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Galvanic Corrosion between Carbon Steel 1018 and Alloy 600 in Crevice with Boric Acid Solution

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This work dealt with the evaluation of galvanic corrosion rate in a corrosion cell having annular gap of 0.5 mm between carbon steel 1018 and alloy 600 as a function of temperature and boron concentration. Temperature and boron concentration were ranged from 110 to 300 ℃ and 2000~10000 ppm, respectively. After the operating temperature of the corrosion cell where the electrolyte was injected was attained at setting temperature, galvanic coupling was made and at the same time galvanic current was measured. The galvanic corrosion rate decreased with time, which was described by corrosion product such as protective film as well as boric acid deposit formed on the carbon steel with time. From the galvanic current obtained as a function of temperature and boron concentration, it was found that the galvanic corrosion rate decreased with temperature while the corrosion rate increased with boron concentration. The experimental results obtained from galvanic corrosion measurement were explained by adhesive property of corrosion product such as protective film, boric acid deposit formed on the carbon steel wall and dehydration of boric acid to be slightly soluble boric acid phase. Moreover the galvanic corrosion rate calculated using initial galvanic coupling current instead of steady state coupling current was remarked, which could give us relatively closer galvanic corrosion rate to real pressurized water reactor.

Keywords *: galvanic corrosion, crevice, nialloy, boron concentration, corrosion product, boric acid deposit*

1. Introduction

In March of 2002, it was observed that the reactor vessel head of Davis-Besse nuclear power plant was severely corroded by boric acid.[1),2)] Many researches are needed to prevent and predict the repeatable accident because the severe accident concerning with boric acid corrosion leads to a threat against safety as well as economic damage. Through extensive researches, main root cause of corrosion, corrosion rate and scenario of the degradation could be accomplished. Therefore numerous basic corrosion tests and their analyses are inevitably needed and also deserve themselves.

Among many tests, galvanic corrosion effect should be also considered. Two metals of alloy 600 and carbon steel consisting of CRDM(control rod drive mechanism) nozzle and reactor vessel head, respectively can be coupled by means of various causes, i.e. formation of boric acid leak path to carbon steel through alloy 600 and formation of some holes to upper plate of carbon steel through the combination of many corrosion mechanisms. Therefore the evaluation of galvanic corrosion through well designed corrosion cell can give us how fast its rate is and whether galvanic corrosion is significant or not.

This work is concerned with the assessment of galvanic corrosion rate in the corrosion cell having annular gap of 0.5 mm between carbon steel 1018 and alloy 600. Galvanic corrosion rate was measured as a function of temperature and boron concentration. The galvanic corrosion rate decreased with time and temperature while the rate increased with boron concentration.

From analyzing experimental results, it was proposed that the adhesive property of corrosion product and boric acid deposit formed on the carbon steel wall was enhanced and the increased amount of boric acid was dehydrated leading to decrease of galvanic corrosion rate as temperature increased. Additionally the galvanic corrosion rate obtained using initial galvanic coupling current instead of

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steady state coupling current was discussed, which would be rather closer to PWR(pressurized water reactor) of real nuclear power plant.

2. Experimental

Fig. 1 shows the schematic diagram of corrosion apparatus. There is an annular gap of 0.5 mm between alloy 600 as a cathode and carbon steel 1018(C 0.15-0.20, Mn 0.60-0.90, P max. 0.04, S max. 0.05) as an anode. Electrical insulation between two metals was accomplished by inserting teflon tube into the annular gap. Solution flow rate was controlled by relief valve to be 10~100 cc/min.

Solution contains boron as boric acid(H_3BO_3) ranging of 2000 to 10000 ppm and 3.5 ppm lithium as lithium hydroxide($LiOH \cdot H_2O$). All solutions used in this experiment were prepared from Millipore deionized water. Dissolved oxygen in the solution reservoir was removed by 12 hrs nitrogen bubbling. During the experiment, hydrogen gas was purged to be constant pressure of 30 psi.

Galvanic current was measured by potentiostat(Gamry instrument) with time as a function of temperature and boron concentration. Temperature was ranged from 110 to 300 ℃. Galvanic coupling was connected when the temperature of the cell where solution was injected was attained at the desired value.

To investigate the film property formed on the carbon steel wall, the second galvanic coupling current at the same or different temperature as the temperature of the first coupling was monitored after the first galvanic coupling followed by 12 hrs break without connection.

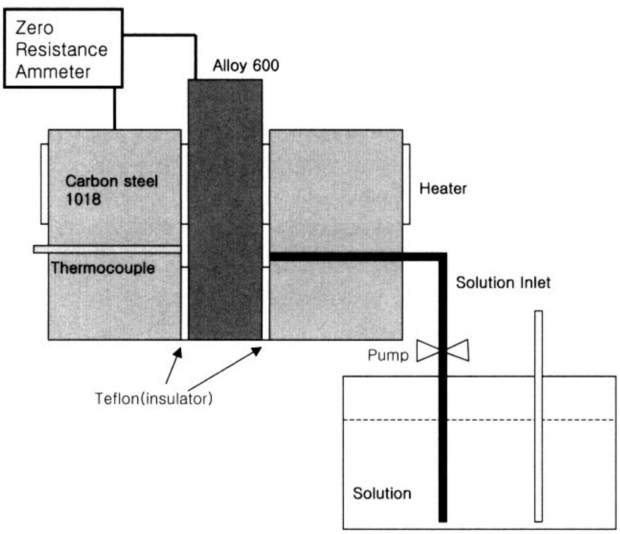

Fig. 1. Schematic diagram showing experimental apparatus.

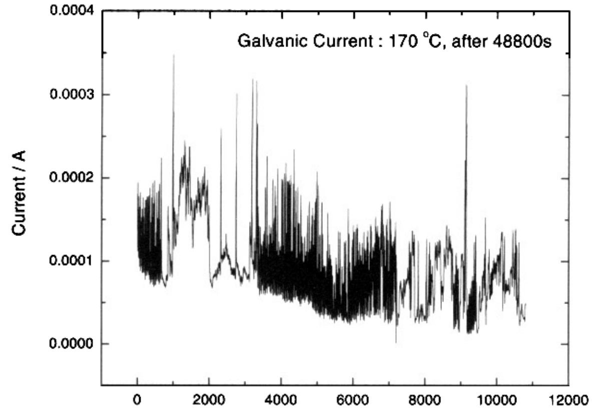

Fig. 2. Typical current transient obtained during galvanic coupling between 1018 carbon steel and alloy 600 in the aqueous solution containing 2000 ppm boron and 3.5 ppm lithium.

3. Results and discussion

Fig. 2 is typical galvanic current transient obtained at 170 ℃ in the solution containing 2000 ppm boron. Galvanic current was decreased with time. It could be also seen that the measured current was fluctuated with time. Corrosion product and boric acid deposit can be formed on the carbon steel wall during galvanic coupling leading to reduction of corrosive area, sometimes blocking of annular gap, followed by detachment from the wall due to impingement by solution flow. This sequence causes galvanic current decrease and then instant increase leading to continual current fluctuation. The amplitude of fluctuation should be reduced with time because the steady state under given condition is attained finally.

As the current fluctuation appeared complicatedly, average current level rather than instantaneous current value could be important and help us reasonably analyze the experimental results. Fig. 3 represents charge passed during each 5000 s with time at 170 ℃ in the solution containing 2000 ppm boron. Charge was decreased and attained at steady state value with time. As two metals were connected, corrosion product such as protective film as well as boric acid deposit was formed on the carbon steel with time accompanying the decrease of active area, which led to galvanic current decrease. Boric acid deposit on the wall can be formed by water steamed out through the annular gap. This galvanic current trend with time was similar to the results shown in EPRI report[3)] which were obtained from the immersion test for carbon steel.

Taking density, molecular weight and oxidation number as 8 g/cm^3, 55 g/mol and 2, galvanic corrosion rate can be calculated from steady state galvanic current as a

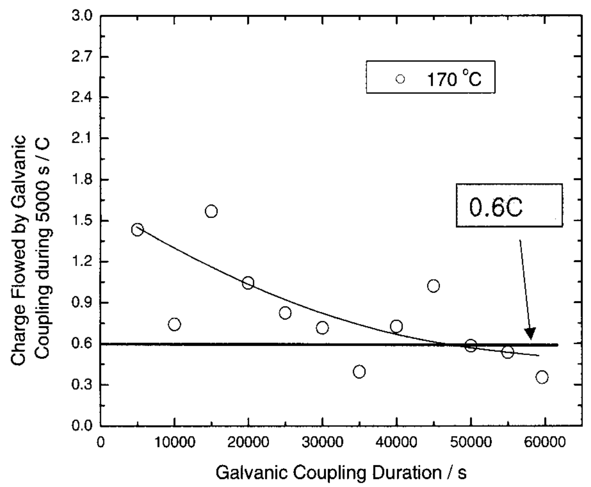

Fig. 3. Plot of charge passed per each 5000 s during galvanic coupling between 1018 carbon steel and alloy 600 against galvanic coupling duration at 170 ℃ in the aqueous solution containing 2000 ppm boron and 3.5 ppm lithium.

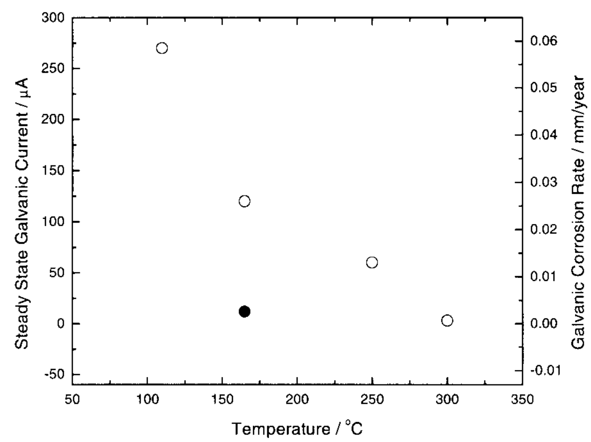

Fig. 4. Steady state galvanic current(left axis) and galvanic corrosion rate(right axis) calculated using steady state galvanic current as a function of operating temperature in the range of 110 to 300 ℃ in the aqueous solution containing 2000 ppm boron and 3.5 ppm lithium. Filled circle(l) presents steady state galvanic current(left axis) and galvanic corrosion rate(right axis) obtained during the second galvanic coupling at 170 ℃ after 300 ℃ pre-coupling followed by 12 hrs disconnection.

function of temperature. Fig. 4 is plot of galvanic corrosion rate obtained from steady state current against operating temperature. Galvanic corrosion rate was decreased from 0.06 to 0.0006 mm/year as temperature was increased from 110 to 300 ℃. It should be noted that the corrosion rate obtained using the steady state corrosion current is not significant. And it should be also remarked that a few tens percent allowance of galvanic corrosion rate is unavoidably incorporated considering the fluctuation of current level.

According to EPRI report published in 2001,[3] there were the reports from Moscow power institute and BNL in which it could be seen that the carbon steel corrosion rate decreased with temperature above 100 ℃.

Decrease of galvanic corrosion rate with temperature seems to be caused by corrosion properties of the corrosion product formed on the carbon steel surface and slightly soluble metaboric acid(HBO_2) produced by the dehydration of the orthoboric acid(H_3BO_3) at 170 ℃.[4] At higher temperature, more stable protective film formed at that temperature can be adhered to the wall even under impingement by solution flow and increased amount of dehydration to less soluble boric acid deposit increases the resistance against galvanic corrosion

Considering that the reaction rate is thermally activated, it is reasonable that the corrosion rate is increased with temperature. Nevertheless, galvanic corrosion rate was decreased as the temperature was ranged from 110 to 300 ℃ indicating that the experimental factors affecting the temperature dependence of galvanic corrosion rate at the present work overwhelm the temperature dependence based upon thermal activation.

Figs. 5(a) and (b) present galvanic corrosion transients obtained from fresh corrosion cell and the corrosion cell re-coupled at 110 ℃ after 12 hrs disconnection of galvanic coupling and simultaneous corrosion cell shut down, i.e. heater off without solution flowing, respectively. In spite of 12 hrs disconnection, galvanic coupling current with time resembled the first galvanic coupling transient in current level and shape. It seems that corrosion products and boric acid deposit formed at 110 ℃ during galvanic coupling are weakly sticky to the carbon steel wall. Hence during re-heating, re-solution flowing and re-coupling after 12 hrs break, almost all corrosion products and boric acid deposit are detached from the wall and dissolved leading to nearly complete recovery up to the galvanic current transient obtained for the fresh corrosion cell. From this, it can be conceivable that corrosion product and boric acid deposit formed at 110 ℃ are not relatively well attached to the carbon steel wall.

It can be also observed sometimes that the current value during initial period of the second coupling is slightly larger than that of the first coupling, which is possibly related to increase of the active area caused by the solution overflow around top region of the crevice sometimes.

Figs. 6(a) and (b) illustrate galvanic corrosion transients obtained during re-coupling at 170 ℃ after 12 hrs disconnection of galvanic coupling and simultaneous corrosion cell shut down for originally 170 and 300 ℃ galvanic coupled corrosion cells, respectively. It could be found that galvanic current level was decreased significantly as

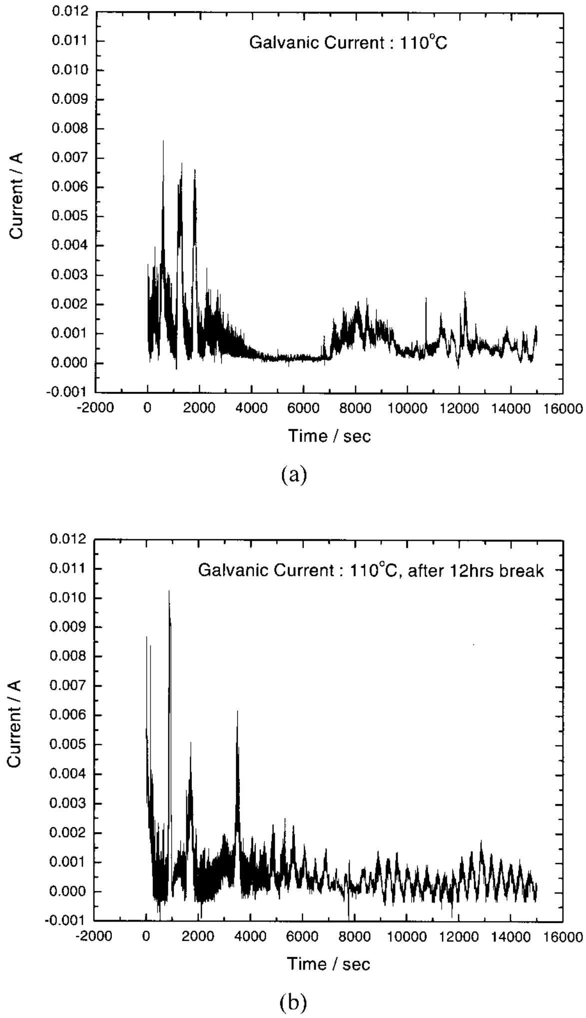

Fig. 5. (a) Current obtained during galvanic coupling at 110 ℃ for fresh sample and (b) current obtained during the second galvanic coupling at 110 ℃ after 110 ℃ pre-coupling for fresh sample followed by 12 hrs disconnection in the aqueous solution containing 2000 ppm boron and 3.5 ppm lithium.

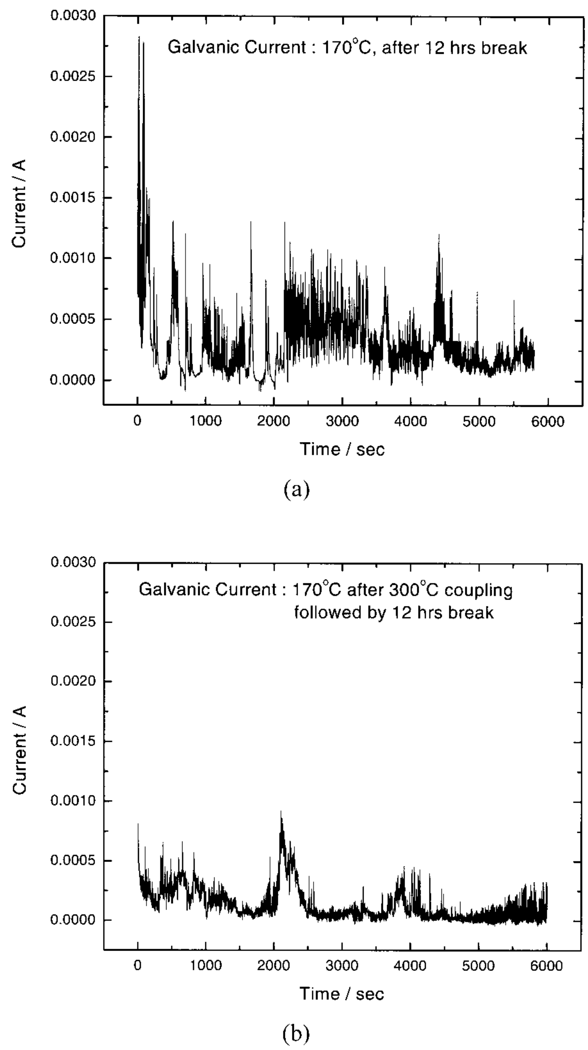

Fig. 6. (a) Current obtained during galvanic coupling at 170 ℃ after 170 ℃ pre-coupling for fresh sample and (b) current obtained during the second galvanic coupling at 170 ℃ after 300 ℃ pre-coupling for fresh sample, followed by 12 hrs disconnection in the aqueous solution containing 2000 ppm boron and 3.5 ppm lithium.

the galvanic coupling specimen pre-coupled at 300 ℃ was compared to the specimen pre-coupled at 170 ℃.

The galvanic corrosion rate can be calculated using steady state current level. Filled circle shown in fig. 4 represents galvanic corrosion rate obtained for the galvanic coupling specimen at 170 ℃ which had been pre-coupled at 300 ℃. As shown in fig. 4, the galvanic corrosion rate for the specimen pre-coupled at 300 ℃ was much smaller than the galvanic corrosion rate for the fresh sample at 170 ℃. From figs. 4 and 6, it is reasonable to think that the corrosion product and boric acid deposit including dehydrated boric acid deposit formed during galvanic coupling at 300 ℃ are so strongly attached to the carbon steel wall that corrosion product and deposit are not detached at 170 ℃. Combining figs. 4~6 results, it is emphasized that the stability and adhesive property of corrosion product and boric acid deposit formed on the carbon steel wall was improved as galvanic coupling temperature increased in the range of 110 to 300 ℃.

While two metals composing of galvanic coupling were disconnected for 12 hrs followed by re-heating to 170 ℃ after 300 ℃ pre-coupling, some amount of the boric acid dehydrated at 300 ℃ should be re-hydrated and some solid boric acid should be dissolved. Therefore it can be expected that quite a large initial current level can be obtained during re-coupling at 170 ℃. Nevertheless initial and steady galvanic current levels for pre-coupled sample at 300 ℃ are smaller than those for pre-coupled sample at 170 ℃ due to adhesive property of the corrosion product and boric acid deposit formed at 300 ℃.

In PWR of real nuclear power plant, pressure difference between inside and outside of reactor vessel head is so large to be about 157 bar that the solution flow rate should be very high if some pinholes through reactor vessel head are formed and exist. Hence it is conceivable that the corrosion product and deposit formed at even high temperature are difficult to be attached to the wall due to strong solution impingement. Therefore in real system having pinhole through upper plate of carbon steel, it is expected that steady state current level would be much larger than that of our lab scale system. This is the reason why initial galvanic current level can give us more valuable information close to real nuclear power plant condition sometimes.

Fig. 7 presents the galvanic corrosion rate calculated from initial current level as a function of operating temperature. Galvanic corrosion rate was ranged from 1.7 to 0.01 mm/year which was much larger value than the value obtained from steady state current level. By the way the galvanic corrosion rate was decreased as temperature was increased like the galvanic corrosion rate obtained from steady state current level. It may be concerned with the corrosion product and boric acid deposit formed already during temperature elevation and solution injection prior to galvanic coupling, which would always underestimate the galvanic corrosion rate obtainable from the fresh sample.

Even though pressure difference between inside and outside of reactor vessel head is very high, it is possible that galvanic corrosion rate dependence on operating temperature should be preserved because the adhesive property of corrosion product and deposit with temperature is still valid.

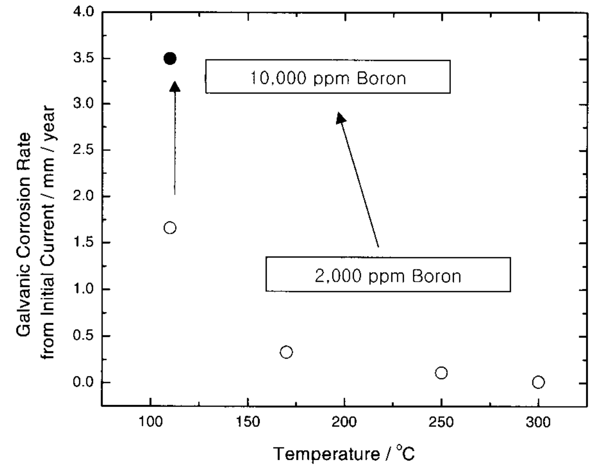

Fig. 8. Plot of galvanic corrosion rate against boron concentration of 2000 ppm(O) and 10000 ppm(l) in the solution.

The effect of boron concentration on galvanic corrosion rate is shown in fig. 8. Galvanic corrosion rate in solution containing 10000 ppm boron was about 2 times larger than that in solution containing 2000 ppm boron. In nuclear power plant condition, it can be occurred that boric acid is concentrated locally instead of the solid deposit formable due to relatively fast water steamed out on the wall leading to increase of galvanic corrosion rate.

Furthermore it should be noticed that the galvanic corrosion rate written here is just averaged value and galvanically corroding region representing highest value, viz. near region where two metals are connected would show much higher galvanic corrosion rate.

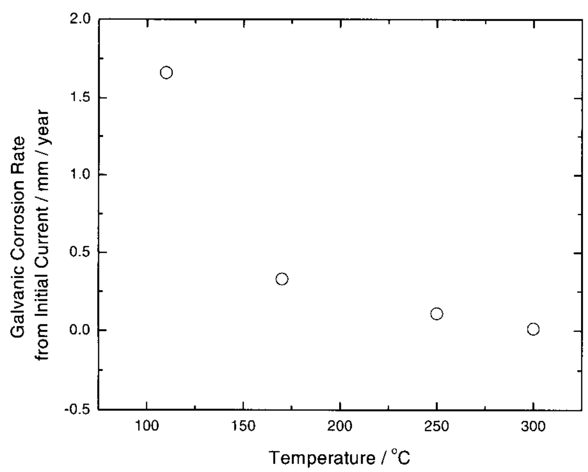

Fig. 7. Galvanic corrosion rate obtained from initial galvanic current as a function of operating temperature in the range of 110 to 300 ℃ in the aqueous solution containing 2000 ppm boron and 3.5 ppm lithium.

4. Conclusions

This work was concerned with the galvanic corrosion rate obtained from the corrosion cell having annular gap of 0.5 mm between carbon steel 1018 and alloy 600 as a function of temperature and boron concentration. The galvanic corrosion rate decreased with time. This occurrence was explained by the increase of corrosion product such as protective film as well as boric acid deposit formed on the carbon steel with time. The galvanic corrosion rate decreased as temperature increased while the corrosion rate increased as boron concentration increased. From these results, it was suggested that the stability as well as adhesive property of corrosion product and boric acid deposit including dehydration of boric acid to be slightly soluble phase was improved as galvanic coupling temperature increased in the range of 110 to 300 ℃. The galvanic corrosion rate determined using initial galvanic coupling current instead of steady state coupling current was commented, which was relatively closer to real PWR if pinholes through the upper plate of carbon steel exist.

Acknowledgement

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