld heat treatment [Kim et al., 2002, 2003; Moon et al., 2003], which reduces potential difference between welding part and base metal. And also galvanic corrosion current can be prevented from flowing by painting.

CONCLUSION

Galvanic current is affected by the area ratio, temperature and the kind of STS for a hot water tank. Corrosion potential of welding part STS 316 was lower than that of STS 304, STS 329, STS 444 in #1, #2 solutions. Therefore, it is suggested that welding part STS 316 acts as anode for the other STSs. The amplitude of galvanic current between welding part STS 316 and STS 304, STS 329, STS 444 in #1 solution is smaller than that of #2 solution. It is reason that chloride ion quantity of #2 solution is more than that of #1 solution. In the flowing current experiment by galvanic cell between welding parts STS 316 and STS 304, STS 329, STS 444, welding part STS 316 is easy to corrode by acting as an anode compared to the other STS. For polarization trends of STS 316, current density of welding part STS 316 is higher than that of standard STS 316.

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