Effect of Acidic and Alkaline Solutions on Electrochemical Corrosion of Zircaloy-2

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Abstract

Electrochemical corrosion of zircalloy-2 in solution containing B-ion as boric acid was tested at room temperature. The results show that the presence of boron has a small effect on the corrosion rates of Zircaloy-2. The tests were conducted in boric concentrations ranged from 50 to 1100 ppm. The effect of boric acid is due to a reduction of PH. Electrochemical corrosion of zicaloy-2 was tested also, in sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions, to compare the results with that of (LiOH) from previous work. The concentrations of these alkaline media ranged from 0.5M to 1M. Both NaOH and KOH have a slight effect on corrosion rate, while LiOH of 1M led to significant increase in corrosion rate. The surface of the specimens was tested by SEM.

Keywords: Zirconium, H_3BO_3 , KOH, NaOH and SEM

1. Introduction

In Pressurized Water Reactors (PWRs), boric acid is added to the primary coolant. Boric acid (H_3BO_3) is added as chemical shim to control the core reactivity according to the nuclear reaction $^{10}B(n, \alpha)$. The alkali, lithium hydroxide (LiOH), is added to the primary coolant for PH control in order to control the corrosion of primary system materials and cladding, and minimize corrosion product transport within the primary system and thereby decreases the activation of out of core components [1-2]. There was a continuous demand to improve uranium utilization and reduce of nuclear fuel cycle cost. This will require extending fuel burnup by means of longer cycle operation, longer total in-reactor residence time, and higher heat rating [2]. For longer fuel cycle operations with higher target discharge burnups, the startup concentrations of boric acid, and thus lithium hydroxide, need to be increased [2]. However, the desire to increase fuel residence time and burnup will result in increased rates of corrosion of fuel cladding alloys (usually zirconium alloys, due to its corrosion resistance and low absorption cross section for neutron) in reactors [3]. In order to explain the accelerated corrosion of cladding in reactor, several hypotheses were suggested such as corrosion hydrogenprecipitation [4], radiation effects in the oxide films [5], metallurgical variables (tin and intermetallic particles) [2, 6, 7], ZrO_2 film thermal conductivity (oxide thicknesses effect) and thermal feedback [2, 8], and primary coolant chemistry (lithium, boron, and oxygen content) [6, 8, 9]. The argument for the possibility of an increase in rate of corrosion due to lithium in-reactor is based on many hypotheses [3, 6, and 10]. Chemical concentration process which extracts water from the solution in the pores to form additional ZrO_2 also act as a concentration mechanism [11].

Many investigations have been documented; evidence from these studies for a lithium-related acceleration of zirconium alloys is somewhat conflicting. The lack of clear evidence of

cladding corrosion enhancement due to lithium, unlike the cases involving hydrogen precipitation, radiation effects in the oxide film, metallurgical variables, ZrO₂ film thermal conductivity has limited the ability to quantify the effect of lithium and boron in PWRs.

The objective of this work is to study the electrochemical of fuel cladding alloy, namely Zircaloy-2, in presence of Na, K, and B ions. To simplify the relationship between the corrosion processes and water chemistry (Li and B), the electrochemical corrosion tests were conducted at room temperature to eliminate the effect of high temperature and pressure.

2. Experimental

2.1 Sample and Solution Preparation

The cladding material used in this study is Zircaloy-2 (Zr-2) was supplied by Nuclear Metallurgical Department. The nominal composition is (Zr, 1.5% Sn, 0.14%Fe, 0.1% Cr, and 0.05% Ni). Zircaloy-2 was received as tube cold rolled and cut into testing specimens. The specimens surfaces were polished with 6 then 1 micron diamond paste, subsequently, cleaned in acetone/ethyl alcohol and then pickled in a solution of HF : HNO₃ : pure H₂O, and finally washed with deionized water and dried. The peripheral region of the specimen for electrochemical testing was covered with insulating resin; leaving an area of 0.5 cm². The preparation process for each specimen was directly conducted before each electrochemical test. Boric acid (H₃BO₃), sodium hydroxide (NaOH), and potassium hydroxide (KOH) were weighed using a balance Mettler Toledo, AG245. Pure deionized water was used for solution preparation and refresh solution was immediately prepared before each test.

2.2. Electrochemical measurements

Anodic oxidation can be used to produce oxide films on zirconium alloys. Compare with autoclave test, it is possible to produce oxide films in short times [12]. The experiments device and the electrochemical parameters are described elsewhere [15-17]. The surface of the formed oxide on specimen was examined by SEM, JEOL JSM 5400.

3. Results and Discussion

3.1. Determination of Corrosion Rate of Zircaloy-2

Using Faraday's Law, we can convert the results of electrochemical measurements (I_{corr} , $\mu\text{A}/\text{cm}^2$) to rates of uniform corrosion (CR, mm/yr) [13].

$$\text{Corrosion Rate (CR)} = \frac{K \cdot I_{\text{corr}} \cdot EW}{\rho}$$

Corrosion Rate (CR), mmpy

K (constant) = 3.27×10^{-3} , mm.g/($\mu\text{A} \cdot \text{cm} \cdot \text{yr}$)

Corrosion Current Density (I_{corr}), $\mu\text{A}/\text{cm}^2$

Equivalent Weight of alloy (EW), gm/equivalent

Density of Zircaloy-2 at room temperature (ρ) = 6.55 g/cc [14].

For alloys, the equivalent weight is more complex. The alloy equivalent weight, EW, is the reciprocal of the total number of equivalents of all alloying elements [19].

$$EW_{\text{alloy}} = \frac{1}{N_{\text{eq}}}$$

$$N_{\text{eq}} = \sum \frac{f_i}{W_i}$$

Where:

f_i is the mass fraction of the i element in the alloy, n_i is the valence of the i element of the alloy, W_i is the atomic weight of the i element in the alloy

Normally alloying elements at concentrations below 1% by mass were not included in the calculation, for example, they were considered part of the basis metal [13].

$$Corrosion\ Rate\ (mmpy) = \frac{EW_{Zr2} = 23.018 \times 0.00327 \times I_{corr} (\mu A/cm^2)}{\rho}$$

3.2. Effect of NaOH and KOH on Electrochemical Corrosion Rate

During the corrosion of zirconium alloys in aqueous environments, an oxide film isolates the alloy from the environment according to the following equation, $Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$.

Effect of LiOH and mixture of LiOH/H₃BO₃ on the electrochemical corrosion of Zirconium, Zr-2, and Zr-4 were studied and well documented in previous investigations [15-17]. These investigations have led to important conclusions; at low and moderate concentrations of lithium hydroxide, there is a slight in the corrosion rate. At high concentrations up to 1M LiOH, acceleration of corrosion rate was observed.

In the lithiated solution, boron added as boric acid has ameliorating effect on the corrosion rate. This ameliorating effect is due to the neutralization (reduction of pH, buffer system) and the interfering of the boric acid with the lithium hydroxide to prevent the formation of porosity.

As presented in Table 1, the corrosion of Zircaloy-2 in aqueous lithiated solutions is sensitive to the concentration of alkali. The Based on SEM analyses, oxide film formed in concentrated lithium hydroxide solution (1M LiOH) was very porous, non-protective, (Fig. 1), the corrosion of Zircaloy was considered to proceed by the diffusion of oxygen ions across the oxide layer [18]. Accelerated corrosion of Zircaloy by porosity generation was suggested by others [11, 19].

Table 1: Effect of LiOH, NaOH, KOH, and H₃BO₃ on the electrochemical corrosion rate

Medium	pH (RT)	I _{corr} (μA/cm ²)	Corrosion Rate (mmpy)
Pure deionized water	6.8	0.1144	1.315×10^{-3}
50 ppm B	5.8	0.2675	3.074×10^{-3}
100 ppm B	5.6	0.2815	3.235×10^{-3}
1000 ppm B	5.1	0.6574	7.554×10^{-3}
2000 ppm B	4.9	0.6608	7.594×10^{-3}
4000 ppm B	4.74	0.6721	7.723×10^{-3}
31000 ppm B	4.7	0.6783	7.795×10^{-3}
10810 ppm B	4.6	0.6896	7.925×10^{-3}
3500 ppm Li[16]	13.5	6.304	72.442×10^{-3}
7000 ppm Li (1M LiOH) [16]	14	55.16	633.867×10^{-3}
11500 ppm Na	13.7	1.759	20.213×10^{-3}
23000 ppm Na (1M NaOH)	13.89	3.205	36.830×10^{-3}
19500 ppm K	13.7	1.256	14.433×10^{-3}
39000 ppm K (1M KOH)	14.0	2.132	24.500×10^{-3}

Fig. 1: SEM micrograph of Zr-2 corroded in 7000 ppm Li as LiOH.H₂O

For the corrosion tests performed in 1M NaOH and 1M KOH as compared to LiOH, there was no accelerated corrosion observed with the addition of NaOH or KOH. Therefore, there is a large dependence upon the cation present in the solution. This observation asserts that the accelerated effect of the lithium hydroxide on the corrosion rate is not only due to a pH impact since the tests performed with KOH and NaOH at equivalent pH lead to no accelerated corrosion. The same observation was documented by many investigators [10, 20, 21]. Furthermore, no other salt of lithium apparently has any effect on zirconium alloy corrosion. Moreover, no effects are observed in fused LiOH [22]. Thus, the phenomenon is neither an effect of PH, [OH⁻], nor of Li⁺ but is a property of LiOH. An approach to explain that, due to the smaller size of the lithium ion versus the sodium and potassium ions [23]. SEM appears no porosity formed in the oxide film in the case of NaOH and KOH (Fig. 2, 3).

Fig. 2: SEM micrograph of Zr-2 corroded in 23000 ppm Na as NaOH

Fig. 3: SEM micrograph of Zr-2 corroded in 39000 ppm K as KOH

3.3. Effect of H₃BO₃ Electrochemical Corrosion Rate

Unlike the ameliorating effect of boric acid on the aqueous solution containing of LiOH, boric acid increases the corrosion rate when it present alone in the solution. As presented in Table 1, with the increase of the concentration of boric acid, a slight increase of the corrosion rate is observed. Moreover, high concentrated solution of boric acid (~11000 ppm B, 1M H₃BO₃) appears capable, at most, only of producing a modest increase in the corrosion rate. The slight effect of boron is because the boric acid is a weak acid and doesn't lead to a reduction in the pH value. In high concentrated solution of boric acid (1M H₃BO₃), no change of the oxide film integrity was observed (Fig. 4-5).

Fig. 4: SEM micrograph of Zr-2 corroded in pure H₂O

Fig. 5: SEM micrograph of Zr-2 corroded in 10800 ppm B as H₃BO₃

3.4. Cyclic Potentiodynamic Polarization (CPP) Curves

The CCP technique provides a reasonable, rapid method for estimating general corrosion rates, passivation behavior for specific sample/solution combinations, and for assessment localized corrosion for passivation types of alloys. In fact, all the polarization curves for Zr-2 in all tests show a negative hysteresis loops indicating no susceptibility to localized corrosion. In Fig. 6. The corrosion test of the alloy in double distilled water, the curve shows the largest potential region over which the specimen remains passive than the other solutions. The more extended the passive region, the better the resistance to the localized corrosion and the better the passivation characteristics [24]. The loop is on the left (negative hysteresis) i.e. the current density during the reverse scan is lower than that for the forward scan at any given potential indicates high resistance of zirconium to passivity breakdown and no susceptibility to localized corrosion [25]. An increase in current at potential above 1.3 V or higher this is associated with the oxidation of water to form oxide rather than with breakdown of the oxide [26]. The same figure was obtained in the case of 1M H₃BO₃ (Fig. 7).

Figure 6: Cyclic Potentiodynamic Polarization Curve for Zr-2 Corroding in Deionized Pure Water at Room Temperature

Figure 7: Cyclic Potentiodynamic Polarization Curve for Zr-2 Corroding in ~ 11000 ppm B as H_3BO_3 at Room Temperature

Figures 8 and 9 show a cyclic polarization graphs of Zr-2 corroded in 1M NaOH and 1M KOH solutions at room temperature. The breakdown potential of passivity (E_{bd}) was observed and the passive region decreases with an increase of sodium and potassium concentration. The loops in these curves are characterized by negative hysteresis indicates the passive film formed on the surface of the specimen after breakdown characterized by self-healing [27,25]. The resistance to corrosion of an alloy increases with an increase in the passive region (ΔE_p) [28]

Figure 8: Cyclic Potentiodynamic Polarization Curve for Zircaloy-2 Corroding in 23000 ppm Na as NaOH at Room Temperature

Figure 9: Cyclic Potentiodynamic Polarization Curve for Zircaloy-2 Corroding in 39000 ppm K as KOH at Room Temperature

Conclusions

1. Boric acid in concentrations ranging from 10 to 1100ppm has a small effect on corrosion rate of Zr2.
2. The effect of boric acid at high concentrations on corrosion of Zr2 is due to reduction in PH.
3. In test solutions containing NaOH and KOH in concentrations ranging from 0.5M to 1M have slight effect on corrosion rate of Zr2.

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