Accelerated Corrosion Tests of Nuclear Reactor Pressure Vessel Materials in NaCl–H$_3$BO$_3$ Solutions$^{*1}$

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Following the 2011 accident at the Fukushima Daiichi nuclear power station, sea water for cooling and boric acid for maintaining a non-critical condition, both corrosive liquids, were injected into nuclear pressure vessels. In order to estimate corrosive characteristics of the pressure vessels an experimental study was undertaken to provide an accelerated corrosion test on SA533B low alloy steel and Inconel 600, materials used in the construction of the pressure vessels. In a typical experiment, samples of these materials were immersed in saturated NaCl and concentrated H$_3$BO$_3$ aqueous solutions at a temperature of 423 K. SA533B suffered little or no corrosion in saturated NaCl solution, significant corrosion in concentrated H$_3$BO$_3$ solution and substantial corrosion in the binary saturated NaCl-concentrated H$_3$BO$_3$ solution. Galvanic corrosion of SA533B was accelerated when Inconel 600 was also immersed in the same solution and the two samples were electrically connected either externally by a wire lead or internally by a screw made of SA533B or both. Corrosion rate in the initial stage was 0.07 mm per hour. The corrosion product on SA533B was porous and easily detachable, indicating corrosion to be progressive without producing a stable protective corrosion layer. The validity of the extreme experimental condition for accelerated corrosion tests is discussed and experimental programs for further investigation are proposed. [doi:10.2320/matertrans.M2012405]

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1. Introduction

On 11th March 2011, a nuclear disaster of Level 7 (INES: International Nuclear Event Scale) occurred at the Fukushima Daiichi nuclear power station of the Tokyo Electric Power Company. As a result, cooling of three reactor pressure vessels became almost impossible. An analysis by the Tokyo Electric Power Company$^1$ estimated that the vessels would have been seriously damaged due to the meltdown of containing nuclear fuels.

The Nuclear and Industrial Safety Agency$^2$ also announced that sea water for cooling and ‘boric acid’ for maintaining a non-critical condition were being injected into the vessels as emergency measures, although it is not clear at present whether the announced ‘boric acid’ was pure boric acid or a boric compound such as sodium pentaborate. Sodium chloride contained in seawater and boric acid are strongly corrosive reagents towards nuclear vessel materials. As a result, the possibility of serious corrosion of vessel materials during a long-term maintenance period prior to their decommissioning must be carefully considered, although cooling water was changed from seawater to light water later in the process.

Even now, there is still insufficient information on the corrosion of reactor pressure vessel materials exposed to severe accidental conditions. In the case of the Three Mile Island nuclear accident in 1979, which was of Level 5, a vessel containing nuclear fuels suffered partial melt-down but was not destroyed$^3$ and seawater was not injected into the vessel. However, it is well known that vessel materials are severely corroded by boric acid. In the case of the David-Besse pressurized water reactor in 2002, a hole was discovered in the head of the vessel and it was verified that it was due to the invasion of boric acid injected for controlling neutron flux to the low alloy steel vessel itself via a crevice with Inconel cladding.$^4$ After this accident, thorough laboratory experiments were carried out.$^5$ As a typical example, a high corrosion rate of 40 mm/year was observed in aerated concentrated H$_3$BO$_3$ at 370.5 K.

The nuclear reactors involved in the accident at the Fukushima Daiichi nuclear power station are of the boiling-water type; the vessels themselves are made of low alloy steel together with stainless steel cladding inside a large part of the vessels. A cladding of nickel-based super alloy is incorporated inside a part of the bottom of the vessels and welded to the sheaths of the control rods. Therefore, if cladding materials of the vessels are damaged and outer steel is exposed to coolant, corrosion of steel proceeds. In addition, if a galvanic couple is formed between steel and corrosion-resistant cladding material, galvanic corrosion is likely to occur. The possibility of such corrosion has not yet been discussed.

Therefore, our purpose in this study is to investigate the nature of the corrosion process and its rate according to the following procedures. The first is to make a model of the damaged vessel in a corrosive coolant environment. The second is to choose appropriate experimental conditions for accelerated corrosion testing. The third is to determine the results of accelerated corrosion tests. Finally, some recommended experimental projects for future investigation are proposed.

2. Proposal of a Model of the Vessel for Accelerated Corrosion Test

Reactors subject to the accident, units 1, 2 and 3 are of the boiling-water type. Reactors, units 1, 2 and 3 were made during different periods but are treated generally without considering this difference in this study.
In Fig. 1, schematic diagrams of the vessel are shown. In Fig. 1(a), a diagram of the usual vessel is shown. Detailed diagrams of vessels are shown in a government report. In general, a reactor is made of low alloy steel 15–16 cm thick, and is internally clad with corrosion-resistant materials such as stainless steel and nickel-based super alloy to prevent corrosion. Degradation of the vessel material is checked by inserting surveillance test specimens with the same composition into the vessel.

The most important matters are degradation of materials by strong neutron radiation and generation of stress corrosion cracking and if it is found that cladded materials are not destroyed, it is concluded that there is no severe corrosion of the vessel material in a short time.

On the other hand, there is insufficient information regarding the present situation of vessels involved in the accidents. According to an analysis by Tokyo Electric Power Company, nuclear fuels in the unit 1 reactor dropped down into the containment vessel from the pressure vessel. In site 2 and 3 reactors, melt-down fuel remains in the pressure vessels. Although the situation depends upon whether a through-hole in the vessels exists or not, it is possible that welded parts of control rods are easily destroyed.

Therefore, a model of a damaged vessel is shown in Fig. 1(b). It is postulated that a part of the welded nickel-based super alloy was destroyed and low alloy steel was directly exposed to coolant; also a through-hole was generated so that a galvanic couple was formed between the welded nickel-based super alloy and the steel. If meltdown fuel remains at the bottom of the vessel, vessel material undergoes local heating by decay products and is highly activated by strong nuclear radiation. In addition, at high temperature and high pressure, injected seawater and boric acid are concentrated by boiling the coolant. After this, although cooling was attempted, melt-down fuels provide a strong source of heat, resulting in exceptionally corrosive circumstances for vessel materials.

3. Experimental Conditions for Accelerated Corrosion Test

Although a simple model of the damaged vessel is presented in Fig. 1(b), there is almost no reliable information on the present situation as yet. It is important that a decision be made urgently concerning what experiments should be done involving appropriate experimental conditions for investigating the possible corrosion of the vessel materials even where there is almost no information without waiting until sufficient information becomes available. In order to investigate the possibility of unexpectedly severe corrosion, experimental conditions for accelerated corrosion test are proposed in some detail below. Of course, test materials and chemical constituents of test solutions should resemble as closely as possible those pertinent to the accident including chemical substances in coolants during the period of the accident. On the other hand, experimental parameters such as temperature, applied pressure, concentrations of chemical substances and so on, should be chosen so as to be suitable for accelerated corrosion tests. Once experimental results at an appropriate experimental condition are obtained, it is expected that experimental parameters will be modified step by step in response to more realistic conditions, as soon as new reliable information on the vessel situation becomes available.

As a test vessel material, a modified low alloy steel, SA533B, used at present as vessel material was chosen, because it is not easy to obtain the material which has the same chemical compositions as the original vessel material subjected to the accident, and furthermore the present commercially available material is useful for further investigation.

In Table 1, chemical compositions of the materials used are shown. As a heat treatment, a SA533B plate 55 mm thick, was quenched after holding at 1153 K for 0.6 ks, and being tempered at a rate of 1.8 ks/25 mm at 923 K. As a reference, some chemical compositions of the vessel material of the damaged Unit 1 reactor are also shown. According to a review on the improvement of vessel materials by Kodaira, some chemical compositions on neutron irradiation embrittlement of vessel material. Also, from the standpoint of corrosion, the copper content can act as a local cathode, resulting in a galvanic corrosion by forming a galvanic couple with iron in low alloy steel. Therefore, employing a presently used low alloy steel with reduced copper concentration means its corrosion is expected to be less than that of the steel subject to the accident. Nevertheless, as shown later, even the present low alloy steel corrodes very severely.

As a reference material for comparing the corrosion characteristic, pure iron was chosen, because pure iron is more easily obtainable, and comparison of the corrosion characteristic is very important allowing the contribution of added elements in the steel to be assessed. Stainless steel is used as cladding inside most parts of the steel comprising the vessel. A cladding of nickel-based super alloy is incorporated on the inside of the base of the steel and welded to the sheaths of the controlling rods. Although the possibility of destruction of the stainless part is not negligible, nickel-based super alloy part-welded to the sheaths of the controlling rods is liable to be destroyed. Therefore, as a test specimen in addition to SA533B, a typical nickel-based super alloy,
Inconel 600 was chosen. The specimen used in this study is expressed as Ni–16Cr–7Fe according to its principal chemical compositions shown in Table 1. The corrosion characteristic of Inconel 600 used as a nuclear material is well known.12)

Seawater was injected as an emergency coolant at the beginning of the accident. “Boric acid” was also sometimes injected in order to maintain the non-critical condition. In general, boric acid, H3BO3 (acidic in nature for pressurized water reactors), and sodium pentaborate, NaB5O8·5H2O (basic in nature for boiling water reactors) are used. Sodium pentaborate, NaB5O8·5H2O is a compound of borax, Na2B4O7·10H2O and boric acid, H3BO3. But, it is not clear what kind of “boric acid” was injected in the emergency.

By considering that a main component of injected seawater is 3 mass% NaCl, it is reasonable that the coolant solution should mainly be treated as the system NaCl–H3BO3–NaB5O8. There are some causes expected to lower the pH of the coolant. The pH of sodium pentaborate decreases with increasing concentration, reaching the almost neutral value of 6.8 at 14 mass%.13) UO22+ ions generated from melted uranium fuel react with H2O2 to lower the pH, according to the following reaction: UO22+ + H2O2 = UO3 + 2H+. Anyway, it is reasonable to suppose that it was not easy to maintain stable chemical compositions and pH of the coolant inside the vessel during the duration of the severe accident. In this study, as an extremely acidic condition, a test solution of the NaCl–H3BO3 system was prepared.

Temperature was set at 423 K for two reasons. According to a report of Tokyo Electric Power Company,1 high temperatures above 473 K continued in the beginning of the accident for units 1, 2 and 3 reactors, and were above 373 K even after 2 months. However, from a reference,3) corrosion rate of SA533B in a saturated H3BO3 solution at 298 K, decreases above 423 K. Therefore, a temperature of 423 K was chosen for an accelerated corrosion test by judging that experiments above 423 K are not always appropriate. To investigate temperature dependence on the corrosion, experiments were also carried out at 298 and 373 K.

A main test solution was a NaCl–H3BO3 mixed solution, and also both a NaCl solution and a H3BO3 solution were used as references. In Table 2, chemical compositions of solutions are shown. The amounts of H2O were fixed at 25.00 g in all three solutions in this study. Concentrations are measured using the unit of molality, mol/kg H2O. Solubilities of NaCl14) in a NaCl solution and H3BO315) in a H3BO3 solution are curve-fitted data obtained from the reference. Mutual solubilities of NaCl and H3BO3 in the mixed solution are not shown, because there is insufficient information on the mutual solubilities. Corresponding to the condition of insufficient cooling during the accident at high temperature and high pressure, NaCl is set up so as to be saturated at any temperature measured. H3BO3 is saturated at temperatures below 373 K, but, is adjusted so as to become more concentrated, but not saturated at 423 K. Solubility of H3BO3 is very high at 423 K, and saturated solution at 423 K has a low molar ratio of H2O/H3BO3, resulting in insufficient water for full ion-solvation. It is therefore not appropriate to investigate corrosion in such a solution, so that the use of the saturated condition was not attempted. In addition, a reference16) shows that when the amount of H2O is substantially decreased, contrarily corrosion decreases. The pH of the mixed solution was 3.23 at 298 K.

In Table 2, the effect of mutual solubilities is not shown, but a reference16) including mutual solubilities of NaCl and H3BO3 in mixed solutions at 303–373 K, shows saturated concentrations are 7.149 mol/kg for NaCl and 6.797 mol/kg for H3BO3 at 373 K.

Although possible irradiation effects on the corrosion of the materials should be investigated, such an experiment cannot be carried out in a standard laboratory. Therefore, any irradiation effect on the materials is out of consideration in this study. But, hydrogen, oxygen and hydrogen peroxide can be generated by the radiohydrolysis of water due to the melted nuclear fuel.3) The effect of oxygen generated by radiohydrolysis is examined by experimenting with oxygen at high pressure in this study.

4. Experimental

Apparatuses used in this study are the same as those used for investigating the galvanic corrosion of a Fe–Zn couple at high temperature and high pressure by one of the present authors.17) Experimental procedures in this study are similar unless otherwise described. A specimen, 3.5 cm long, 1 cm wide with a given thickness was cut and polished with progressively finer emery paper finishing with a grade of 800, and then washed with acetone. The specimen was covered.
with Teflon tape except for an area on each side of 1 cm × 2 cm. After the immersion experiment, the part of the specimen covered with Teflon was checked and found not to be corroded. This fact indicates that insulation of the specimen except for the exposed surface area is sufficient. The specimen was connected with a rod (lead) made of the same material by a screw made of acryl resin, and set up in an autoclave.

The autoclave was set up so that the specimen was hanging into the solution inside a glass beaker with a volume of 70 mL. When the specimen was inserted into the solution, the lower part of the specimen was inserted into the region where insoluble NaCl and H₃BO₃ remained at the bottom of the beaker, but there was no apparent difference between the corrosion characteristics of the specimen observed. The test solution was degassed by a flow of nitrogen gas and when the temperature reached 363 K, the flow of nitrogen gas was stopped and the stopcocks of the gas inlet and outlet were closed. When the temperature reached 373 K, the stopcock of the gas outlet was opened for an instant to release residual nitrogen and then the stopcock was closed to retain water vapor within the autoclave. An experiment at 373 K was carried out at this condition. For the experiments at 423 K, the temperature was increased after this. It took about 1.2 ks to heat and cool from room temperature to 423 K. In addition, an experiment at a total applied pressure of 2 MPa was carried out by applying oxygen. In the case of this experiment, in order to avoid an abrupt increase of temperature by injecting oxygen due to adiabatic compression, a total pressure of 1.7 MPa was attained by applying oxygen when the temperature reached 393 K, and then, to keep the applied pressure at 2 MPa oxygen was applied at 423 K. An experiment was then carried out using this pressurized oxygen condition.

Electrochemical experiments, such as measurements of electrode potential and current, polarization measurement, galvanic potential and current were carried out. As a reference electrode, a Ag:AgCl electrode was used. Surface observation of the specimens was carried out using an optical microscope and EPMA.

5. Results

Experiments were done according to experimental condition proposed in the previous section, that is, at 423 K in a NaCl–H₃BO₃ mixed solution for 14.4 ks (4 h) unless otherwise described.

In Fig. 2, electrode potentials for specimens used in this study are shown. Potentials versus Ag:AgCl electrode were stable until reaching about 10 ks. The potentials are about −0.30 V for Ni–16Cr–7Fe alloy, −0.45 V for SA533B and −0.55 V for pure iron. The potential of Ni–16Cr–7Fe alloy is the most positive among the specimens measured, and that of iron is the most negative. Therefore, iron and SA533B can become anodic and Ni–16Cr–7Fe alloy cathodic, indicating galvanic corrosion of iron or SA533B will proceed when coupled with Ni–16Cr–7Fe alloy. The difference of electrode potential between coupled specimens indicates that galvanic corrosion of iron can be more remarkable than that of SA533B. After about 10 ks had elapsed, the electrode potential of Ni–16Cr–7Fe alloy became unstable with time.

Also, the electrode potential of Fe transferred toward the noble direction with time, and as a result a reversal of potential can occur. Reversal of electrode potential was observed for Fe/Ni–16Cr–7Fe and SA533B/Ni–16Cr–7Fe couples when the time exceeded around 14.4 ks, although long term experiments were not intended in this study.

In Fig. 3, the results of polarization measurements for SA533B and Ni–16Cr–7Fe alloy are shown. Reproducibility of measurements, especially that of Ni–16Cr–7Fe alloy was lacking. The solution used is a weak acid, pH ranging from 3 to 4. Therefore, it is considered for SA533B that cathodic reactions are both the generation of hydrogen and reduction of dissolved oxygen, and the anodic reaction is dissolution of iron contained in SA533B. Reaction mechanisms are discussed later.

The cathodic reaction on Ni–16Cr–7Fe alloy is similar to that on SA533B. Corrosion current density for SA533B obtained by extrapolating measured anodic and cathodic polarization curves is about 500 A·m⁻², that is, a corrosion rate of 0.07 mm/h assuming that the corrosion rate is independent of time. The potential difference between SA533B and Ni–16Cr–7Fe alloy is less than 200 mV, and in the case of a galvanic couple, the cathodic current on Ni–16Cr–7Fe alloy is not negligible. By considering that the anodic current of SA533B is equal to the sum of cathodic current densities on SA533B and Ni–16Cr–7Fe alloy,
corrosion current density of SA533B is estimated to be about 600 A·m$^{-2}$, that is, a corrosion rate of 0.08 mm/h. In this case, the contribution of the galvanic couple is estimated to be about 100 A·m$^{-2}$. The corrosion of SA533B itself is remarkable and is accelerated by the formation of a galvanic couple. However, the reproducibility of polarization measurements is low and an analytical value has a considerable error, because there is some uncertainty in the extrapolation method.

In Fig. 4, galvanic corrosion currents of a couple of SA533B and Ni–16Cr–7Fe alloy measured by two methods are shown: one is with a continuous connection and the other one minute on-off cycling. Both the current profiles are essentially similar to each other, although the current measured by on-off cycling is a little larger than with a continuous connection.

In Fig. 5, electrode potential corresponding to Fig. 4(b) is shown. Potentials of SA533B and Ni–16Cr–7Fe alloy were measured alternatively at intervals of ten minutes. SA533B was polarized anodically by about 20 mV by coupling with Ni–16Cr–7Fe alloy, indicating that the corrosion characteristic of the couple is cathodically controlled. Anodic current density at the anodically polarized potential of 20 mV, as shown in Fig. 3, is 30 A·m$^{-2}$, which is in good agreement with 40 A·m$^{-2}$ measured in the initial stage of the galvanic coupling.

The effects of several experimental factors on the galvanic corrosion of the SA533B/Ni–16Cr–7Fe alloy couple were investigated, as shown in Figs. 6 to 9.

In Fig. 6, a comparison of corrosion between two kinds of galvanic couples, is shown. The galvanic current for Fe/Ni–16Cr–7Fe alloy is significantly larger than that for SA533B/Ni–16Cr–7Fe alloy, which corresponds to the fact that the potential difference between iron and Ni–16Cr–7Fe alloy is larger than that between SA533B and Ni–16Cr–7Fe alloy as shown in Fig. 2. Galvanic current density for SA533B/Ni–16Cr–7Fe alloy is about 40 A·m$^{-2}$ in the initial stage and then decreases with time, the average value for 14.4 ks being about 5 A·m$^{-2}$. On the other hand, the current density for Fe/Ni–16Cr–7Fe alloy was 200 A·m$^{-2}$ in the initial stage, leading to a stable value of about 30 A·m$^{-2}$ after an extended period. Calculated galvanic corrosion rate is 0.004 mm/h, or 3.4 cm/y, showing that the contribution of galvanic corrosion is certainly not negligible.

In Fig. 7, comparison of galvanic potential and current of the SA533B/Ni–16Cr–7Fe alloy couple for the three kinds of solutions is shown. A very low value of 0.04 A·m$^{-2}$ in NaCl solution, but high values, 1 A·m$^{-2}$ in H$_3$BO$_3$ solution and 5 A·m$^{-2}$ in mixed solution, respectively, were obtained. Why such a difference exists, will be discussed later. The galvanic potential in each solution was relatively stable during the measuring period.
In Fig. 8, temperature dependence of corrosion current is shown. At 373 K, a relatively large current flows. Therefore, even when the temperature is lowered from 423 to 373 K, galvanic corrosion is decreased but it is not negligible. From a reference,4) it is verified that corrosion in H₃BO₃ solution is not changed much in the range 373 to 423 K. At 298 K, current density was a low value of 0.01 A·m⁻².

In Fig. 9, the effect of applied oxygen pressure on the galvanic corrosion is shown. At an applied pressure of 2 MPa by oxygen, galvanic current is at most doubled initially as the electrical circuit is closed when compared with that where oxygen is absent. Therefore, the contribution of oxygen on the corrosion is not great, compared with the reduction of hydrogen ions.

In Fig. 10, the results of cross-sectional observation of corroded specimens in NaCl and in H₃BO₃ solutions are shown. In NaCl solution, corrosion was scarcely detected. In H₃BO₃ solution, corrosion products were observed on the surface and they appeared to be layered and detached layer by layer leaving a rough surface. A thin layer was observed at a depth of 10 µm from the surface, showing that oxidation internally proceed and layered corrosion products are formed. Corrosion rate was 0.040 mm/h (35 cm/y). A reference5) shows 14.463 cm/y at 423 K for 162 ks immersion in a concentrated H₂BO₃ solution, although the concentration is not indicated. This corrosion rate is lower than that of our value for 14.4 ks immersion, possibly due to the fact that the former is an average value obtained for a longer period than the latter.

In Fig. 11, the results obtained in the mixed solution are shown. The corrosion in the mixed solution is greater than that in H₂BO₃ solution. Corrosion products are very porous and easily detached manually. The galvanic specimen looks more porous than a non-galvanic specimen and the surface of the former is rougher than that of the latter. Corrosion rates are 0.065 mm/h for a non-galvanic specimen and 0.075 mm/h for a galvanic specimen. However, for the specimen with a rough surface, knowledge of the minimum thickness is the most important issue for estimating the risk of rupture of the specimen. The corrosion rate estimated by measuring the minimum thickness was 0.082 mm/h.

In Fig. 12, corrosion of an internal galvanic couple for 14.4 ks immersion is shown. The couple was formed by

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**Fig. 8** Dependence of galvanic current density on temperature for a SA533B/Ni–16Cr–7Fe alloy couple.

**Fig. 9** Dependence of galvanic current density on atmospheric gas composition for a SA533B/Ni–16Cr–7Fe alloy couple.

**Fig. 10** Surface morphologies of SA533B in NaCl and H₃BO₃ solutions after 14.4 ks immersion.
connecting together a small piece of SA533B and a piece of Ni–16Cr–7Fe of the same size; this was achieved by machining a screw thread on the former and rotating this into a corresponding threaded hole in the latter until tight. In appearance, SA533B was severely corroded and corrosion products on SA533B are easily detached. An enlarged photograph shows that the interface is not smooth and Ni–16Cr–7Fe alloy appears to be corroded. The corrosion rate of SA533B determined by measuring the thickness of the corrosion layer is 0.066 mm/h.

In order to investigate the effect of the ratio of cathodic area/anodic area, another internal galvanic couple with a ratio of 36.5/1 was used; a hole was made in the center of a disc (5 mm thick, 20 mm diameter) of Ni–16Cr–7Fe alloy, into which a screw of SA533B of 4 mm diameter was inserted. Cross-sectional views of two specimens are shown in Fig. 13. Top parts of the SA533B screws were more corroded than their bottom parts, indicating that at the top parts, evolved hydrogen is readily detached and the corrosion proceeds. On the other hand, at the bottom parts, evolved hydrogen is trapped and the metal is isolated from direct contact with the solution thus hindering corrosion. Corrosion rates of top parts of two SA533B specimens were different from each other; one was 0.26 mm/h and the other was 0.52 mm/h. These values are very high, compared with the corrosion rate of about 0.07 mm/h for a cathodic area/anodic
area ratio of 1/1. In addition, it is well known that a nickel-based super alloy such as Inconel is corrosion-resistant in general, but, crevice corrosion sometimes occurs. The possibility of crevice corrosion will be checked, if a long-term experiment is carried out.

In Table 3, comparison of the corrosion rates is shown. The results obtained from both of the polarization measurements and cross-sectional observation of the specimen are in agreement with each other. However, the result obtained by polarization measurement is a rounded value, because the analysis is dependent upon the calculation method, as shown previously. The values obtained by cross-sectional observation are directly measured. But considering the experimental errors, accurate estimation of the effect of galvanic corrosion is not easy. As shown in Fig. 4, the measured average value of 5 A·m\(^{-2}\), equivalent to 0.0006 mm/h is difficult to be detected from the cross-sectional observation of the specimen. Nevertheless, in the initial stage of immersion, galvanic current density of 0.005 mm/h was detected, that the corrosion is accelerated at least in the initial stage. Corrosion rate in NaCl–H\(_2\)BO\(_3\) is about 0.07 mm/h (60 cm/y), both for non-galvanic and galvanic specimens.

### Table 3 Calculated corrosion rates of SA533B at 423 K.

<table>
<thead>
<tr>
<th></th>
<th>NaCl</th>
<th>H(_2)BO(_3)</th>
<th>NaCl–H(_2)BO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not coupled</td>
<td>0.040 mm/h (35 cm/y)</td>
<td>0.065 mm/h (57 cm/y)</td>
<td>0.075 mm/h (External) (66 cm/y)</td>
</tr>
<tr>
<td></td>
<td>0.066 mm/h (Internal) (58 cm/y)</td>
<td>0.07 mm/h* (60 cm/y)</td>
<td>0.08 mm/h* (70 cm/y)</td>
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*From the polarization analyses (see Fig. 3)

6. Discussion

The reaction mechanism is now discussed based upon the experimental results. Iron is the major component of SA533B; the other minor metallic components are more corrosion-resistant than Fe. As a result, a principal anodic reaction is the oxidation of Fe to dissolved Fe\(^{2+}\) ions.

\[
\text{Fe} = \text{Fe}^{2+} + 2e^{-} \quad (1)
\]

Boric acid, H\(_2\)BO\(_3\) is a weak acid and is partially dissolved in H\(_2\)O.\(^{13}\)

\[
\text{H}_2\text{BO}_3 \rightarrow \text{B(OH)}_3^- + \text{H}^+ \quad (2)
\]

A cathodic reaction in an acidic solution is the reduction of hydrogen ions to generate hydrogen gas.

\[
2\text{H}^+ + 2e^- = \text{H}_2 \quad (3)
\]

The net reaction resulting from the combination of reactions (1) and (3) is the following.

\[
\text{Fe} + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2 \quad (4)
\]

It follows that corrosion of Fe in H\(_2\)BO\(_3\) solution is accompanied by hydrogen evolution. At the elevated temperature of 423 K, hydrogen overpotential may be lower than that at room temperature and reaction (4) is likely to proceed.

It was found that pH measured at 298 K before and after the immersion experiment of 4 h duration in the NaCl–H\(_2\)BO\(_3\) solution changed from 3.23 to 3.83, which indicates the consumption of hydrogen ions during the corrosion process. In addition, hydrogen generation was verified by surveying the internal pressure of the experimental vessel: the pressure was increased from the saturated water vapor pressure of about 0.5 MPa at 423 K to a total pressure of about 0.8 MPa within 1 h and then it remained at an steady value during the experiment.

Hydrolysis of Fe\(^{2+}\) ions proceeds in the solution.\(^{18}\)

\[
\text{Fe}^{2+} + 4/3\text{H}_2\text{O} = 1/3\text{Fe}_3\text{O}_4 + 2\text{H}^+ + 1/3\text{H}_2 \quad (5)
\]

Hydrogen ions are generated according to reaction (5), but consumed in reaction (4), so that corrosion of Fe is accelerated. The solution after an immersion experiment looks blue-colored. The surface of SA533B is black-colored so that in the solution surrounded by deaerated water vapor, corrosion does not reach the point corresponding to the formation of Fe\(_2\)O\(_3\). Therefore, it is considered that the corrosion product formed in the initial stage is Fe\(_2\)O\(_4\).

At a high oxygen pressure or where dissolved oxygen is not removed from solution by degassing, oxygen reduction proceeds as a cathodic reaction in acidic solution in addition to reaction (3).

\[
1/2 \text{O}_2 + 2\text{H}^+ + 2e^- = \text{H}_2\text{O} \quad (6)
\]

The effect of oxygen on the corrosion of Fe was verified, as shown in Fig. 9.

For the corrosion in NaCl–H\(_2\)BO\(_3\) mixed solution, the effect of added Cl\(^{-}\) ions must be also considered as follows.

\[
\text{Fe}^{2+} + \text{Cl}^- = \text{FeCl}^+ \quad (7)
\]

At a rough estimate, the ratio of [FeCl\(^+\)]/[Fe\(^{2+}\)] is 33 by applying an association constant of 4.57 (mol/kg)\(^{-1}\) at 423 K for this reaction\(^{19}\) and a saturated chloride ion concentration of 7.23 mol/kg and by assuming that activity coefficients of ions are unity. As a result of the formation of soluble FeCl\(^+\) ions, the concentration of Fe\(^{2+}\) ions is lowered promoting the dissolution of Fe\(^{2+}\) ions, so that the corrosion of Fe is also accelerated. This may be the reason why SA533B was scarcely corroded in neutral NaCl solution but its corrosion in H\(_2\)BO\(_3\) solution was accelerated by adding NaCl.

In the Fe–B–O system,\(^{20}\) many complex iron borates are known. In the experiment in H\(_2\)BO\(_3\) solution,\(^4\) FeB\(_2\)O\(_4\) was identified as a corrosion product. For the formation of FeB\(_2\)O\(_4\), Fe\(^{2+}\) ions react with B(OH)\(_4^-\) ions, followed by a dehydration step.

\[
\text{Fe}^{2+} + 2\text{B(OH)}_4^- = \text{FeB}_2\text{O}_4 + 4\text{H}_2\text{O} \quad (8)
\]

From the experiment in H\(_2\)BO\(_3\) in this study, the formation of a corrosion product involving Fe, B and O was verified by EPMA, but a stoichiometric FeB\(_2\)O\(_4\) is not identified. Corrosion products obtained in NaCl–H\(_2\)BO\(_3\) solution involved Fe, B, O and Cl.

Consider now the reaction mechanism for galvanic corrosion via the SA533B/ Ni–16Cr–7Fe alloy couple. There
are external and internal galvanic couples: an external one results from a lead wire, the connection point being positioned external to the solution; an internal one results from a connection within the solution. At first, the case of external galvanic corrosion is considered. Electrode potentials of both specimens are close to each other and anodic and cathodic reactions proceed on the surface of SA533B, but anodic oxidation of Ni–16Cr–7Fe alloy is negligible due to the fact that the corrosion of this couple is cathodically controlled, as shown in Fig. 5. As a whole, pH of the bulk solution is increased but pH on Ni–16Cr–7Fe alloy is higher than that on SA533B. Reaction on each specimen is not likely to be affected, because the specimens are separated from one another. In principle, corrosion reaction mechanism of the internal couple is the same as that of the external couple. But, the pH distribution on the surface of internal couple is inhomogeneous, especially at the boundary of both specimens. As the result, corrosion near the boundary of both specimens was substantial due to this phenomenon as illustrated in Figs. 12 and 13. Also, the specimens of the internal couple in this study are mechanically connected, so that crevice corrosion is likely to occur at the boundary of both specimens. Although the experimental system is different from that of this study, authors21) investigated the following case. From the results of pH distribution measurements adjacent to the iron onto which Zn had been partially electrodeposited in a neutral NaCl solution, Zn2+ ions are dissolved and hydrated, resulting in lowering the pH on the surface of the Zn and in spreading an acidic region toward the surface of Fe from the Fe/Zn boundary. Therefore, in the cases of Figs. 12 and 13 in this study, a more acidic area is spreading toward the Ni–16Cr–7Fe side from the boundary interface of SA533B/Ni–16Cr–7Fe alloy. That results in the possibility of corrosion of the Ni–16Cr–7Fe alloy.

When the SA533B sample was immersed in the solutions, as shown in Figs. 10 and 11, it was scarcely corroded in NaCl solution but was corroded significantly in H3BO3 solution and substantially corroded in a mixed solution. In the case of the galvanic corrosion experiments, as shown in Fig. 7, there was a very low corrosion current in NaCl solution, and was a low current in H3BO3 and a substantial corrosion current in the mixed solution. So, galvanic corrosion characteristic in the examined solutions is similar to corrosion characteristic of non-coupled specimen, in spite of different experimental methods. A reference23) shows that the contribution of galvanic corrosion is not important, compared with the corrosion of SA533B itself in H3BO3 solution. However, in the mixed solution as shown in this study, galvanic corrosion increased in comparison with that in H3BO3 solution. Although a measured average galvanic current density of 5 A·m−2 in the mixed solution is not great, it must be pointed out that the contribution of galvanic corrosion is dependent upon the ratio of cathodic area/anodic area. In the case of a galvanic couple of an area ratio of 36.5/1, the corrosion of SA533B was greatly accelerated, shown in Fig. 13. If stainless steel and/or nickel based super alloy cladding inside the steel vessel are destroyed, a galvanic couple with a large cathodic area (S\textsubscript{c}) and a small anodic area (S\textsubscript{a}) can be formed in a highly electro-conductive concentrated coolant.

As a first approximation, anodic current is proportional to the area ratio S\textsubscript{a}/S\textsubscript{c}22) which is likely to be in the range 100 to 1000. Therefore, even if the corrosion current measured at a galvanic couple of the same areas of cathode and anode is relatively low, it is possible that substantial galvanic corrosion occurs depending upon the cathode/anode area ratio. Assuming that some corrosion resistant cladding is destroyed and as a result, SA533B is exposed to the coolant, anodic current flows locally on SA533B and the coolant near the SA533B becomes more acidic; consequently, it is expected that a small area of SA533B is locally attacked and a through-hole is likely to be made, as if the hole were made intentionally using a mechanical drill. Further, if a through-hole is made, flow-accelerated corrosion can occur.

According to the references, corrosion profiles observed in this study are discussed. Potter and Mann showed that a mild steel corroded in high temperature aqueous solutions with a thick laminated film according to a linear time law.23) The growth mechanism of oxide films during the gaseous oxidation of metals was reviewed by Atkinson.24) And, by analogy to gaseous oxidation, Robertson18) discussed the mechanism of growth of the layers of Fe3O4 on mild steel in high temperature aqueous solutions. A SA533B specimen was corroded in H2BO3 solution by forming laminated corrosion products as shown in Fig. 10, and by forming laminated layer products as shown in Fig. 11. The laminated products look to be non-protective and easily detachable. Therefore, the corrosion rate is expected to obey a linear time law, as pointed out by Potter and Man.23) Hydrogen generation acts to detach layered products.

Some comments for further investigation are presented.

In this study, experiments at high temperature and high pressure were carried out in a beaker of a small volume of 70 mL. There is no problem if the corrosion is not significant, but in the case of significant corrosion as in this study, the corrosion characteristic is likely to be influenced by the size of the vessel.

If the dissolution rate of Fe2+ ions is high, the solution is easily concentrated and becomes saturated with dissolved ions in a short period. As a result, corrosion products are easily formed and dissolution of Fe2+ ions is limited. In the case of a corrosion rate of 0.07 mm/h analyzed in Table 3, Fe2+ ions are estimated to be dissolved from the specimen surface area of 4 cm² at a rate of 0.4 mol/h. As a result, the corrosion characteristic is not influenced by the size of vessel for a short immersion time, but if an experiment in a small vessel continues, the corrosion rate is underestimated. On the other hand, it does not follow that experiments should be carried out in vessel of large volume. It is reasonable to do experiments in a small vessel for simulating the situation in which the solution is concentrated by insufficient circulation and significant evaporation. Because it is not easy to do an experiment in a vessel of large volume for simulating a reactor pressure vessel, it is reasonable to do experiments using vessels with different sizes and to extrapolate the experimental results.

When the solution flows, a protective corrosion layer is not easily formed and flow-accelerated corrosion occurs. This problem is well known in the usual operation period of a reactor.25) Assuming that a through-hole is made at the bottom
of the reactor pressure vessel, flow-accelerated corrosion will be serious. If a pressure difference of 0.4 MPa between the inside and outside of the reactor vessel and a coolant height in the vessel of 5 m are assumed, the flow rate calculated by Torricelli’s formula (2 gh)\(^{0.5}\), approximates to the high velocity of 30 m/s. However, if the solution flows at high speed, it is not easily concentrated; because the two effects are contrary to each other it is not possible to predict which effect will be dominant with regard to corrosion.

The solution system in which seawater and ‘boric acid’ are injected, is generally expressed as the NaCl–H\(_3\)BO\(_3\)–Na\(_2\)B\(_4\)O\(_7\) system. In this study, as an extremely acidic condition, the NaCl–H\(_3\)BO\(_3\) system was chosen. As a result, the corrosion of SA533B is significant, and as shown in Figs. 12 and 13, when SA533B and Ni–16Cr–7Fe alloy are connected with each other and then if a crevice is formed between them, the boundary becomes acidic and corrosion is accelerated. In further investigations, experiments should be carried out in NaCl–H\(_3\)BO\(_3\)–Na\(_2\)B\(_4\)O\(_7\).

In this study, accelerated experiments were performed by modeling an extremely serious situation for the corrosion of the reactor pressure vessel subjected to the accident at Fukushima Daiichi nuclear plant. At present, cooling water is changed from sea water to light water, and evaporation of the coolant is substantially decreased by decreasing the temperature below 373 K, and the concentration of the coolant is changed very little. However, for at least two months reactor pressure vessels subjected to the accident were exposed in a very serious situation. Even if the situation is improved at present, hysteresis of vessel materials remains. As shown in this study, corrosion products on SA533B are very porous and easily detached. Therefore, corrosion products involve NaCl and H\(_3\)BO\(_3\), and a stable protective corrosion layer is not easily formed, even if the situation is improved. For the corrosion study on reactor vessels subject to the accident, it is necessary to do experiments taking into consideration the possible hysteresis of vessels.

7. Conclusions

In emergency, corrosive seawater and ‘boric acid’ were injected into the reactor vessels of Fukushima Daiichi nuclear power station. In general, the solution system is considered to approximate to NaCl–H\(_3\)BO\(_3\)–Na\(_2\)B\(_4\)O\(_7\) system. Experimental conditions for accelerated corrosion tests were considered for SA533B and Ni–16Cr–7Fe alloy (Inconel 600) as vessel materials. Experiments for non-galvanic SA533B and galvanic couple with Ni–16Cr–7Fe alloy were carried out especially in a saturated NaCl-concentrated H\(_3\)BO\(_3\) solution.

The results are:

1. SA533B is scarcely corroded in NaCl solution, significantly corroded in H\(_3\)BO\(_3\) solution and substantially corroded in NaCl–H\(_3\)BO\(_3\) solution.
2. The corrosion of SA533B is accelerated by forming a galvanic couple with Ni–16Cr–7Fe alloy.
3. The corrosion rate in the initial stage is 0.07 mm/yr, on the assumption that the corrosion rate is constant with time, this is equivalent to 60 cm/yr.
4. Corrosion products are porous and easily detached, and as a result a protective corrosion layer is not formed.

As the next step, the possibility of significant corrosion should be checked in a wide range of experimental conditions. Some comments for further investigation are presented.

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