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Galvanic effect of magnetite on the corrosion behavior of carbon steel in deaerated alkaline solutions under flowing conditions

Geun Dong Song^{a,b}, Soon-Hyeok Jeon^a, Yeong-Ho Son^a, Jung Gu Kim^b, Do Haeng Hur^{a,*}

^a Nuclear Materials Safety Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 305-353, Republic of Korea ^b Department of Advanced Materials Science and Engineering, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Suwon 440-746, Republic of Korea

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ABSTRACT

The effect of magnetite on the corrosion of carbon steel was investigated in simulated secondary water of pressurized water reactors at 60 °C by using the immersion and electrochemical tests. The corrosion rate of carbon steel was increased by the galvanic coupling with magnetite, and was more accelerated with increasing the area ratio of magnetite to carbon steel. From the electrochemical behavior of carbon steel and magnetite, it was verified that the corrosion of carbon steel is accelerated by a galvanic corrosion mechanism. This phenomenon is expected to be an acceleration factor on the corrosion of carbon steel piping.

1. Introduction

The magnetite layer, which is normally the protective oxide layer, is covered on the inner surface of carbon steel piping by the corrosion processes in the alkalized reducing conditions of pressurized water reactors (PWRs) [1]. These layers are rapidly dissolved or removed in the turbulent flow region, and wall thinning of carbon steel piping is accelerated. Consequently, this process can lead to failures in the carbon steel pipelines [2–4].

In the secondary system of PWRs, the corrosion of carbon steel piping is controlled by protective properties of the magnetite layer. Factors affecting the degradation of the magnetite layer formed on carbon steel have been well identified and quantified: pH [5,6], temperature [7], dissolved oxygen [8,9], flow velocity [10,11], the presence of solid particle [12] and material composition [13–15]. Water chemistry such as pH, dissolved oxygen, and temperature affects the stability of magnetite layer, while fluid dynamics affects the mass transfer of soluble iron from the surface of the magnetite layer. In addition, solid particles such as corrosion products in flowing water mechanically destroy the protective magnetite layer, resulting in the accelerated corrosion of carbon steel piping.

Although the effects of various factors mentioned above have been evaluated comprehensively [16–19], there is another factor that should be considered in evaluating the corrosion behavior of carbon steel piping. Magnetite layers formed on carbon steel are partially removed in areas where turbulence is severe, and then the exposed metal surface of carbon steel is electrically connected with the remaining magnetite layer. Magnetite has a high electrical conductivity of $2.5 \times 10^4 \Omega^{-1} \text{ cm}^{-1}$ [20] and a relatively low band gap of 0.1 eV [21], indicating that magnetite behaves as a metal. That is, a galvanic cell between the exposed metal surface of carbon steel and magnetite can be formed. Recently, it has been reported that the galvanic coupling with magnetite accelerates the corrosion of secondary system materials, such as carbon steel [22–25], Alloy 600 [26], and Alloy 690 [27,28] in various environments.

As briefly described above, the galvanic coupling with magnetite is expected to be an additional acceleration factor on the corrosion of carbon steel piping in the secondary system of PWRs. However, this effect has still not been considered. Thus, the objective of this paper is to investigate the galvanic effect with magnetite on the corrosion behavior of carbon steel. To evaluate the corrosion behavior of pure magnetite and its effect, the magnetite specimens were prepared by the electrodeposition method. The galvanic corrosion behavior between carbon steel and magnetite was investigated in simulated secondary water by using the immersion and electrochemical corrosion tests. Based on the experimental results, a new additional acceleration factor on the corrosion of carbon steel piping in PWRs is discussed and proposed.

2. Experimental procedures

2.1. Material and test solution

Carbon steel specimens were machined from SA106Gr.B pipe material into a size of 10 mm \times 5 mm \times 1 mm for electrochemical corrosion tests, and a size of 20 mm \times 20 mm \times 1 mm for immersion

E-mail address: dhhur@kaeri.re.kr (D.H. Hur).

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^{*} Corresponding author.

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Table 1

Chemical composition of SA106Gr.B (wt.%).

С	Si	Р	S	Cr	Mn	Ni	Cu	Мо	Fe
0.19	0.23	0.012	0.005	0.4	1.05	0.2	0.1	0.1	Bal.

tests. The chemical composition of carbon steel is given in Table 1. The specimens were ground using silicon carbide papers down to grit #1000, and then ultrasonically cleaned in acetone.

An alkaline aqueous solution of pH 9.5 at 25 °C was used in this investigation. The pH of the test solution was adjusted using ethanol amine, which is an organic chemical agent used to control the pH of secondary water in PWRs. All corrosion tests were carried out under a deaerated condition at 60 °C. To maintain the deaerated condition, the test solutions were continuously purged with high-purity nitrogen gas (99.999%) at a flow rate of 100 cm³/min during testing. This test environment was chosen to simulate a secondary water chemistry of PWRs [29].

2.2. Preparation of magnetite coupon and electrode

To evaluate the effect of magnetite on the corrosion behavior of carbon steel, it is necessary to prepare a dense, thick, and rigid magnetite coupon for immersion tests and magnetite working electrode for electrochemical corrosion tests, respectively. Therefore, in this study, the magnetite coupon and magnetite electrode were prepared by the electrodeposition of the magnetite layer on the whole surface of the carbon steel substrate. The electrodeposition solutions consisted of 2 M sodium hydroxide, 0.1 M triethanolamine, and 0.043 M ferric sulfate hydrate. The electrodeposition process of magnetite was conducted in a conventional corrosion cell with three electrodes using a potentiostat. A saturated calomel electrode (SCE) and a pure graphite rod were used as a reference and counter electrode, respectively. The magnetite layer was electrodeposited in the deposition solution at an applied potential of $-1.05 V_{SCE}$ at 80 °C for 1800 s. The detailed electrodeposition process of magnetite is given in previous studies [30–33].

The morphology of the electrodeposited magnetite layer was investigated by a focused ion beam-scanning electron microscope (FIB-SEM). To observe the cross section of the electrodeposited magnetite, the sample was milled using FIB in the vertical direction of the magnetite layer. In addition, an X-ray analysis of the electrodeposited magnetite layer was performed using an X-ray diffractometer with a Cu-K α radiation ($\lambda = 1.5406$ Å).

2.3. Immersion corrosion test

Carbon steel coupons coupled and uncoupled to magnetite were used in the immersion corrosion test. In case of the coupled specimens, the area ratio (AR) of magnetite to carbon steel was controlled to be 1 and 20, respectively. To make the coupled specimen with the AR of 1, a carbon steel coupon (20 mm \times 20 mm \times 1 mm) with holes in all corners was prepared as shown in Fig. 1(a). The magnetite layer was electrodeposited on the whole surface of the carbon steel coupon described above. This magnetite deposited coupon was used as a magnetite coupon. These two materials were electrically connected by tightening a polytetrafluoroethylene (PTFE) bolt and nut. In case of the AR of 20, a carbon steel disc (radius: 3.2 mm, thickness: 1 mm) with an internal thread in the center and a magnetite coupon (20 mm \times 20 mm \times 1 mm) with holes in all corners and the center were prepared as shown in Fig. 1(b). The carbon steel disc was located in the center of the magnetite coupon, and then these two materials were electrically connected by tightening a carbon steel bolt. After that, all crevices of these coupled specimens including bolts and nuts were coated with a water-repellent agent to prevent the permeation of the test solutions, as shown in Fig. 1. Four samples for each condition were

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Fig. 1. Schematic for the preparation of the specimensgalvanically coupled with magnetite used in the immersion corrosion test: (a) AR of 1 and (b) AR of 20.



Fig. 2. Schematic of the test apparatus for the immersion corrosion test.

exposed to the test solution for the weight loss measurement and surface analysis.

Fig. 2 shows the schematic of the test apparatus for the immersion corrosion test. The test apparatus consisted of a hot plate, water bath, specimen holder, and reaction flask equipped with a reflux condenser, gas sparger, overhead stirrer, and thermocouple. The specimen holder was made in the form of a regular dodecagon using PTFE. In order to expose all specimens to the same fluid dynamic condition, the samples were placed in each side of the specimen holder, which is equidistant 60 mm from the center. After that, this specimen holder was loaded to the end of the overhead stirrer shaft and rotated at a rate of 320 rpm to make a fluid flow at the surface of specimens during the immersion corrosion test. When this angular velocity is converted into a linear velocity, the flow rate of the test solution at the surface of the specimen is calculated to be 2 m/s, excluding the effect for the motion of the test solution by the rotation of the specimen holder.

The immersion corrosion test was conducted for 500 h. After the test was completed, the samples were ultrasonically cleaned in acetone,

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Fig. 3. Schematic for a magnetite working electrode prepared using the electrodeposition method.

dried in a desiccator, and then the weight change of the sample was measured using an electrical balance with a precision of 10 µg. In addition, the corrosion morphology of the samples was investigated by a FIB-SEM. The surface chemistry of the oxide layers was also analyzed using a X-ray photoelectron spectroscopy (XPS) with an Al K α X-ray source (1486.6 eV) operated at 15 kV and 150 W under a base pressure of 2.7 \times 10⁻⁷ Pa. To analyze the interior of the oxide layer, the surface of the samples was etched using 1.0 keV argon ion beam for 20 s. After that, XPS spectra for the interior of the oxide layer were recorded.

2.4. Electrochemical corrosion test

A carbon steel specimen with a dimension of 10 mm \times 5 mm \times 1 mm was spot-welded to a pure iron wire, which was then covered with a PTFE tube for electrical insulation. The area around the weld junction was coated with an epoxy resin to prevent crevice corrosion. This specimen was used as a carbon steel working electrode for electrochemical tests. A magnetite working electrode was prepared by the electrodeposition of the magnetite layer on the whole surface of the carbon steel electrode stated above, as shown in Fig. 3.

Potentiodynamic polarization tests were performed using a potentiostat and a three-electrode cell. An SCE and platinum wire were used as a reference and counter electrode, respectively. After the open circuit potential (OCP) was stabilized, polarization scans for carbon steel and magnetite were started from 10 mV below the OCP to the anodic direction or from 10 mV above the OCP to the cathodic direction. The scan rate was 1 mV/s. Each anodic and cathodic polarization curve was finally combined in one graph. In addition, a zero resistance ammeter (ZRA) was used to measure the actual galvanic corrosion potential (E_G) and galvanic current density (i_G) between carbon steel and magnetite. The ARs were 1 and 20. After the individual OCPs of carbon steel and magnetite were stabilized, the actual E_G and i_G of the couple were measured for 3600 s.

In the case of the electrochemical measurement, the test solution was agitated using a magnetic stirrer at a rate of 1000 rpm to create a fluid flow. All electrochemical corrosion tests were conducted at least three times to confirm their reproducibility.





Fig. 4. SEM images of the magnetite layer electrodeposited on the surface of carbon steel at an applied potential of -1.05 VSCEin the electrodeposition solution at 80 °C for 1800 s: (a) top view and (b) cross section.



Fig. 5. XRD patterns of the magnetite layer electrodeposited on carbon steel at an applied potential of -1.05 VSCEin the electrodeposition solution at 80 °C for 1800 s.



Fig. 6. Weight change of carbon steel coupled and uncoupledto magnetite after the immersion corrosion test in the flowing solutionat a flow velocity of 2 m/s at 60 $^{\circ}$ C for 500 h.

3. Results

3.1. Characteristic of the electrodeposited magnetite layer

Fig. 4 shows the SEM images of the electrodeposited magnetite layer on the carbon steel substrate. As shown in Fig. 4(a), the polyhedral shaped-magnetite particles were densely formed on the carbon steel substrate, and the interstices between them were not observed. This magnetite layer was homogeneously electrodeposited over the whole carbon steel substrate. In addition, there were no defects such as crack, pore, or crevice at the interface between the magnetite layer and the substrate, as shown in Fig. 4(b). This indicates that the magnetite layer was tightly bonded to the carbon steel substrate. The average thickness of the magnetite layer was approximately 5 μ m. In addition, the X-ray diffraction (XRD) patterns of this layer corresponded to pure crystalline magnetite (JCPDS card no. 19-0629), as shown in Fig. 5. Consequently, these results indicate that the electrodeposited magnetite electrode and coupon are very effective to evaluate the electrochemical corrosion behavior of magnetite itself and its effect on the corrosion behavior of carbon steel, without the exposure of the carbon steel substrate to the test solution.

3.2. Immersion corrosion behavior

Fig. 6 shows the weight change of carbon steel coupled and uncoupled to magnetite after the immersion corrosion test in flowing solutions at a flow velocity of 2 m/s at 60 °C for 500 h. The weight loss of uncoupled carbon steel was $0.14 \,\mu\text{g/cm}^2\text{h}$, while that was significantly increased by the galvanic coupling with magnetite. When the AR was 1, the weight loss of carbon steel was increased to $0.30 \,\mu\text{g/cm}^2\text{h}$. Furthermore, as the AR was increased to 20, the weight loss of carbon steel was drastically increased to $0.86 \,\mu\text{g/cm}^2\text{h}$. This result indicates that the corrosion rate of carbon steel is accelerated by about 6-times owing to the increased AR.

The corrosion morphologies of carbon steel for each condition after the immersion corrosion test were presented in Fig. 7. The oxide layer formed on uncoupled carbon steel was very thin and discontinuously covered on the surface. In case of carbon steel coupled to magnetite with the AR of 1, a relatively thick and porous oxide layer was formed on the whole carbon steel surface, compared to uncoupled carbon steel. A few crack were also observed on the surface of this oxide layer. As the AR was increased to 20, many defects such as pores and trenches were observed in the oxide layer formed on carbon steel, and the thickness of the oxide layer was more increased. This observation directly supports the accelerated corrosion of carbon steel by the galvanic coupling with magnetite. In addition, it is noted that although the oxide layer formed on coupled carbon steel was much thicker than that of uncoupled carbon steel, the weight loss was larger as shown in Fig. 6. This means that the dissolution-out rate of carbon steel in coupled conditions is remarkably larger than that in uncoupled conditions. The porous and defective feature of the oxide layers could be evidence that a rapid dissolution occurred in the oxides formed on coupled carbon steel.

Fig. 8 shows the XPS spectra of Fe2p core-level from the interior of



Fig. 7. SEM images showing the corrosion morphologies of carbon steel coupled and uncoupled to magnetite after the immersion corrosion test in the flowing solutionat a flow velocity of 2 m/s at 60 °C for 500 h.



Fig. 8. XPS spectra of Fe2p core-level from the oxide layer formed on the surface of carbon steel with and without the coupling to magnetite after the immersion corrosion test: (a) Uncoupled, (b) AR of 1 and (c) AR of 20.

the oxide layer formed on carbon steel coupled and uncoupled to magnetite after the immersion corrosion test. The Fe2p spectra of the oxide layer for all conditions were fitted with peaks corresponding to ${\rm Fe}^{2+}$ and ${\rm Fe}^{3+}$, as shown in Fig. 8. The peaks with binding energy at

about 709 eV (satellite at 714.8 eV) and 711 eV can be attributed to Fe^{2+} and Fe^{3+} in the oxide form, respectively [34,35]. Meanwhile, they showed a difference in the ratios of Fe^{2+} to Fe^{3+} calculated from the area for each peak of the deconvoluted XPS spectra. The ratio of Fe^{2+} to Fe^{3+} in the iron oxide formed on uncoupled carbon steel was approximately 0.54, while that was decreased by the galvanic coupling with magnetite. Especially, as shown in Fig. 8(c), the spectral feature of Fe^{3+} in oxide form was significantly increased when the AR was increased to 20. In this case, the ratio of Fe^{2+} to Fe^{3+} was approximately 0.32. This significant increase of the Fe^{3+} contribution in the oxide form means that the increased AR results in the oxidation of Fe^{2+} to Fe^{3+} in the oxide layer formed on the surface of carbon steel.

3.3. Electrochemical corrosion behavior

The potentiodynamic polarization tests for each material and condition were carried at least three times as shown in Fig. 9, and a high reproducibility was confirmed. In addition, it is necessary to verify that the polarization curves of a magnetite working electrode were obtained from the reactions occurring between the electrolyte and the surface of the magnetite electrode itself without interference from the carbon steel substrate. Fig. 10 shows the SEM images of the surface and cross section of the magnetite working electrode after the polarization test. Compared to the original feature in Fig. 4, only the outer surface of the magnetite electrode was slightly corroded without the damage of the carbon steel substrate after the test. The representative results shown in Fig. 9 were rearranged in Fig. 11 for elucidating the galvanic corrosion behavior between carbon steel and magnetite by the application of the mixed potential theory. To evaluate the effect of the AR, polarization curves of magnetite with an area of 20 cm² were also presented in Fig. 11, which were calculated from those with an area of 1 cm^2 .

In stagnant test solutions, the corrosion potential ($E_{\rm corr}$) of carbon steel was about 290 ~ 300 mV lower than that of magnetite, as shown in Fig. 11(a). This means that carbon steel and magnetite will act as an anode and cathode, respectively, when these two materials are electrically connected. In this couple, the anodic current density of carbon steel is expected to increase. Furthermore, that will more increase with increasing the AR.

In flowing test solutions, both the $E_{\rm corr}$ of carbon steel and magnetite were shifted in the positive direction compared to those in stagnant test solutions, as shown in Fig. 11(b). The corrosion current densities of carbon steel and magnetite were also increased. This is because the mass transfer rate is increased by the presence of a fluid flow. Carbon steel still behaves as the anode of the galvanic couple with magnetite in flowing test solutions. Therefore, if carbon steel and magnetite are electrically connected, the extent of galvanic corrosion of carbon steel is expected to more increase than that in stagnant test solutions. Based on the result of the potentiodynamic polarization tests, the galvanic coupling with magnetite anodically shifts the E_{corr} of carbon steel to the galvanic potential of the couple, and this shifting results in the increased corrosion current of carbon steel. Although the specific current values determined from the electrochemical measurements do not directly reflect the corrosion rate of carbon steel obtained in the immersion test, it is considered that this galvanic effect is still valid in the immersion test conditions. Therefore, the accelerated corrosion of carbon steel by magnetite in Fig. 6 is caused by the change in the electrochemical corrosion behavior of carbon steel by the galvanic coupling with magnetite described above.

To evaluate quantitatively the effects of a fluid flow, the galvanic coupling with magnetite and the AR on the corrosion rate of carbon steel, corrosion parameters were estimated from the polarization curves in Fig. 11. The corrosion current densities of carbon steel for each condition were calculated by using the Tafel extrapolation method from cathodic polarization curves in a potential range between -50 and -100 mV below the E_{corr} . The galvanic current densities of the couple with the AR of 1 and 20 were also predicted by the mixed potential



Fig. 9. Reproducibility of potentiodynamic polarization tests for each material and condition: (a) carbon steel-stagnant test solutions, (b) carbon steel-flowing test solutions, (c) magnetite-stagnant test solutionsand (d) magnetite-flowing test solutions.

theory. The changes in the corrosion current density of carbon steel caused by the three factors mentioned above were summarized in Fig. 12. The corrosion current density of carbon steel is expected to increase by about 5-times by the fluid flow. That will increase by about 11-times when considering both the fluid flow and the galvanic coupling with magnetite (AR of 1). Furthermore, the accelerated corrosion of carbon steel caused by these two factors becomes more severe (about 16-tmes) owing to the increased AR from 1 to 20. Consequently, the corrosion rate of carbon steel can be drastically accelerated in a region where these three factors are combined.

Fig. 13 shows the actual E_G and i_G of carbon steel coupled to magnetite obtained from the ZRA measurements in stagnant and flowing test solutions at 60 °C. As shown in Figs. 13(a) and (b), the actual E_G values of the couple with the AR of 1 and 20 were located between the E_{corr} of carbon steel and magnetite in both stagnant and flowing test solutions. The actual E_G of the couple was shifted in the more positive direction with increasing the AR. This means that the increased AR put the coupled carbon steel in a more oxidizing condition. These changes in the thermodynamic condition can affect the ratio of Fe²⁺ to Fe³⁺ of the oxide layers formed on carbon steel, as shown in Fig. 8. Furthermore, the actual i_G of carbon steel coupled to magnetite had an increased anodic current density as shown in Figs. 13(c) and (d), confirming that carbon steel was the anodic member in the galvanic couple with magnetite. That was increased by the presence of the fluid flow. When the AR was increased, the actual i_G was also increased significantly in both stagnant and flowing test solutions. These tendencies are in good agreement with results predicted from the polarization curves via the mixed potential theory in Figs. 11 and 12. Therefore, the galvanic corrosion behavior between carbon steel and magnetite can be quantitatively predicted by the application of the mixed potential theory, and clearly confirmed using the ZRA technique.

4. Discussion

The results obtained in this study can be summarized as follows: the corrosion of carbon steel was accelerated by a galvanic coupling with magnetite. A large AR of magnetite to carbon steel more accelerated the corrosion of carbon steel. In addition, the morphology and stoichiometry of the oxide layer formed on carbon steel were significantly changed by the galvanic coupling with magnetite. This galvanic coupling of carbon steel with magnetite can be discussed as an acceleration factor on the corrosion of carbon steel piping in the secondary system of PWRs.

The surface of carbon steel piping is typically covered with the magnetite layer under the alkalized reducing conditions of PWRs. This magnetite layer contains pores through which soluble irons released from carbon steel diffuse to the oxide/water phase boundary [4,36]. Therefore, the small area of carbon steel is exposed to the reducing secondary water due to the pores at the oxide/steel interface. In this case, the exposed surface of carbon steel is galvanically coupled to a





Fig. 10. SEM images of the magnetite layer electrodeposited on the surface of carbon steel after the polarization test in the test solution at 60 $^{\circ}$ C: (a) top view and (b) cross section.

relatively large area of magnetite, as shown in Fig. 14(a). Consequently, the corrosion is accelerated from the small area of carbon steel owing to the galvanic coupling with magnetite. In addition, this galvanic corrosion process will also occur by exfoliation or spallation mechanism, which mechanically removes the magnetite layer formed on carbon steel [36,37]. The generation and collapse of bubbles can repeat in the area immediately downstream of an orifice where the local static pressure of flowing water drops below the vapor pressure [38]. That is, cavitation can occur in severe turbulent flow and destroy the magnetite layer at the local areas, resulting in a formation of galvanic cell between carbon steel and magnetite as shown in Fig. 14(b).

The same situation is expected to occur in the regions such as elbows, tees and bends where flow accelerated corrosion (FAC) is most severe by a turbulent flow with a higher flow velocity. In these areas, the dissolution rate of magnetite rapidly increases. At this time, the dissolution of magnetite would be balanced by the formation of magnetite at the interface between a metal and magnetite. However, the thickness of the magnetite layer becomes thinner due to its rapid dissolution [39,40]. Although magnetite is continuously formed, it is immediately removed out in this severe condition. According to the Dooley's paper [36], the layer can be as thin as a few angstroms. It should also be noted that the magnetite layer was absent at the local areas where the most wall thinning was observed in elbows and tees of carbon steel piping collected from an operating PWR [39,41]. It is therefore reasonable to say that the metal surface of this local area is exposed to flowing water. In addition, corrosion product particles presented in flowing water can erode the magnetite layer formed on the surface of carbon steel [12]. The removal of magnetite layer by erosion is most severe in the extrados of elbows where the pattern of the turbulent flow changes [42]. When the magnetite layer is removed by FAC and erosion, therefore, the metal surface of carbon is exposed to flowing water. In these situations, the exposed metal surface of carbon steel is electrically connected with the neighboring magnetite layer. Accordingly, galvanic corrosion can occur between carbon steel and magnetite, resulting in an accelerated corrosion of carbon steel. This galvanic corrosion process between carbon steel and magnetite exposed to severe turbulent flow in elbows is schematically presented in Fig. 15. Under these conditions, the corrosion of carbon steel is more accelerated by an unfavorable area ratio of a large cathode (neighboring magnetite) and a small anode (exposed metal).

The result shown in Fig. 6 demonstrates that the corrosion of carbon steel is accelerated by the galvanic coupling with magnetite through the immersion corrosion test. Furthermore, it was also verified that the corrosion of carbon steel is more accelerated with increasing the AR. Although the oxide layers of carbon steel coupled to magnetite were



Fig. 11. Potentiodynamic polarization curves of carbon steel and magnetite in the test solutions at 60 °C: (a) stagnant conditionsand (b) flowing conditions.



Fig. 12. The change in the corrosion current density of carbon steel caused by effects of a fluid flow, the galvanic coupling to magnetite and the AR in the test solutions at 60 °C.

thicker than that of uncoupled carbon steel as shown in Fig. 7, these oxide layers are expected to be removed under the severe turbulent conditions of operating PWRs as shown in Fig. 15. This is because the fluid dynamic conditions in regions such as elbows, tees and bends in the secondary system of PWRs is more severe than the experimental

conditions used in this study. Consequently, if the oxide layer formed on carbon steel is completely removed under the severe turbulence condition, the difference in the weight loss between carbon steel coupled and uncoupled to magnetite shown in Fig. 6 will be more increased. Many experimental results showed that the protective oxide layer on carbon steel was rapidly dissolved or destroyed by the mass transfer effect and erosion at flow velocities above certain levels [11,12,39,42]. Therefore, it is again considered that the thick oxide layer in Fig. 7 remains only because our test flow does not reach a critical turbulent condition.

Fig. 16 schematically presents the electrochemical corrosion behavior in the situations shown in Figs. 14 and 15, based on the result of potentiodynamic polarization tests in Fig. 11. The electrochemical behavior of carbon steel and magnetite demonstrates that the corrosion current of carbon steel is more increased by not only the mass transfer effect but also a galvanic corrosion mechanism. This galvanic corrosion mechanism is also supported by the results obtained from ZRA measurements in Fig. 13. Thus, wall thinning of carbon steel piping will be more accelerated owing to the galvanic corrosion mechanism described above under operating conditions of PWRs.

Based on the above results and discussion, we propose that the galvanic effect with magnetite must be considered as an additional acceleration factor in evaluating the corrosion of carbon steel piping in the secondary system of PWRs. In addition, the extent of galvanic corrosion depends on the difference in the OCPs and the polarization behavior of the coupled materials, which would be affected by



Fig. 13. Galvanic corrosion behavior of carbon steel coupled tomagnetite obtained from the ZRA measurements in the test solutions at 60 °C: (a) E_G-stagnant test solutions, (b) E_G-flowing test solutions, (c) i_G-stagnant test solutionsand (d) i_G-flowing test solutions.

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Fig. 14. Schematics of the galvanic corrosion process between carbon steel and magnetite exposed to the reducing secondary water.



Fig. 15. Schematic for the galvanic corrosion between carbon steel and magnetite occurring in a pipe bend.



Current (log i)

Fig. 16. Schematic electrochemical behavior of carbon steel and magnetite occurring in a pipe bend.

temperature. Thus, extensive experimental works are ongoing to validate the galvanic effect in the high temperature ranges up to 230 °C.

5. Conclusions

The corrosion behavior of carbon steel piping in the secondary system of PWRs has been known to be affected by various factors such as water chemistry and fluid dynamics. This paper provides a new additional acceleration factor on the corrosion of carbon steel, which is accelerated owing to not only various factors reported up to now but also a galvanic coupling with magnetite. To prove this acceleration factor, the magnetite specimen was prepared by using the electrodeposition method, and the immersion and electrochemical corrosion tests were conducted in simulated secondary water of PWRs at 60 °C. From the result of the immersion corrosion test, it was clearly confirmed that the galvanic coupling with magnetite accelerated significantly the corrosion of carbon steel. In addition, the electrochemical behavior of carbon steel and magnetite showed that carbon steel acts as an anode of the galvanic couple with magnetite, resulting in an increased corrosion current. Therefore, the galvanic coupling of carbon steel with magnetite is proposed as an additional acceleration factor on the corrosion of carbon steel piping in the secondary system of PWRs.

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