Repassivation Potential E_R for Crevice Corrosion of Type 304 Stainless Steel/FPM-Crevice in Neutral NaCl/NaF Solutions

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The effects of fluoride ion on the crevice corrosion for a FPM/metal of a type 304 stainless steel were studied in terms of repassivation potential (E_R) measurements in neutral NaCl/NaF mixed solutions at 303 K. It was found that the E_R values shifted to the noble direction by presence of F^- , sufficient concentrations of which promoted uniform dissolution of the nobly polarized stainless steel. There was a good correlation between E_R and V_{crev} .

Key words : fluoride, chloride, repassivation potential, stainless steel, crevice corrosion

1. Introduction

The repassivation potential, E_R has been successfully developed as a evaluation method for the crevice corrosion susceptibility by Tsujikawa *et al.*^{1)~6)} E_R is recognized to be a well reproducible electrochemical parameter for repassivation of crevice corrosion. Under chloride^{1)~4)}, bromide⁵⁾ and seawater⁶⁾ environments, the E_R values have been found to be coincide with the critical crevice corrosion potential, V_{crev} , above which crevice corrosion can initiate and continue to grow. Much work has been published on the causes and effects for the crevice corrosion of stainless steels by E_R measurements in chloride solutions^{2), 6)~9)}. However, there has not been a report concerning effect of fluoride ion on E_R for stainless steels in aqueous solutions.

In a previous study¹⁰⁾, the effect of fluoride ion on crevice corrosion for type 304 stainless steel was studied in terms of V_{crev} , in neutral NaCl solutions. It was found that fluoride ion has an inhibitive effect to the chloride ion-induced crevice corrosion.

The subjects of this paper are to examine the effect of fluoride ion on E_R for type 304 stainless steel in neutral NaCl solutions, and then to compare the E_R with the V_{crev} reported previously¹⁰⁾.

2. Experimental Method

2.1 Test Material

Test material used in this work was a type 304 (bright annealed) stainless steel sheet with thickness of 0.4 mm. The chemical composition of the steel is shown in Table 1.

2.2 Crevice electrode

Rectangular test pieces with 15×50 mm/ea. were cut out from the steel sheet. Each test piece surface was mechanically wet-polished using SiC paper up to 240 grid. The crevice electrode assembly is shown in Figure 1. A fluoro rubber (FPM) gasket, a test piece and a support plate with a lead wire were held together in an acrylic holder to be tightened by an acrylic screw at the back side of the support plate, with a constant fastening torque of 1×10^{-1} N·m. The acrylic holder has a hole of 11.3 mm in diameter and the FPM gasket has that of 8.0 mm in diameter. This means that the exposed area (crevice-free surface) is 50 mm² and the shielded one (metal/FPM crevice) is also 50 mm².

2.3 Test Solutions

Test solutions were prepared from reagent grade NaCl and NaF, and distilled water with

Table 1 Chemical composition of the test material (mass%).

C	Si	Mn	P	S	Ni	Cr	Cu	Mo	N	O
0.062	0.57	1.15	0.028	0.003	8.42	18.21	0.02	0.01	0.0493	0.0052

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Fig. 1 Assembly of crevice electrode (mm).

a specific electric conductivity less than $2 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$. The upper limit of concentrations for NaCl and NaF in the test solution was $5 \times 10^{-1} \text{ kmol} \cdot \text{m}^{-3}$ (in the following, simply represented in unit M). The pH range of the test solutions was 5.3–6.7. The solution was supplied without further adjusting the pH. The temperature of the test solution was held at 303 K by a thermostat, and the solution was deaerated by purified nitrogen gas bubbling before and throughout each polarization experiment.

2.4 E_R Measurements

The E_R measurements were performed using a computer-controlled potentiostat/galvanostat (HZ-1A, Hokuto Denko Co., Ltd), and a X-T recorder (The current was recorded as a function of time). A three-electrodes cell consisting of a saturated calomel electrode (SCE) as the reference electrode and a smooth Pt sheet as the counter electrode was used. All potential values given below are expressed in the SCE scale.

Measurement of E_R was based on the works of Tsujikawa *et al.*^{1), 11), 12)} and the procedure was illustrated in Figure 2. The crevice electrode was polarized to the noble direction (positive scan) from the natural corrosion potential with a scanning rate of $5 \times 10^{-3} \text{ V} \cdot \text{min}^{-1}$ and held galvanostatically for 2 hours at the current of $2 \times 10^{-4} \text{ A}$. Then the crevice electrode was polarized to the less noble direction (negative scan) with a scanning rate of $1 \times 10^{-3} \text{ V} \cdot \text{min}^{-1}$ until a current decreased to $5 \times 10^{-5} \text{ A}$. Then, polarization was stepped down by an increment of $1 \times 10^{-2} \text{ V}$ every 3 hours un-

Fig. 2 Procedure for E_R measurement.

til the current showed a decreasing tendency. E_R was determined as a potential at which the current decreased to the passive level and showed no increasing tendency. Reproducibility of E_R measurements was good. The E_R values given below are expressed the mean value of three-times measurements.

3. Results and Discussion

3.1 Cyclic polarization curves

Cyclic polarization curves obtained in NaCl solutions are shown in Figure 3. A hysteresis was observed in each curve and E_R moved to the less noble direction with increasing NaCl concentration. Effects of NaCl concentration on the E_R agree with the data reported by Tsujikawa *et al.*, for type 444^{3), 12)} and type 316^{12), 13)} stainless steels. Appearance of the specimen after a cyclic polarization test in $5 \times 10^{-1} \text{ M}$ NaCl solution is shown in Figure 4. The crevice corrosion occurred on the crevice surface (metal/FPM-crevice) and the maximum corrosion depth of that was $80 \mu\text{m}$. Similarly, the maximum corrosion depths at crevice surfaces after the tests in each $1 \times 10^{-2} \sim 1 \times 10^{-1} \text{ M}$ NaCl solutions were in a range of 70 to $100 \mu\text{m}$, which was not dependent upon NaCl concentration.

Cyclic polarization curves obtained in NaF solutions are shown in Figure 5. In $1 \times 10^{-2} \sim 1 \times 10^{-1} \text{ M}$ NaF solutions, contrary to the curves obtained in NaCl solutions, each polarization curve in the negative scan was almost identi-

Fig. 3 Cyclic polarization curves for FPM/304 ss-crevice in the NaCl solutions at 303 K.

Fig. 4 Appearance of the specimen after a cyclic polarization test in the 5×10^{-1} M NaCl solution.

cal with the one in the positive scan. Namely, hysteresis was not observed. General metal dissolution was observed in each solution during the galvanostatic polarization at a current of 2×10^{-4} A. In 5×10^{-1} M NaF solution, a potential shifted to the noble direction during the galvanostatic polarization at a current of 2×10^{-4} A. The polarization curve in the negative scan differed from the one in the positive scan. This phenomenon is assumed that the protective film was formed on the specimen surface. Appearance of the specimen after a cyclic polarization test in 5×10^{-1} M NaF solution is shown in Figure 6 as a typical example in the NaF solution. The uniform dissolution occurred on the crevice-free surface of which luster was lost. On the crevice surface, corrosion products were deposited. Thus in NaF so-

Fig. 5 Cyclic polarization curves for FPM/304 ss-crevice in the NaF solutions at 303 K.

Fig. 6 Appearance of the specimen after a cyclic polarization test in the 5×10^{-1} M NaF solution.

lutions, hysteresis was not observed in the cyclic polarization curves, which means that only uniform dissolution occurs on the crevice-free surface and that no crevice corrosion will grow on the crevice surface.

Cyclic polarization curves obtained in 5×10^{-2} M NaCl/ X NaF ($X = 0 \sim 5 \times 10^{-1}$ M) solutions are shown in Figure 7 as a typical example in the NaCl/NaF mixed solutions. E_R moved to the noble direction with increasing NaF concentration. It is interesting that current-fluctuations were observed during the negative

Fig. 7 Effect of NaF concentration on the cyclic polarization curve for FPM/304 ss-crevice in the 5×10^{-2} M NaCl solutions at 303 K.

scan, and frequency of that occurrence was drastically enhanced with increasing NaF concentration. These results suggest that there are competitive effects between the aggressive Cl^- and the inhibitive F^- ions for growing crevice corrosion.

3.2 E_R in NaCl/NaF Solutions

E_R values obtained in $1 \times 10^{-2} \sim 5 \times 10^{-1}$ M NaCl/ X NaF ($X=0 \sim 5 \times 10^{-1}$ M) solutions are summarized in Figure 8. The data indicate that the effect of increasing NaF concentration is to shift E_R to the noble direction in fixed NaCl concentration. However, in 1×10^{-2} M NaCl/ 5×10^{-1} M NaF solution, the cyclic polarization curve was identical with the one in absence of Cl^- (5×10^{-1} M NaF) as indicated in Figure 5. In that solution, crevice corrosion did not occur at all and only uniform dissolution occurred on the crevice-free surface. Thus, it was found that the fluoride ion has an inhibitive effect to the chloride ion-induced crevice corrosion and promotes the uniform dissolution to the steels.

3.3 Comparison of E_R and V_{crev}

Figure 9 shows the relationship between the values of E_R and V_{crev} ¹⁰⁾ obtained in the NaCl/NaF mixed solutions. The V_{crev} values were quoted from the experiment of previous paper¹⁰⁾ performed in the same condition as the present one. There was a good correlation between E_R and V_{crev} . The correlation coefficient was 0.98. Coincidence of V_{crev} and E_R values

Fig. 8 Effect of NaF concentration on the E_R values for FPM/304 ss-crevice in NaCl solutions at 303 K.

Fig. 9 Relationship between the E_R values and the V_{crev} values¹⁰⁾ obtained in NaCl/NaF mixed solutions at 303 K.

means that they are the critical potentials which are equivalent to both initiation and repassivation of crevice corrosion¹⁾. It is concluded that the E_R measurement is also applicable to NaCl/NaF mixed solutions.

4. Conclusions

- 1) In neutral NaF solution, crevice corrosion does not occur, and only uniform dissolution occurs on the crevice-free surface.
- 2) E_R is shifted to the noble direction by presence of F^- , sufficient concentrations of which promote the uniform dissolution to the nobly polarized stainless steel in neutral NaCl solution.
- 3) There is a good correlation between E_R

and V_{crev} . Then, the E_R measurement can be applied to NaCl/NaF mixed solutions.

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