Corrosion behavior of Zircaloy-4 in aqueous solution of methanol at 320 °C under gamma-irradiation

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Abstract
It has been pointed out that high concentration dissolved hydrogen is one of the important factors of PWSCC (primary water stress corrosion cracking) in the primary systems of pressurized water reactors. Application of a substitution for hydrogen may be a fundamental countermeasure of PWSCC. The authors are developing a new water chemistry technology of a hydrogen alternative to suppress PWSCC. In the present paper, corrosion tests of Zircaloy-4 were performed in deaerated 5x10^{-3} mol dm^{-3} methanol solution at 320 °C in the absence and presence of gamma-irradiation. The nominal absorbed dose of the test water was 100 kGy. After the immersion tests, the specimens were analyzed. Weight gain per unit surface area, thickness of oxide film and hydrogen storage were measured. In addition, Raman spectroscopy was carried out, to investigate possible deposition of organic compounds on surface of the specimens. The corrosion behavior of Zircaloy-4 without irradiation agreed with literature data. It was concluded that the presence of methanol did not affect the corrosion behavior of Zircaloy-4. The corrosion behavior of Zircaloy-4 hardly depended on 100 kGy gamma-irradiation. On the Raman spectra of the specimens after the immersion tests, the Raman peaks ascribed to polyethylene or graphite were not found. The deposit of decomposition products of methanol would be negligible if any. It seems that polymerization is not the major process in thermal decomposition and radiolysis of methanol, but methanol decomposes into CO_2 or carboxylic acids.

Key words: Pressurized water reactor, Corrosion, Zircaloy-4, High temperature, Methanol, Gamma-irradiation, Weight change, Oxide film thickness, Hydrogen storage

1. Introduction

It has been pointed out that high concentration DH (dissolved hydrogen) is one of the important factors of PWSCC (primary water stress corrosion cracking) in the primary systems of PWRs (pressurized water reactors) (Nakagawa, et al., 2003). Application of a substitution for hydrogen may be a fundamental countermeasure of PWSCC. The authors have been developing a new water chemistry technology of a hydrogen alternative to suppress PWSCC. In the past, survey of appropriate reductants was performed, and methanol was selected as the most promising chemical agent (Domae, et al., 2010). Also corrosion test results of stainless steels in high temperature water containing methanol without irradiation and under gamma-irradiation were reported (Domae, et al., 2011). So far, our experimental results have demonstrated that methanol is still the promising candidate of hydrogen alternative.

In the present paper, corrosion behavior of fuel cladding materials was investigated in methanol solution at 320 °C in the absence and presence of gamma-irradiation, based on (1) weight gain per unit area, (2) thickness of oxide film and (3) hydrogen storage. It is considered that direct effect of gamma-rays on the corrosion of fuel claddings is unlikely and gamma-rays affect the corrosion of fuel claddings through radiolytic products of water. Not only corrosion behavior but also deposition of organic compounds on the fuel cladding materials is concerned, because additional
deposits on the fuel claddings may result in anomalous corrosion, deterioration of heat transfer efficiency and so on. Raman spectroscopy was applied, to analyze qualitatively organic deposit on the specimens. Raman spectroscopy cannot quantify chemical substances. But, Raman spectroscopy is sensitive to functional groups of organic materials.

2. Experimental

2.1 Corrosion test

Zircaloy-4 was supplied as a tube of outer diameter 10.72 mm and inner diameter 9.48 mm. The Zircaloy-4 tube was cut circumferentially by 50 mm length, and the 50 mm tube was further cut into two parts in the axial direction. The Zircaloy-4 specimens were immersed in 5x10^{-3} mol dm^{-3} methanol solution (20 ml) in stainless steel tubes. The methanol solutions were deaerated with Ar, and sealed with stainless steel plug (Fig. 1). The volume of the stainless steel tubes was approximately 44 ml. The stainless steel tubes are placed in an electric furnace (Fig. 2) and heated to 320 °C. Totally 5 tubes were placed in the electric furnace for several reasons. The first reason is to fix the position of each tube and to reproduce γ-ray dose rate. The second reason is that the test water in several tubes was to be analyzed. In the case of gamma-irradiation, the whole electric furnace was irradiated by γ-rays.

Test conditions are listed in Table 1. The two runs 1 and 2 were carried out as shown in Table 1. Run 2 is an immersion test in 5x10^{-3} mol dm^{-3} methanol solution at 320 °C for 500 h without irradiation. On the other hand, run 1 simulates immersion under irradiation. To avoid expensive irradiation for long time, the irradiation was completed in 2 days. The absorbed dose was nominally 100 kGy. According to Garbett et al. (2000), absorbed dose rate in a PWR core is following: γ-rays 3.33 kGy/s, fast neutrons 6.67 kGy/s and α-rays 6.39 kGy/s. If the primary coolant is irradiated in a PWR core for several seconds, the absorbed dose of 100 kGy in the present work well simulates the irradiation in a PWR core although types of ionizing radiation are different. Almost all of methanol will be decomposed after 100 kGy irradiation from the radiation chemical aspect. It is considered that the 100 kGy gamma-irradiation simulates methanol decomposition in a PWR core. In run 1, the specimen and the test water were kept in the stainless steel tube after 100 kGy gamma-irradiation. Then, the stainless steel tube was again heated to 320 °C and kept for 500 h without...
irradiation.

It is possible to know the effect of methanol on the corrosion behavior of Zircaloy-4 if the test result of run 2 is compared with literature date on corrosion test of Zircaloy-4 without methanol. Comparison of the result of run 1 with that of run 2 leads to clarification of the effect of gamma-irradiation.

### 2.2 Dosimetry

Gamma-ray irradiation was carried out with the $^{60}$Co $\gamma$-ray source in Takasaki Advanced Radiation Research Institute of Japan Atomic Energy Agency. Dose rate was measured with alanine dosimeter (Hitachi Cable, Ltd., AMINOGRAY). In the present work, $\gamma$-rays are weakened in the stainless steel tubes and the electric furnace. The dosimeters were put in the stainless steel tubes as shown in Fig. 2 (b) and irradiated for 30 minutes under the same condition as the corrosion tests. The dose rates were 3.23 kGy/h and 1.73 kGy/h for dosimeter No. 1511 and No. 1512 in Fig. 2 (b), respectively. For the stainless steel tube with the Zircaloy-4 specimen, dose rate was 3.23 kGy/h. The irradiation time was 45.13 h, and the accurate absorbed dose of the test water in the presence of the Zircaloy-4 specimen was 146 kGy.

### 2.3 Analyses of specimen

After run 1 and run 2, the Zircaloy-4 specimens were analyzed as follows:

1. Weight measurement
   Weight of the specimens was measured before and after the corrosion test. From the difference of the weight, weight gain per unit area was calculated.

2. Transmission electron microscopy/Energy dispersive X-ray analysis
   Surface of the specimens was coated with Au, and thin samples were cut from the specimens with focused ion beam (FIB, SII SMI3050MS). The cross-section of the specimens was observed with transmission electron microscope (TEM, JEOL JEM2100F). On the same cross-sectional view, elemental distribution of C, O, Cr, Fe, Ni, Zr, Au and Sn was analyzed with energy dispersive X-ray spectroscopy (EDX).

3. Hydrogen storage
   Hydrogen storage in the Zircaloy-4 specimens after the corrosion tests was analyzed with hydrogen analyzer (Horiba EMGA-621A).

4. Raman spectroscopy
   Raman spectra of surface of the Zircaloy-4 specimens were observed with the Raman modular system (Kaiser Optical Systems Inc., HoloLab532). From the Raman spectra, metal oxides on the surface were identified. Furthermore, it is clarified if organic compounds containing C-C bond or C-H bond are deposited or not.

### 3. Results and discussion

#### 3.1 Weight change

Weight change of the specimens is shown in Table 2. In corrosion behavior of the fuel cladding materials, weight gain per unit area is one of the important indices. Surface area of the Zircaloy-4 specimen is following:

$$A = \frac{(1.072 \cdot \pi \cdot 5 + 9.48 \cdot \pi \cdot 5)}{2} = 15.87 \text{cm}^2$$

(1)

The weight gain per unit area is shown in the sixth column of Table 2.
In literature, corrosion rate of Zircaloy-4 has been reported as 0.45 mg dm\(^{-2}\) d\(^{-1}\) at 360 °C without irradiation (McDonald, et al., 1984), although weight gain of Zircaloy-4 in the early stage of corrosion is not linear (Hillner, et al., 2000). This corrosion rate corresponds to 9.4 and 10 mg dm\(^{-2}\) at 500 and 546 h, respectively. In the present work, immersion time at 320 °C is 500h without irradiation and 546 h in the presence of gamma-irradiation. Anyway, the corrosion rates 9.4 to 10 mg dm\(^{-2}\) well agree with 10 to 11 mg dm\(^{-2}\) in Table 2 although temperature is lower in the present work.

It is concluded that weight gain of Zircaloy-4 is not affected by 5x10\(^{-3}\) mol dm\(^{-3}\) methanol addition or gamma-irradiation of 146 kGy.

### 3.2 TEM/EDX analyses

Cross-sectional view of the specimens Zr1 and Zr2 is shown in Fig. 3 and Fig. 4, respectively. Effect of gamma-irradiation on surface morphology was not observed. From the mapping of Zr and O, ZrO\(_2\) oxide film of approximately 700 nm is formed on the both specimens. Inhomogeneous distribution of Fe, Ni, Cr and Sn was not observed except the Fe-Cr compound which is well known in Zircaloy-4. It seems from the mapping of C that any C-containing compound is not present on surface of the both specimens.

Oxide film thickness is an important index of corrosion behavior of Zircaloy-4. In literature, oxide film thickness of 3 µm is after immersion in Li-free solution at 360 °C in a batch autoclave for 100 days (Pêcheur, et al., 2000). Linear interpolation of the literature data results in 630 nm and 680 nm after 500 h and 546 h, respectively. These values seem consistent with the present result of 700 nm thickness at 320 °C for 500 or 546 h.

From the comparison above, the 5x10\(^{-3}\) mol dm\(^{-3}\) methanol addition and the gamma-irradiation of 146 kGy do not affect ZrO\(_2\) oxide film thickness.

### 3.3 Hydrogen storage

Hydrogen storage of the specimens Zr1 and Zr2 was measured after the corrosion tests, as shown in Table 3. The hydrogen concentration was 22 ppm in the presence of gamma-irradiation of 146 kGy, and 17 ppm without irradiation.

Appropriate literature value to be compared with the present results could not be found. At least, effect of gamma-irradiation of 146 kGy on hydrogen storage in Zircaloy-4 is small.

### 3.4 Raman spectroscopy

Raman spectra of the specimens Zr1 and Zr2 after the immersion tests are shown in Fig. 5. There is no Raman peak on the Raman spectrum of Zircaloy-4 before the corrosion test, because Zircaloy-4 consists of not metal oxides but metals. On the other hand, many sharp Raman peaks are seen on the Raman spectra of the specimens Zr1 and Zr2. Several standard Raman spectra are compared with the Raman spectra of the specimens Zr1 and Zr2 in Fig. 6. The Raman spectrum of the specimen Zr2 apparently coincides with that of ZrO\(_2\) powder. Therefore, oxide film on the surface of the specimen Zr2 predominantly consists of ZrO\(_2\). From the Raman spectrum of Zr2, presence of any other oxides is not confirmed. The major Raman peaks of the specimen Zr1 also agree with those of ZrO\(_2\) powder. Major
component of the oxide film on the surface of the specimen Zr1 is no doubt ZrO$_2$. However, on the Raman spectrum of the specimen Zr1, several additional Raman peaks are observed. The peak positions are 968 cm$^{-1}$ and 787 cm$^{-1}$. These Raman peaks are different from those of major spinel type oxides of FeCr$_2$O$_4$, Fe$_3$O$_4$, NiFe$_2$O$_4$ and NiCr$_2$O$_4$, which are considered to be stable in high temperature water. It is discussed below if these Raman peaks are assigned to organic compounds.

As described in Introduction, organic deposit on fuel claddings is concerned if methanol is added in the PWR primary coolant. It is considered that organic deposit would be graphite or polymerized large molecules because small organic molecules seem to be volatile around 320 °C.

Raman spectroscopy is a powerful tool to detect functional groups of organic compounds. For example, the broad
Raman peaks of graphite in Fig. 6 are assigned to the C-C bond in graphite structure. The graphite structure is not so strict, and the Raman peaks are broad. Polyethylene is a typical polymer which consists of only C and H. Chemical bond in polyethylene is the C-C bond or the C-H bond. Therefore, the Raman peaks of polyethylene in Fig. 6 are assigned to the C-C bond or the C-H bond. It is natural that the C-C bond and the C-H bond are comprised in any large organic molecule. If graphite or any large organic molecules are deposited on the specimen Zr1, the same Raman peaks of graphite or polyethylene must be observed in the Raman spectrum of the specimen Zr1. However, there is no Raman peak in the wave number range from 1600 to 1000 cm\(^{-1}\). It is concluded that organic deposit on the specimen Zr1 would be very little if any.

Fig. 4 TEM photograph of cross sectional view of specimen Zr2 (a) and elemental mapping: (b) Zr, (c) O, (d) C, (e) Fe, (f) Ni, (g) Cr, (h) Au and (i) Sn. The mapping of Zr and O clearly shows the oxide film thickness of approximately 700 nm. In the oxide film, inhomogeneous distribution of Fe, Ni, Cr and Sn was not observed. The mapping of C shows absence of organic deposit.

The results of Raman spectroscopy of the specimens Zr1 and Zr2 are summarized as follows. For the both
specimens, the surface oxide predominantly consists of ZrO$_2$, and any organic deposit could not be detected. These results agree with the elemental mapping by EDX in Fig. 3 and Fig. 4. For the specimen Zr1, unknown sharp Raman peaks at 968 cm$^{-1}$ and 787 cm$^{-1}$ were observed. It is speculated that methanol is decomposed into small molecules such as CO$_2$ or carboxylic acids: it seems that methanol is not polymerized but oxidized in high temperature water under gamma-irradiation.

![Raman spectra of specimens Zr1 and Zr2, and Zircaloy-4 before immersion test.](image)

Fig. 5 Raman spectra of specimens Zr1 and Zr2, and Zircaloy-4 before immersion test. Many sharp peaks are observed on the Raman spectra of Zr1 and Zr2 whereas there is no apparent peak on the Raman spectrum of Zircaloy-4 before the test.

![Comparison of Raman spectra of specimens Zr1 and Zr2 with several standard spectra.](image)

Fig. 6 Comparison of Raman spectra of specimens Zr1 and Zr2 with several standard spectra. Most of the sharp peaks on the Raman spectra of Zr1 and Zr2 agree with ZrO$_2$ powder. On the Raman spectra of Zr1 and Zr2, no specific peaks attributed to graphite or polyethylene are observed.
3.5 Addition of organic compound in primary coolant

Addition of methanol in the primary coolant of PWRs undoubtedly increases TOC (Total Organic Carbon) concentration. TOC in the primary coolant concerns additional deposit on fuel claddings. On the other hand, zinc addition has been employed world-wide in many PWR plants. In zinc water chemistry, acetate is continuously added as counter anion of zinc. Even in case of high concentration zinc, no effect on fuel claddings has been reported (Fruzzetti and Wood, 2006). This fact means that not only zinc but also acetate has actually no effect on fuel claddings. In addition, most of methanol will oxidized into CO₂, as shown in the present paper. Therefore, methanol water chemistry would be compatible with the present management of water chemistry. Occurrence of SCC of fuel claddings seems unlikely. But, it is necessary to discuss details in future after the optimal concentration of methanol and steady-state concentrations of the decomposition products are determined.

In AP-1000 which is one of the third generation nuclear reactors, TOC concentration is limited, according to Reid, at al. (2012). It might be necessary to predict TOC concentration in the primary coolant of AP-1000 if methanol water chemistry is applied.

4. Conclusion

The corrosion tests of Zircaloy-4 have been carried out in 5x10⁻³ mol dm⁻³ methanol solution at 320 °C in the presence and absence of gamma-irradiation. The weight gains per unit area of the both specimens were actually the same, and consistent with the literature value. From the cross-sectional view of the both specimens observed with TEM, thickness of the oxide film was approximately 700 nm, irrespectively of gamma-irradiation. This thickness is consistent with the literature value. The oxide film consists of ZrO₂ and any other oxide was not found, according to the EDX elemental mapping. The Raman spectra also demonstrated the presence of ZrO₂ and absence of any major spinel type oxides. The hydrogen storage of the both specimens was in the same level. It is concluded that addition of 5x10⁻³ mol dm⁻³ methanol and gamma-irradiation of 146 kGy hardly affect the corrosion behavior of Zircaloy-4.

The Raman spectroscopy showed that deposit of organic compounds on Zircaloy-4 in the presence of 5x10⁻³ mol dm⁻³ methanol was little under gamma-irradiation of 146 kGy if any.

Methanol is still the promising hydrogen alternative. So far, it has been demonstrated that general corrosion environment of stainless steels in the presence of methanol is similar to hydrogen condition (Domae, et al., 2010, Domae, et al., 2011). In the present work, it has been clarified that addition of methanol does not affect the corrosion behavior of fuel cladding materials.

In the next step, radiation chemistry of methanol should be thoroughly studied under high dose irradiation. In future SCC test of nickel base alloy will be performed.

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References


