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Flow Accelerated Corrosion Behavior of Low Alloy Steel at Elevated Temperature

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Abstract

Flow accelerated corrosion behavior of piping steel in the range of 25 to 270 was studied using Rotating Cylinder Electrode (RCE). Electrochemical corrosion potential (ECP) and electrochemical corrosion current density was measured with temperature and rotating velocity through polarization test. ECP dropped at the rate of -1.51mV/ which is attributed to the formation of magnetite on steel surface. It shifted upward with rotating condition in all temperature range by the diffusion mechanisms of oxidizing agent. It can be discriminated activation between mass transfer process from the comparison between electrochemical corrosion current and deposition current on steel surface

1. Introduction

In nuclear industry, erosion-corrosion or flow-accelerated corrosion (FAC) in single-phase liquid lines has become a major problem. Many works have been done on FAC of carbon steel since the accident of Surry steam line rupture due to the localized pipe wall thinning at elbow in 1986 [1]. FAC is a process whereby the normally protective oxide layer on carbon or low alloy steel dissolves into a stream of flowing water or a water-steam mixture. FAC process is known to be divided into the two subsequent processes. The first is the production of soluble ferrous ions at the oxide-water interface, while the second is the transfer of the ferrous ions into the bulk water across the diffusion boundary layer [2].

Large-scale loop for simulating high temperature and high flow rate is essential for the investigation of flow accelerated corrosion behavior in nuclear power industry. But it has some drawbacks in terms of difficulty in maintaining reproducible water environment, testing elaborate electrochemical experiment, and so on. Thus many types of facility have been developed to test the velocity sensitive corrosion behavior with ease, such as rotating disk electrode, rotating cylinder electrode, jet impinging electrode, and so on [3]. The objectives of this study are to develop rotating cylinder electrode that is suitable for high temperature water environment, and provide methodology in assessing velocity sensitive corrosion process, also in suggesting application of such methodologies to actual power plant situation.

2. Experimental Procedures

2-1. Rotating Cylinder Electrode (RCE) setup

Fig. 1 shows schematic diagram of RCE. External motor is adapted as magnetic type so that inner rod can rotate without penetrating between external and internal pressure boundaries. Rotating rod is intended to design large diameter so as to maintain stable rotation even when operated 3000rpm. Anti-vibration guide has been installed at lower part of RCE to reduce unstable vibration generated by unintended misalignment of each part. The main design concept of RCE is insulating electrode housing against external fluid using nonmetallic sealant around 300 . Polytetrafluoroethylene (PTFE) disk was introduced to protect water penetration to the stainless steel connections. To prevent distortion of nonmetallic disk in high temperature water and provide tight seal even in severe conditions, stainless steel disk was inserted outer part of PTFE disk, closed tight by the frictional force of bolt. Besides protecting leakage, and extracting corrosion parameter outside of the autoclave safely is of importance. Platinum wire which is covered with shrinkable PTFE was wired outside of electrode surface, directly connected to data acquisition system. Rulon was adapted to insulate between contact parts, which is stronger and more resistant to high temperature than usual PTFE. Contact parts are covered with PTFE lest it should contact external autoclave, which acts as large cathode if inadvertently connected. Diameter of RCE is 70mm, which is equivalent to the linear velocity at the rate of 11m/sec on electrode surface when rotated to 3000rpm. From the inspection of the specimen after the experiment, solution leakage was not found.

2-2. Corrosion Experiment

To verify the performance of the RCE at simulated LWR environment, polarization tests were performed. Water chemistries used in this test were de-ionized water and weak alkaline solution adjusted by lithium hydroxide measured at room temperature to pH 10.6. Scan rate was 0.5mV per second. 3 hours of nitrogen purging at ambient temperature before experiment was conducted. Electrochemical Corrosion Potential (ECP) in this study was determined at the point where anodic half-cell current, i_a, and cathodic half-cell current, i_c, are equal. Corrosion current density was measured through Tafel extrapolation method by the intersection between anodic and cathodic reaction near corrosion potential. IR drop effect due to solution resistance was compensated by current interrupt method. For experiment below 100 , saturated calomel reference electrode was used as reference electrode. For experiment above 100 , reference electrode and auxiliary electrode was used external pressure-balanced type Ag/AgCl electrode and platinum, respectively, and all data were converted to SHE scale. Correction of potential in reference electrode by temperature differences was carried out according to Macdonald’ s calculation [4].

3. Results and Discussion

3-1. Effect of temperature

Fig. 2 shows the temperature dependence of the Electrical Corrosion Potential (ECP). The potential versus temperature lines for other alloys lie within the region of water stability, that is, between the oxygen and hydrogen evolution lines [5]

ECP increased slightly up to intermediate range (~150) then it dropped to converge into other's data. The decrease both of oxidation potential and of reduction potential with temperature may result in the decrease of a mixed potential where both anodic and cathodic reaction are competitive. The ECP study of structural materials in recirculated system [6] reveals that increasing surface coverage with magnetite leads to decreasing ECP irrespective of kinds of metal. Fig. 3 is the diagram of temperature dependence of the thermodynamic half-cell potential for oxidation of ferrous species. From 25 to 100 , oxidation reaction as like conversion of metal ion into ferrous hydroxide compound, namely $Fe(OH)_2$ and ã or ä-FeOOH, governs the entire anodic reaction, therefore it leads to increase of ECP up to the intermediate temperature. Then, ECP goes close to magnetite oxidation line above 150 , which indicates that conversion into magnetite, rather than hematite on the electrode surface dictated entire ECP over 100 . Slope of ECP with temperature over 150 is -1.51mV/ which is consistent with theoretical value of temperature gradient of magnetite oxidation as -1.38mV/ .

3-2 Effect of rotation rate on electrode potential

Fig. 5 is the plot of corrosion potential against temperature and rotation speed. Sensitivity of corrosion potential with respect to rotation speed did not appear until solution temperature reached at 200 . Such upward shift of corrosion potential with rotating velocity may be due to the active migration of reducing agent, namely, dissolved oxygen content in the autoclave, on the metal electrode with the turbulent flow [7]. The predicted dissolved oxygen content from inverse calculation of potential-DO relationships [8] is approximately 20ppb, which locates upper shelf of potential-DO curve at ambient temperature. Soon ECP shifts down to the transient regime of potential-DO curve with the elevation of temperature, which implies that velocity sensitiveness against ECP becomes larger from ambient temperature to higher one. Corrosion potential does not affect rotation speed any more when migration mechanism caused by diffusion-driven process is restricted by the concentration of dissolved oxygen. On the contrary, corrosion potential shows sensitive with intermediate amount of oxidizing agent. From the RCE results with the dissolved oxygen contents [9] revealed that corrosion potential was not sensitive to rotating velocity where oxygen content lay below 10ppb and above 1000ppb, whereas it became sensitive between 30 and 100ppb.

Fig. 6 is the ECP profile with temperature and rotating speed at pH 10. 6. Between room temperature and 100℃, ECP increased slightly with temperature for both static and rotating state. At room temperature, where piecewise transformation of steel into hydroxyl compound is dominated, increasing solution pH may accelerate activation process across double layer. Thus ECP gradient versus temperature becomes positive. When the solution temperature is raised so that generation of magnetite is activated rather than iron hydroxide generation, ECP somewhat drops regardless of rotating status to change its slope.

3-3 Effect of rotation rate on electrode kinetics

Fig. 7 is the result of electrochemical corrosion current calculated by Tafel method with dimensionless hydrodynamic parameter, Reynolds number. It shows increment with rotating speed in all condition. Previous polarization result showed that increase of cathodic half cell current was larger than that of anodic half cell current with rotating speed. This implies the mass transfer behavior where corrosion kinetics is dominantly governed by the migration of the oxidizing agent. Corrosion current at pH 7 is lower than that at pH 10.6 where solution resistivity at pH 7 is higher than that at pH 10.6 due to the effect of chemical agent, namely lithium hydroxide. The rate of current increase at pH 7 at 200 and at pH 10 at 150 is notable, which results from the competition between activation and mass transfer process. Liquid temperature is known to influence the chemical reaction during the FAC process as well as the protective layer formation. The overall temperature effect on material loss due to FAC can be described by a bell-shaped curve which reaches a maximum at around 180 for wet steam conditions [10] The maximum is the result of competition between two reactions. The first is the formation rate of ferrous hydroxide induced by Schikorr reaction with temperature below the maximum. The other is formation of a protective layer of magnetite, which becomes less porous with the formation of hematite at higher temperatures. At room temperature, velocity exponent of the limiting current, which represents mass transfer kinetics, shows 0.402 for alkaline solutions. On the other hand, velocity exponent of the corrosion current density, which is considered to be constituted in serial mechanisms, namely, converting into ferrous ion in addition to the mass transfer process shows more or less retarding behavior with a value of 0.113 [11]. That implies oxidation process such as oxidation of steel into hydroxyl compounds, formation of passive film, acts as the restraint of entire corrosion kinetics. At 150 , both the corrosion current density and the cathodic deposition current density rose so high as to reach the upper limit of mass transfer controlled corrosion, which implies activation process do not affect entire corrosion process any more. When the temperature rises above 150 , coverage of surface magnetite acts as barrier against migration and diffusion of ionic species. Thus it hinders corrosion and mass transport process to a certain extent.

4. Conclusions

RCE was applied in order to test velocity-sensitive corrosion behavior in nuclear power plant environment with ease. From corrosion experiment at the elevated temperature, it was revealed that RCE was effective device in performing velocity sensitive test in high temperature, high pressure water environment. Characterization of ECP and electrochemical corrosion current density can be varied with temperature by the competition of activation and mass transfer process.

ACKNOWLEDGMENTS

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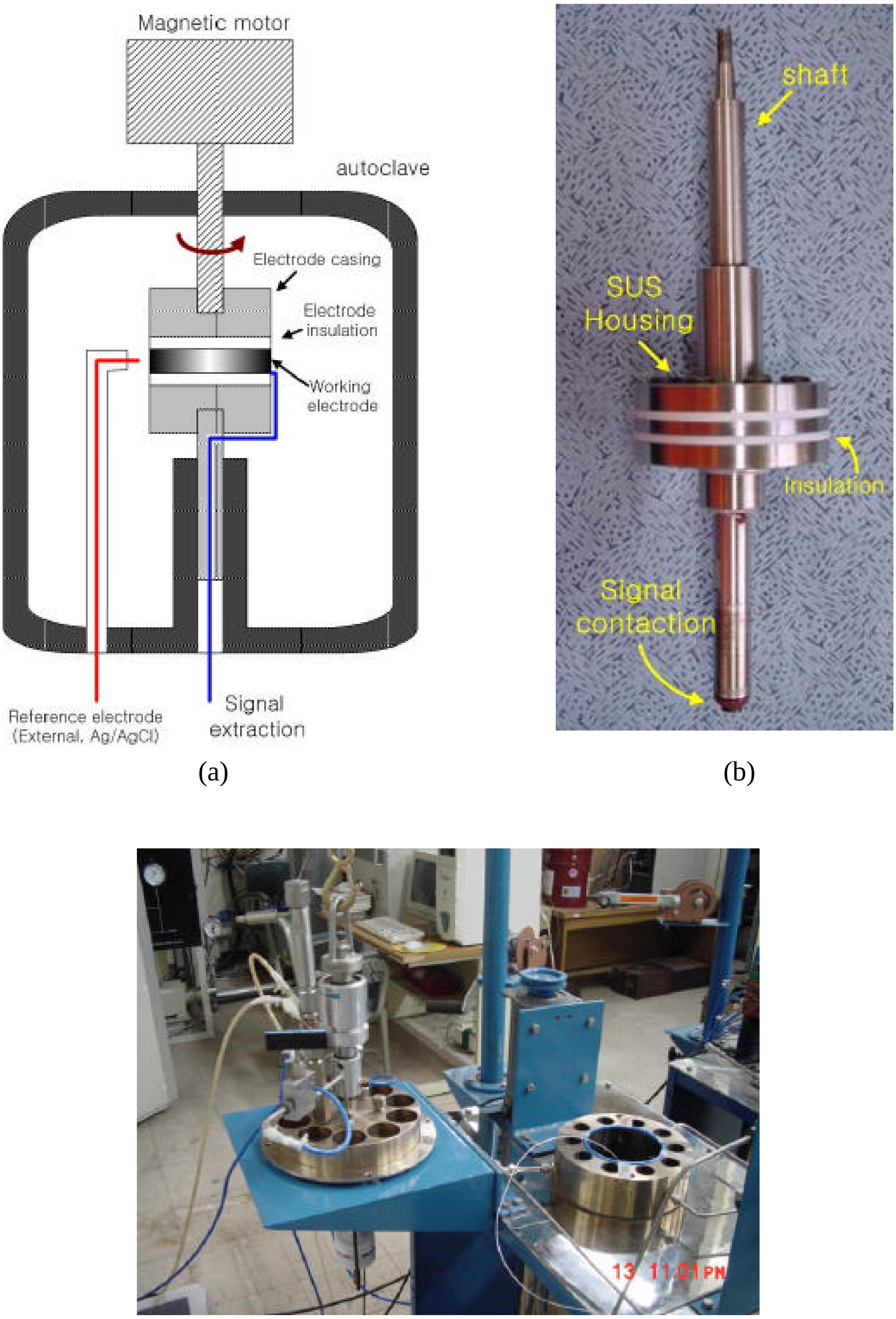

(a)

(b)

(c)

Fig. 1. Schematic illustration of rotating cylinder electrode

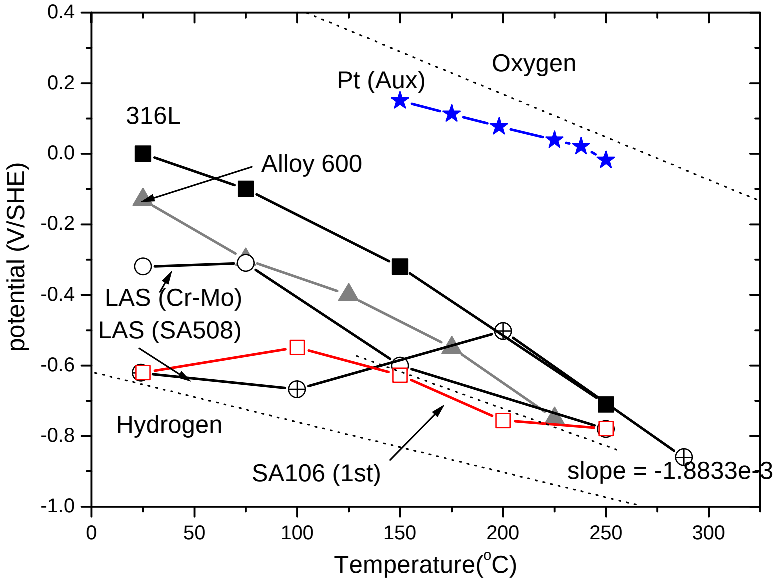

Fig. 2. Dependence of Electrochemical Corrosion Potential (ECP) on solution temperature

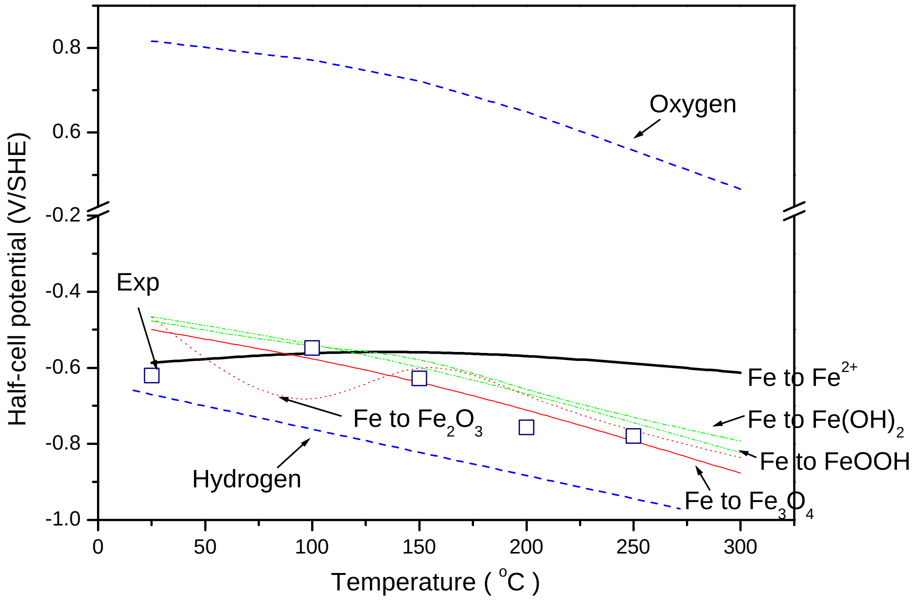

Fig. 3. Temperature dependence on the thermodynamic half-cell potential of oxidation of ferrous species

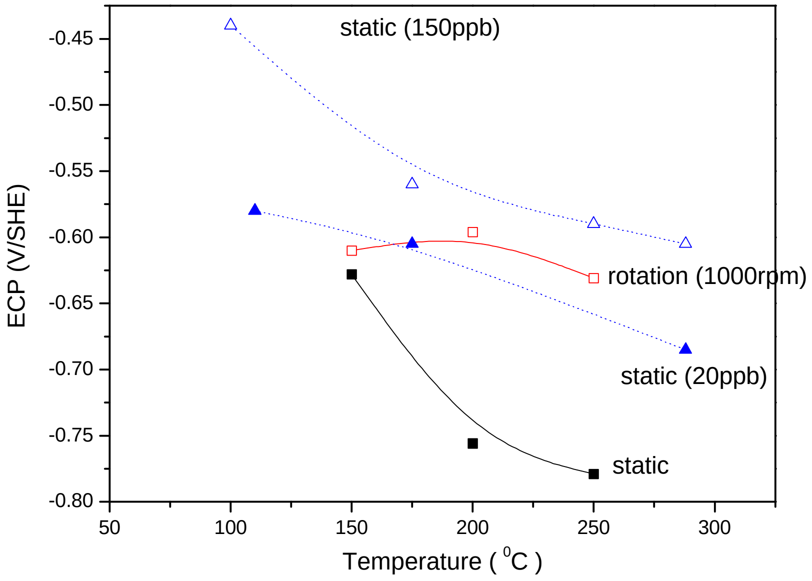

Fig. 5. ECP profile with temperature and rotating speed at pH 7

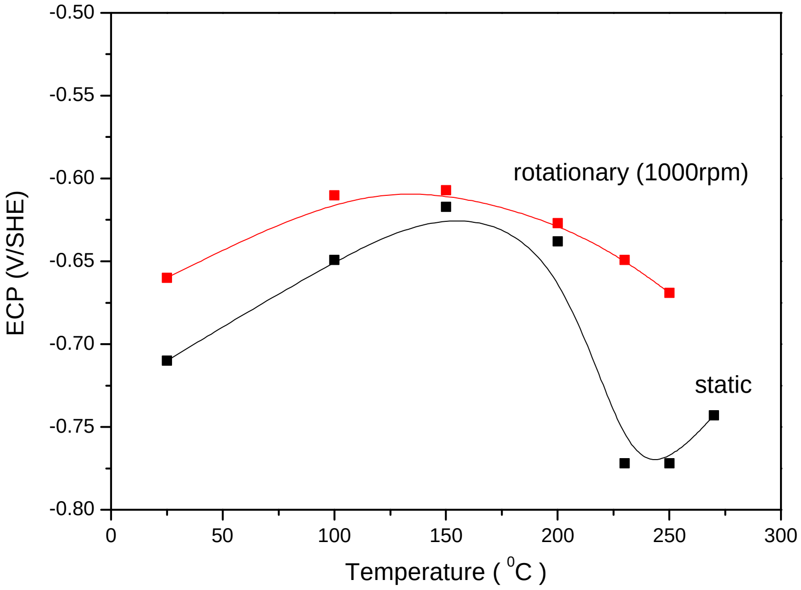

Fig. 6. ECP profile with temperature and rotating speed at pH 10.6

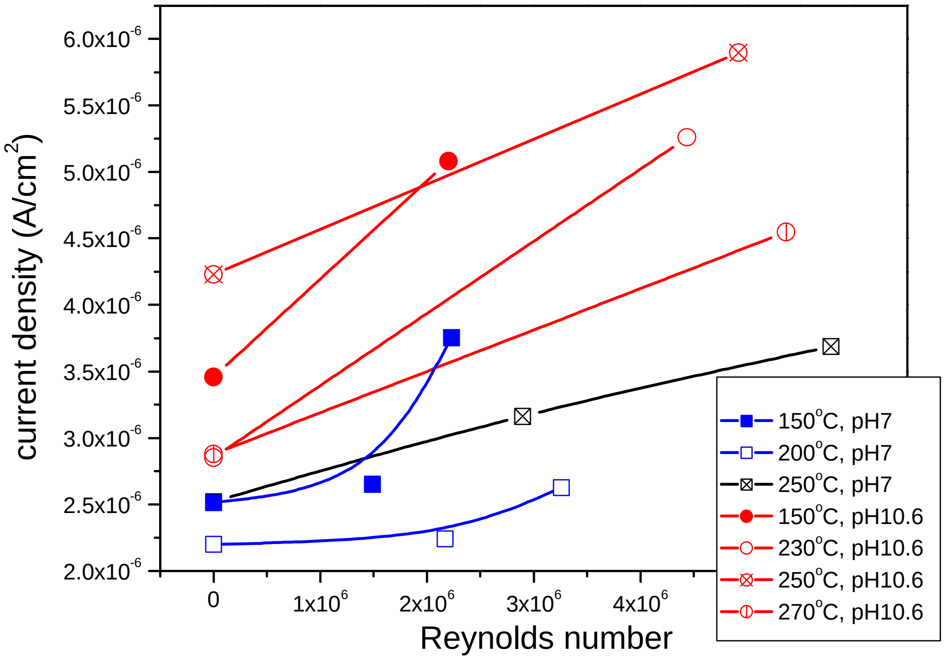

Fig. 7. Variation of corrosion currents with hydrodynamic condition