IR drop of the crevice corrosion for ferritic stainless steel by electrochemical approach

EUN-YOUNG NA
Research Institute of Energy Resources Technology, Chosun University, Gwangju 501-759, Korea
E-mail: eyna@chosun.ac.kr

Published online: 16 September 2005

It is very difficult to examine the problem of crevice corrosion, due to the irregularity of the corrosion initiation time and place and the velocity of corrosion propagation [1], and the reproducibility of the results is always a problem in crevice corrosion studies. Thus, it is very difficulty to explain the mechanism of progression of crevice corrosion. In addition, despite the increasing consumption of ferritic stainless steel, little research has been done on the problem of crevice corrosion for this metal. The mechanism of IR drop focuses on the outer surface of the passive sample and the existing electric potential difference inside of the crevice. There have been several studies which proved the existence of the IR drop inside the crevice, a phenomenon which is connected to the IR drop theory, through both experiment and by mathematical modeling. In these studies, it was proposed that the mechanism of progression of crevice corrosion results from chemical changes in the crevice solution [2–7]. However, these studies did not reach any firm conclusion as to the IR mechanism involved during the crevice corrosion induction period. The aim of this study was to investigate the initiation of crevice corrosion for ferritic 430 stainless steel using a newly developed technical method involving the use of a microcapillary tube, and to measure the potential difference between the crevice bottom and opening, which was too small to be measured directly. Therefore, in this study, we focused on measuring the IR drop of the ferritic 430 stainless steel within the crevice by the electrochemical approach. The potential and current were measured in directly by measuring the potentiodynamic and potentiostatic polarization by means of the depth profile technique using a microcapillary tube which was inserted into the crevice.

The sample was mounted in a fast curing epoxy with a copper wire soldered on one side, and ground to expose the 10 × 20 mm outer surface. The 3 × 16 × 0.2 mm artificial crevice was attached each sample. The electrode potential on the crevice wall was measured by positioning the microcapillary tube at the vertical boundary on the crevice wall. A model CMS-100 potentiostat manufactured by Garmry Corp. was used to measure the electrochemical corrosion. A carbon rod and a saturated calomel electrode (SCE) were used for the counter and reference electrodes, respectively. 1 N H_2SO_4 solution was used as the corrosion solution for the passivation of the surface, and 0.1 N NaCl was added to provide the Cl^- ion, which is known to break down the passive film. Three different solution temperatures were used viz. 20 °C, 30 °C, and 50 °C. For the electrochemical evaluation, the potentiodynamic polarization test was used with a scanning rate of 600 mV/h from −600 mV versus SCE to +1,200 mV versus SCE in the positive direction. N_2 gas was provided at a flow rate of 150 cm^3/min for 30 min before the test, in order to remove any dissolved oxygen. Then, the potentiostatic polarization test was used to measure the passive current density and crevice corrosion initiation time.

The anodic polarization curve of the 430 stainless steel at the different solution temperatures is shown in Fig. 1. These curves indicate that the corrosion electric potential values decreased as the solution temperature increased, exhibiting values of −523, −544, and −548 mV versus SCE at the solution temperatures of 20 °C, 30 °C, and 50 °C, respectively. On the other hand, the critical current density values increased as the solution temperature increased, exhibiting values of 25.12, 50.12, and 79.43 mA/cm^2 at the solution temperatures of 20 °C, 30 °C, and 50 °C, respectively. The passive current density increased, while the break down potential values decreased, as the solution temperature increased. However, these data show that the passive region included −200 mV versus SCE for the different solution temperatures. The influence of the crevice corrosion initiation time and the current density of the solution temperature can be seen in the potentiostatic polarization curves shown in Fig. 2. Fig. 2 shows the dependence of the current density values on the elapsed time. The crevice corrosion initiation time decreased as the solution temperature increased. For the solution temperatures of 20 °C, 30 °C, and 50 °C, it took 1,408 s (23 min), 780 s (13 min) and 750 s (12 min) for crevice corrosion to develop, respectively. The corresponding current densities for these temperatures were 1.87, 2.50, and 2.87 mA/cm^2 respectively. A passive potential of −200 mV versus SCE, in the passive region of the polarization curve, was applied to the crevice opening of the sample, and the results are shown in Fig. 3. Even though a passive potential of −200 mV versus SCE is applied to the crevice, because the depth of the crevice is more than 1 mm, due to the potential drop, the passive potential reaches −220 mV versus SCE. Also, the potential was lowered

0022-2461 © *2005 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-005-4507-x

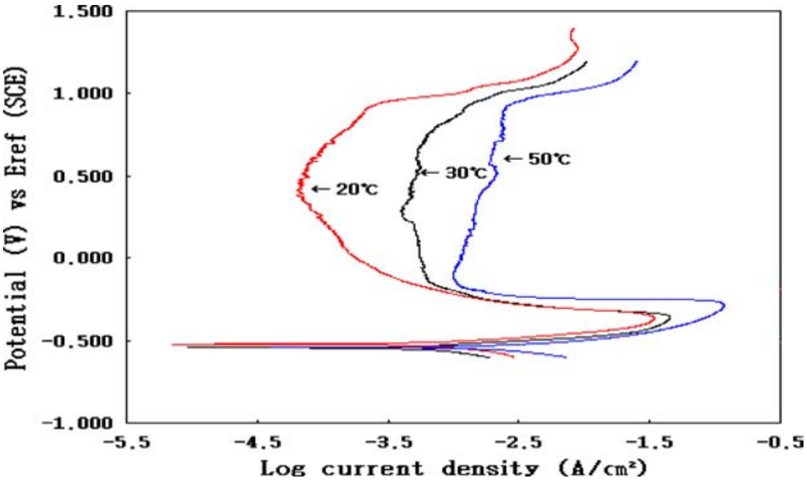
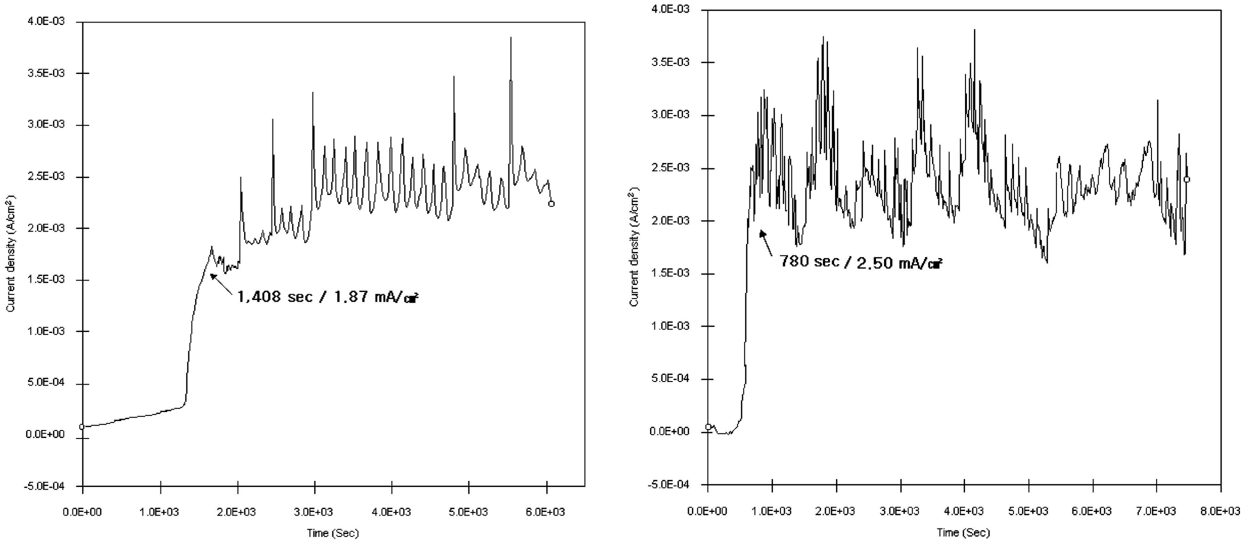
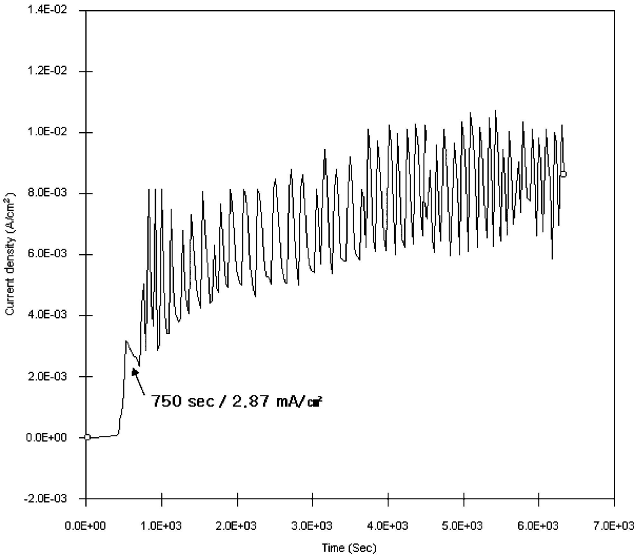


Figure 1 Polarization curves of 430 stainless steel at different solution temperatures.



(a) 20℃

(b) 30℃



(c) 50℃

Figure 2 The relation between the current density and time for crevice corrosion in 1N H_2SO_4 + 0.1N NaCl for different solution temperatures; (a) 20 °C, (b) 30 °C, and (c) 50 °C.

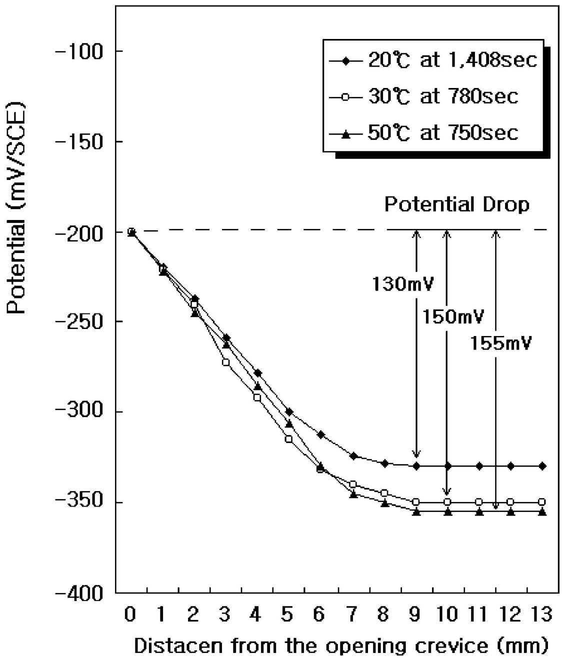
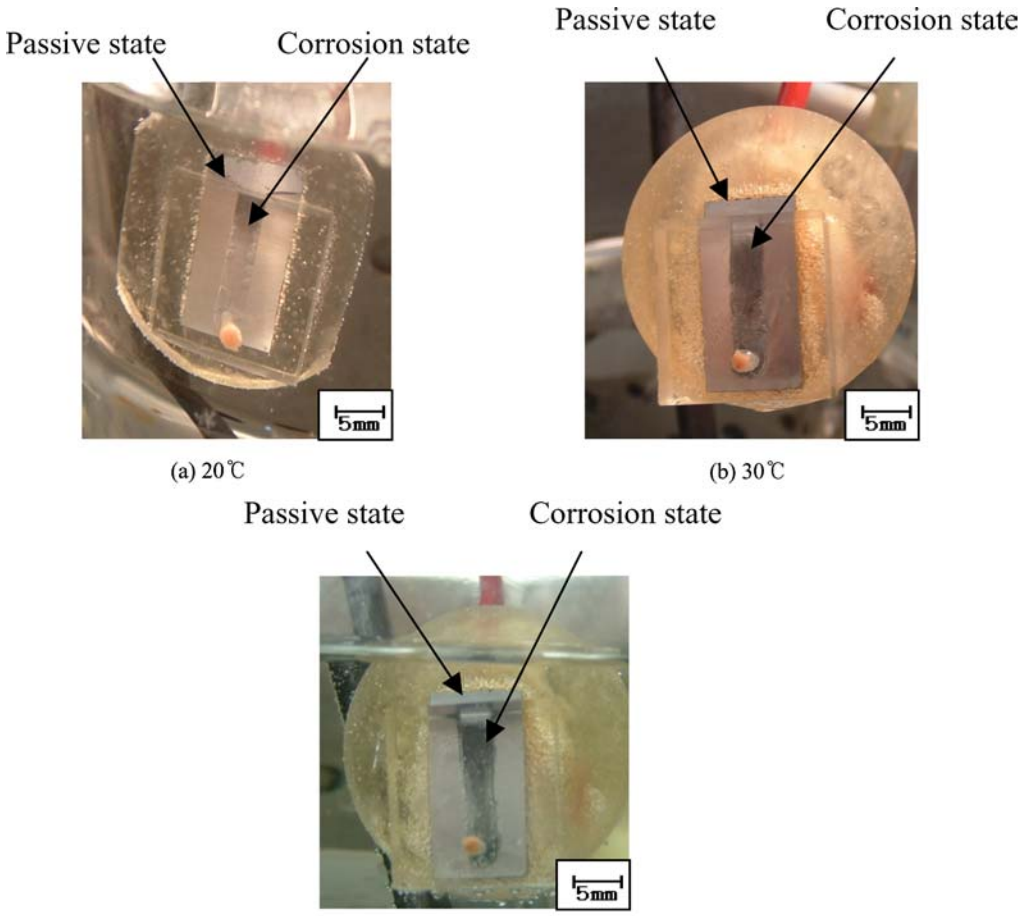


Figure 3 Electrode potential profiles inside the crevice measured in the upside-down position at various solution temperatures.

as the depth of the crevice increased. The measured maximum potentials of the inside of the crevice were −330, −350, and −355 mV versus SCE at the solution temperatures of 20 °C, 30 °C, and 50 °C, respectively. The potential differences were measured at the opening and the bottom of the crevice. In case, the potential drop exceeds the critical potential required to cause the corrosion to change from the passive to the active sate. Fig. 4 shows the ferritic 430 stainless steel crevice corrosion states for the different solution temperatures. That is, at each temperature, active crevice corrosion is develops at a certain depth inside the crevice but the outer surface of the sample remains in the passive state.

In this study, we used a new method, based on the microcapillary tube, to investigate the high potential difference which exists between the crevice bottom and opening, and which is difficult to explain with the existing theory of crevice corrosion initiation. Firstly, the results of this study showed that E_{cor} (the corrosion potential) and E_{b} (the break down potential) decreased as the solution temperature increased whereas, I_{crit} (the critical current concentration) values and I_{p} (the passive current density) increased. Also, the crevice corrosion rapidly increased as the solution temperature increased. Secondly, in the passive state, a passive potential of −200 mV versus SCE potential was applied to the sample surface, and the passive film in the crevice was broken down. The breakdown of the film is due to the potential changes from the passive to the active state between the inside and outside of the crevice. Therefore, this potential drop allows the crevice corrosion to



(a) 20℃

(b) 30℃

(c) 50℃

Figure 4 Photographs of crevice corrosion samples in 1N H_2SO_4 + 0.1N NaCl for different solution temperatures; (a) 20 °C, (b) 30 °C, and (c) 50 °C.

be evaluated, by measuring the potential in a narrow crevice with the new micro capillary tube measuring system. This means that the IR drop mechanism in the crevice is more objective for the evaluation of corrosion and the results are easier to reproduce. Also, it is hoped that the micro capillary tube method will constitute a more useful tool for the study of crevice corrosion than the existing methods.

References

1. M. S. DESA and C. M. RANGEL, *Br. Corrosion J.* **23** (1988) 186.
2. K. CHO and H. W. PICKERING, *J. Electrochem. Soc.* **137** (1990) 3313.
3. Y. XU and H. W. PICKERING, *ibid.* **140** (1993) 658.
4. B. A. KEHLER, G. O. ILEVBARE and J. R. SCULLY, *Corrosion J.* **57** (2001) 1042.
5. K. CHO, M. I. ABDULSALAM and H. W. PICKERING, *J. Electrochem. Soc.* **145** (1998) 1862.
6. M. WANG and H. W. PICKERING, *ibid.* **142** (1995) 2986.
7. B. A. SHAW, P. J. MORAN and P. O. GARTLAND, *Corros. Sci.* **32** (1991) 707.

Received 6 May
and accepted 6 May 2005