

A Study on the Crevice Corrosion for Ferritic Stainless Steel by Micro Capillary Tube Method

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(2004년 8월 24일 접수 : 2004년 11월 23일 채택)

Abstract: The aim of this study is to investigate the initiation and propagation of crevice corrosion for ferritic stainless steel in artificial crevice based on micro capillary tube method. The 430 stainless steel in artificial crevice is potentiostatically polarized in different sodium chloride solutions. Potentiodynamic and potentiostatic polarization data were measured in situ. The potentials in the crevice were measured by depth profile using the 0.04 mm diameter micro capillary tube inserted in the crevice. The potentials in the crevice ranged from -220 mV to -360 mV vs SCE from opening to bottom of crevice, which are lower than the external surface potential, -200 mV vs SCE. Such a potential drop induced the change of the metal surface state from passive to active. The surface of metal is located in passive state in -200 mV but the inner surface keeps active state below -220 mV. Thus these results show that the IR drop mechanism in the crevice was more objective for evaluation and the method was easier to reproduce. Therefore the potential drop is one of the reasons for crevice corrosion by measuring the potentials in narrow crevice with a new micro measuring system.

Key words: ferritic stainless steel, crevice corrosion, potentiostatic polarization, IR drop mechanism, micro capillary tube

1. Introduction

Ferritic stainless steel is a body centered cubic structure even after heat treatment in normal temperature a Fe-Cr series alloy with 12~30 wt% of Cr.¹⁾ Corrosion resistance and strength are improved as Cr content increases. Also the price of material is cheaper than austenite stainless steel due to the low contents of Ni, while austenite stainless steel is very sensitive to stress corrosion cracking in hot chloride environment. On the other hand, ferritic stainless steel is known to have a good stress corrosion resistance.²⁻⁴⁾ For this reason, the consumption of ferritic stainless steel is increasing in automobile material, domestic electric appliances, and water heaters, etc.

It is very difficult to examine the crevice corrosion due to random initiation, propagation, position and composition rate, so there is a great difficulty in explaining the mechanism of crevice corrosion.⁵⁾ Almost all of the traditional mechanism of crevice corrosion rely on acidification, mass transport, and forms, but exclude the electrode potential and its distribution within the crevice. The mechanism of IR drop is interested in the outer surface of passive sample with higher voltage and inside of crevice is positioned on lower potential. The potential difference exists between the inner and outer sides of crevice. Especially, some researchers proved that IR drop inside crevice is connected to the IR drop theory by mathematical modeling. It was proposed in the mechanism progress of crevice corrosion from chemical

change of crevice solution.^{6,7)} Nevertheless, they did not conclude that the IR mechanism could be operated during the induction period. Also, the cause of many localized corrosion studies can be reexamined by IR drop process. The mechanism of IR Drop puts its interest in the outer surface of passive sample and existing electric potential difference of inside crevice. That is, active crevice corrosion can be developed at the position of a certain distance in the inside crevice direction in any situation, and the outer surface of the sample still maintains the passive state. The mechanism's $IR > \Delta\phi^*$ criterion, where $\Delta\phi^*$ is the difference between the applied potential, ESURF, and the electrode potential of the active/passive transition, EA/P, has also been measured in crevice corrosion.

This study used technical method developed for micro capillary tube to measure the potential difference between the crevice bottom and opening, which was too narrow to measure potentials. Therefore, this research focused on the ferritic 430 stainless steel with the crevice. The artificial crevice was assembled onto the sample. The different concentrations of solution ranged from 0.01N to 0.5N NaCl are used for an important factor of corrosion environment. The potential and current were measured in potentiodynamic and potentiostatic polarization by using a 0.04 mm micro capillary tube in the crevice.

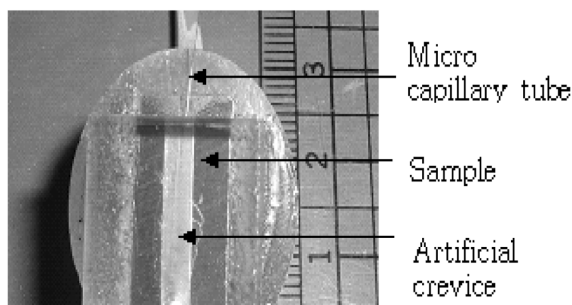
2. Experimental procedures

The composition of experimental material 430 stainless steel is shown in Table 1. The size of all samples is $10 \times 20 \times 5$ mm. Samples were mounted in a fast curing epoxy with

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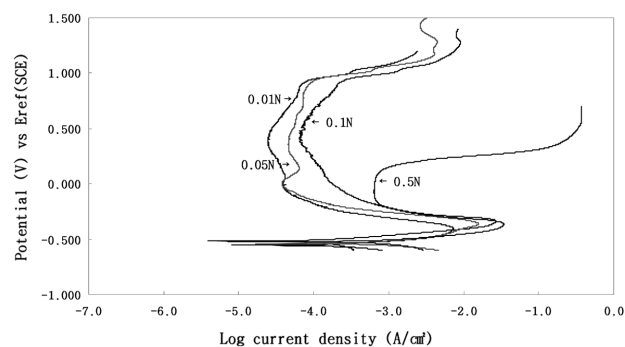
Table 1. The chemical composition of 430 stainless steel.

Element	Fe	Cr	Ni	Mo	C
Wt %	82.26	16.46	0.32	0.0024	0.055
Element	Si	Mn	P	S	
Wt %	0.36	0.50	0.035	0.004	

**Fig. 1. Experimental set of crevice corrosion.**

a copper wire soldered to back side, and grounded to expose 10×20 mm crevice surface. The 430 stainless steels were mechanically polished with fine SiC paper to 1200grit and polished with $0.2 \mu\text{m}$ final aluminum oxide (Al_2O_3) powder. Prior to tests, samples were cleaned ultrasonically with ethyl alcohol. The $3 \times 16 \times 0.2$ mm of artificial crevice was attached on the sample. The experimental set of sample, artificial crevice, and micro capillary tube in the crevice are shown in Fig. 1. The potentials in the crevice were measured by the micro capillary tube inserted in the crevice.

The potentiostat (CMS-100) was used as electrochemical corrosion measuring system of Gamry Co.^{8,9)} A high density graphite and a saturated calomel electrode (SCE) were used for the counter and reference electrodes. All potentials are referenced to the SCE respectively. $1\text{N H}_2\text{SO}_4$ solution was used as a corrosion solution for passivation of the surface and NaCl was added for providing Cl^- which is known to break the passive film. All tests were performed at room temperature. For the checking of Cl^- effect, four kinds of NaCl concentration such as 0.01N, 0.05N, 0.1N and 0.5N were selected. For the electrochemical evaluation methods, a potentiodynamic polarization test was carried out with scanning rate 600 mV/hr from -600 mV vs SCE to $+1,200 \text{ mV vs SCE}$. The change of potential and current density in the artificial crevice were measured by depth profile to outer crevice under the applied potential -200 mV vs SCE . The corrosion behavior of corrosion potentials and passive current density were analyzed. N_2 gas was purged by $150 \text{ cm}^3/\text{min}$ for 30 minutes before the test to remove dissolved oxygen.

**Fig. 2. Polarization curves of 430 stainless steel.**

3. Results and discussion

The polarization curves of 430 stainless steel in the sulfuric acid solution containing four different concentrations of sodium chloride such as $1\text{N H}_2\text{SO}_4 + 0.01\text{N}$, 0.05N , 0.1N and 0.5N NaCl are shown in Fig. 2. The summary of corrosion potential (E_{cor}), critical current density (i_{crit}), passivation current density (i_p) and break down potential (E_b) are shown in Table 2.

In Fig. 2, all curves indicated that corrosion potential values tended to decrease as sodium chloride concentration increased. On the other hand, critical current density and the passive current density values increased, while break down potential values decreased. In case of -200 mV vs SCE , all curves showed the in passive state despite of different sodium chloride concentrations. The influence of crevice corrosion initiation time and current density of sodium chloride concentration would be shown by potentiostatic polarization curve, Fig. 3. In Fig. 3, the upper part is the current density change with applied potential and lower part is the detailed current density change with time.

The current density at the inside of the crevice increased with increasing NaCl concentration. The crevice corrosion initiation time, namely break down of passive film was shortened as sodium chloride concentration increased.

In case of low concentration, such as 0.01N NaCl , the change of current density did not appear until $86,400 \text{ s}$ (24 h) in the testing period. On the other hand, in case concentrations were 0.05N , 0.1N , and 0.5N , current density suddenly increased to $1,720 \text{ s}$ (29 min), $1,408 \text{ s}$ (23 min) and 550 s (9 min). The current density was measured as 0.96 , 1.87 , and 6.60 mA/cm^2 respectively.

Many studies indicated that the differences of Cl^- ion concentration and dissolved oxygen concentration should be arisen between inner and out of the narrow crevice.¹⁰⁻¹²⁾ The

Table 2. The summarization of potentiodynamic polarization data.

NaCl concentration	Corrosion potential (mV/SCE)	Critical current density (mA/B θ)	Passivation current density (mA/B θ)	Break down potential (mV/SCE)
0.01N	-517	6.31	0.03	951
0.05N	-523	15.85	0.05	949
0.1N	-539	25.12	0.06	921
0.5N	-554	31.62	0.63	142

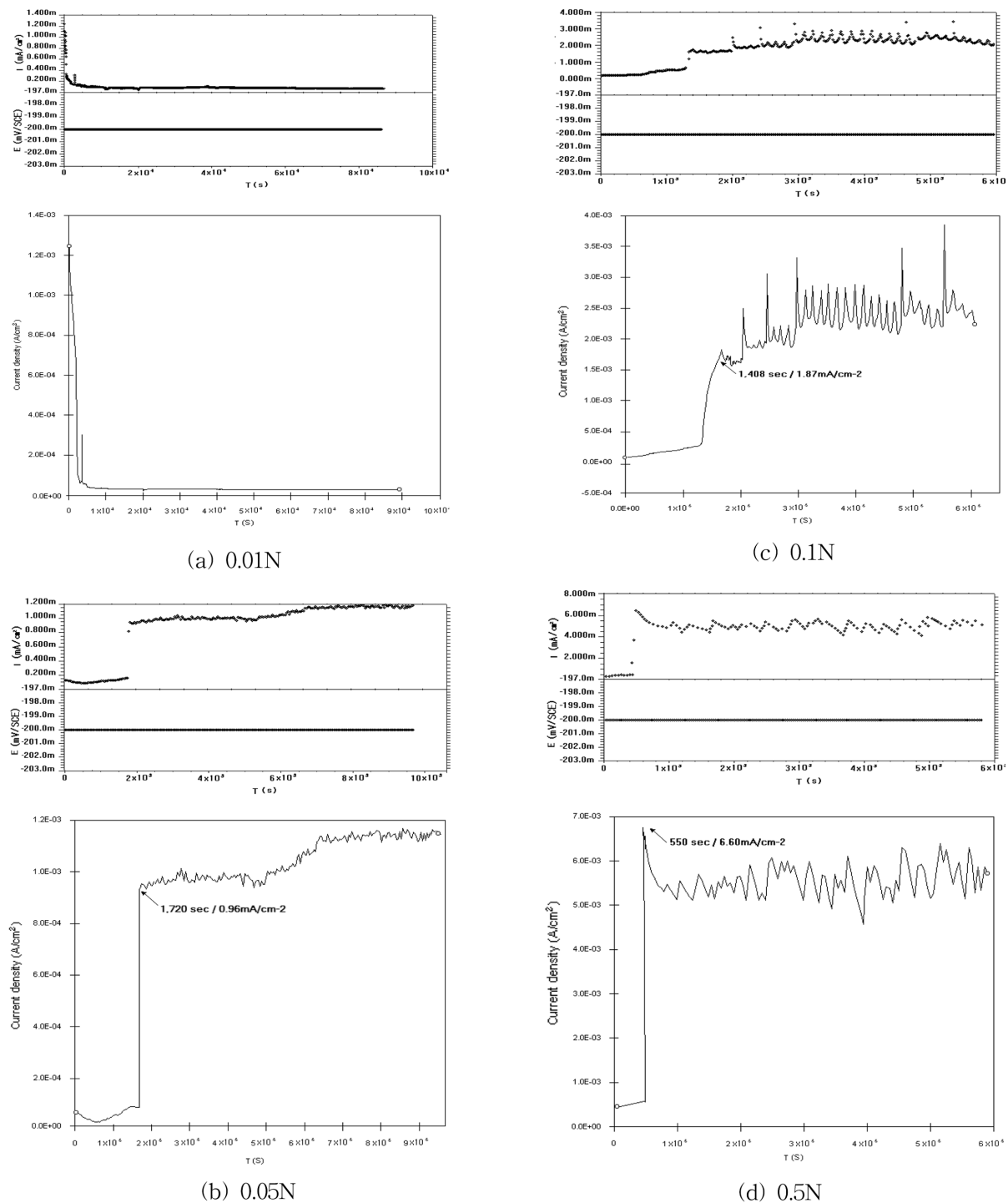


Fig. 3. The relation between the current density and time for crevice corrosion in 1N sulfuric acid solution with different sodium chloride of (a) 0.01N (b) 0.05N (c) 0.1N and (d) 0.5N

ions of Fe^{2+} , FeOH^+ , H^+ , OH^- , Na^+ , Cl^- , etc. in the inside of crevice are controlled by diffusion, electrical transfer, and chemical reaction.¹³⁾ If the ion concentration exceeds the concentration of minimum break content, the passive film will begin to breakdown. The break down of passive film is accelerated by increased Cl^- ion concentration. Also the difference of concentration will induce potential change as Nernst equation, that is;

$$E = E_0 + 0.0592 \log \frac{[M^{n+}]}{n}$$

n : the number of charge transfer

M^{n+} : concentration of material

The cause of IR drop inside the crevice is thought as the following; certain aggressive ions (mostly Cl^- and H^+) are promoted to transfer inside the solution and change local

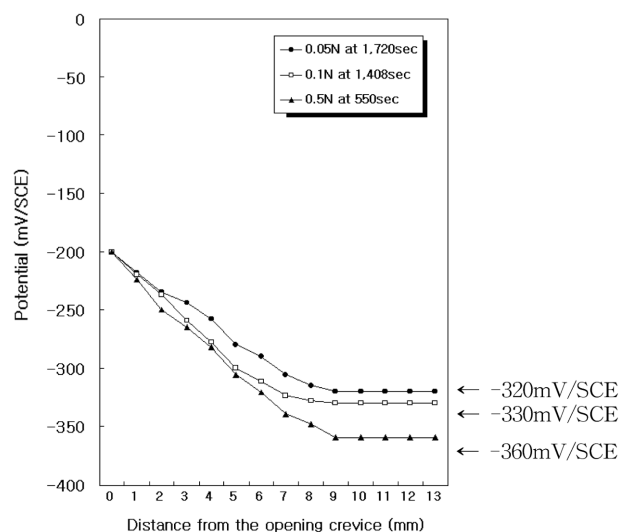


Fig. 4. Potential distribution profiles inside a crevice with variation of NaCl concentration

chemical reaction inside the crevice, break the passive film, and the potential of the inside crevice drops more than the outside due to potential difference between the outside and inside dependent on ion transfer.

The -200 mV vs SCE in the passive region of the polarization curve was applied to crevice opening of sample. The results are shown in Fig. 4. In Fig. 4, the potentials were lowered with increasing depth of crevice. Such a potential change has arisen by the difference of Cl^- ion concentration as mentioned above.

The measured maximum potentials of the inside of crevice were -320, -330 and -360 mV vs SCE for 0.05, 0.1 and 0.5N solutions respectively.

The potential differences were measured at the opening and the bottom of the crevice. In case, potential drop exceeds the critical potential from passive to active state. The environment of film should be located in active state. It was also found that the drop of potential values induced the film to breakdown state, which caused the crevice corrosion.

Fig. 5 shows the 430 stainless steel crevice corrosion states with different sodium chloride solutions. In Fig. 5 at the concentration of 0.01N no crevice corrosion was detected. whereas at 0.05N, 0.1N and 0.5N appeared a large of amount crevice corrosion as shown in Fig.3 (b), (c), (d) and Fig. 4.

4. Conclusions

The crevice corrosion of the ferritic stainless steel was investigated by the micro capillary tube technique for 1N H_2SO_4 with different concentrations of 0.01N, 0.05N, 0.1N and 0.5N NaCl.

First, E_{cor} (corrosion potential) and E_b (breakdown potential) decreased as NaCl concentration increased. on the other hand, i_{crit} (critical current concentration) and i_p (passive current density) values increased with NaCl concentration. Also,

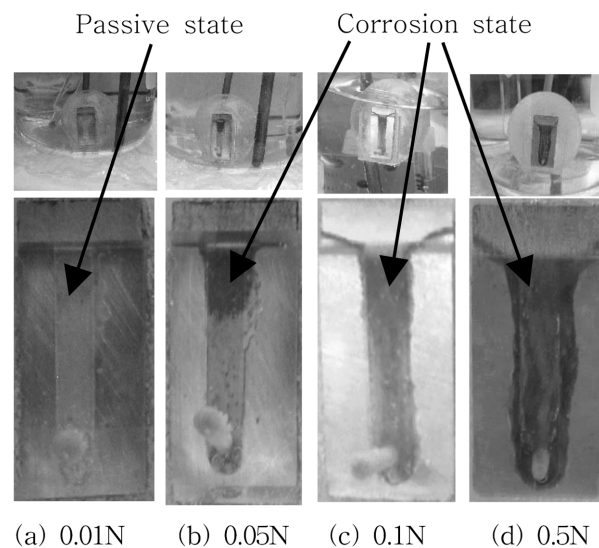


Fig. 5. Surface of crevice corrosion samples in different solution

crevice corrosion rapidly increased as the concentration of NaCl increased, except 0.01N concentration.

Second, under the passive state -200 mV vs SCE potential was applied to the sample surface, then the passive film in the crevice was broken. The breakdown of film is due to potential changes from passive to active state due to concentration differences of inner and outer crevice. The potential change with crevice depth and current density increased rapidly as the increasing Cl^- concentration. Therefore we could confirm that the potential drop was one of the reasons for crevice corrosion by measuring the potentials in narrow crevice with a new micro measuring system. Meanwhile, the IR drop mechanism in the crevice was more objective for evaluation and the method was easier to reproduce.

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