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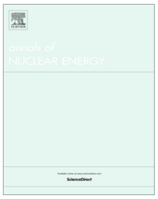

Electrochemical corrosion of Zircaloy-2 under PWR water chemistry but at room temperature

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ABSTRACT

Electrochemical corrosion of Zircaloy-2 was tested at room temperature in lithium hydroxide (LiOH) concentrations that ranged from 2.2 to 7000 ppm and boric acid (H_3BO_3) concentrations that ranged from 50 to 4000 ppm. Following the corrosion experiments, the oxide films of specimens were examined by SEM to examine the oxide existence. LiOH concentrations as high as 1 M (7000-ppm lithium) can lead to significantly increased electrochemical corrosion rate. It is suggested that the accelerated corrosion in concentrated solution is caused by the synergetic effect of LiOH, pH and porosity generation. In solutions containing 100 ppm of lithium, the presence of boron had an ameliorating effect on the corrosion rates of Zircaloy-2. Similar to acceleration of corrosion by lithium, the inhibition by boron is due to a combined effect of pH neutralizing and its participation in the corrosion process.

1. Introduction

The pressurized water reactor (PWR) coolant chemistry, typically 2.2 ppm lithium as LiOH (buffer reagent) and 1200 ppm boron as H_3BO_3 (chemical shim reagent) at the start of a cycle in the case of light water reactors (Pêcheur et al., 1996). However, an incentive exists to extend the average fuel rod discharge burnups with longer fuel cycle operations. For longer fuel cycle operations with higher target discharge burnups, the startup concentrations of boric acid, and thus lithium hydroxide, need to be increased (3.5 ppm Li and 1400 ppm B) (Pêcheur et al., 1996; Cheng et al., 1996). However, local boiling regimes at the fuel rod surface can lead to a local enrichment of lithium (and boron) on the surface of the cladding (Billot et al., 1994). Moreover, high concentrations of lithium can be present in thick porous oxide films or within crud layers deposited on fuel cladding (Pêcheur et al., 1996).

Zirconium alloys are used as fuel cladding and pressure tube material in the primary circuits of nuclear reactors (Ramasubramanian et al., 1989). The corrosion of Zirconium alloys in water reactors is dependent on the water chemistry [LiOH and H_3BO_3] of the primary coolant, hydride effect, metallurgical variable, thermal feedback, and radiation effects in the oxide film (Pêcheur et al., 1996; Cheng et al., 1996). As a result, in PWRs operating with an elevated lithium regime (3.5 ppm Li), there is some concern that, for longer fuel cycle operations with higher target discharge burnups, accelerated corrosion rate is observed and may require removal of fuel before the end of its reactivity capability if maximum oxide thicknesses exceed some selected value (Cheng et al., 1996; Van Swam and Shann, 1991; Baur et al., 1994). Therefore, the effect of higher startup lithium concentration, 3.5 ppm, has been of interest to fuel users and the impact of lithium hydroxide/boric acid additions on the corrosion rate of zirconium alloys has been studied for lithium levels in the coolant between 2.2 and 7000 ppm for many years (Cheng et al., 1996; Billot et al., 1994, 2002; Billot and Giordano, 1991; Shann et al., 1991; Polley and Evans, 1993; Swam and Polley, 1993; Karlsen and Vitanza, 1994; Sabol et al., 1994; Willse et al., 1994; Cox et al., 1996; Garzarolli et al., 2000; Kido et al., 2000). 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 metallurgical and hydride effects, has limited the ability to quantify the effect of lithium in PWRs.

We report here such investigations on the electrochemical corrosion of Zircaloy-2 using potentiostat in lithiated and borated water at room temperature to eliminate the effect of high temperature and pressure.

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2. Experimental

2.1. Sample preparation

Zircaloy-2 was supplied by Nuclear Manufacture and Materials division, EAEA, Egypt. The nominal composition is (Zr, 1.5% Sn, 0.14% Fe, 0.1% Cr, and 0.05% Ni). Zircaloy-2 was received as tube; the tube was lengthwise cut, cold rolled and then cut into test specimens. The specimen surface was polished with 6 µ diamond paste, next cleaned in acetone/ethyl alcohol and then pickled in a solution of HF: HNO_3: pure H_2O, 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 cm^2. The preparation for each specimen was directly conducted before each electrochemical test. Lithium hydroxide and boric acid (H_3BO_3) 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. pH was measured directly after preparation of the solution only.

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 (Oskarson, 2000). The equipment consisted of a potentiostat (EG&G Princeton Applied Research, Model 352/252 Corrosion Analysis Software, version 2.23), computer, and an electrolytic cell. A two graphite electrodes and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively (see Fig. 1). The potentiostat was operated with cyclic potentiodynamic polarization (CPP) scan; initial delay (ID) 600 s, initial potential equal −0.1 versus open circuit potential (OC), vertex at 0.2 versus reference electrode potential, final potential at 0.1 versus reference electrode potential, and the scan rate of potential was 0.5 mV/s. Typically about 700 ml of water or solution was added to the cell before each test. All electrochemical measurements were measured at room temperature and open to atmosphere. The surface of the formed oxide on specimen was examined by SEM, Using SEM Model Quanta 250 FEG (Field Emission Gun).

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}, µA/cm^2) to rates of uniform corrosion (CR, mm/yr) ASTM G102, 1994.

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

Corrosion Rate (CR), mmpy. K (constant) = 3.27×10^{-3}, mm g/(µA cm yr). Corrosion Current Density (I_{corr}), µA/cm^2. Equivalent Weight of alloy (EW), gm/equivalent. Density of Zircaloy-2 at room temperature (ρ) = 6.55 g/cc IAEA Publications, 2008.

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 (ASTM G102, 1994).

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

$$N_{eq} = \sum \frac{fini}{Wi}$$

where fi = the mass fraction of the i element in the alloy, ni = the valence of the i element of the alloy, Wi = 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 (ASTM G102, 1994).

$$EW_{zr-2} = 23.018$$

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

3.2. Effect of LiOH on electrochemical corrosion rate

The corrosion rate data for Zr-2 with increase in LiOH concentration, corresponding to 2.2–70 ppm lithium, show erratic results (Table 1). These erratic results were reported also by many investigators when tests were conducted in autoclave (Billot et al., 1994; Mnolescu et al., 1982; Cox and Wong, 1991; Ramasubramanian and Balakrishnan, 1994) and in our previous work (Abdel–Hakim Kandil et al., 2014). This dichotomy is significant, however, is not understood. In fact, the effect of lithium hydroxide on the corrosion rate seems to depend not only on the concentration of LiOH.

An attempt is made to determine the influence of increasing the lithium content in the primary coolant of PWRs (with lithium content, 2.2 and 3.5 ppm) on fuel cladding corrosion. The measurements led to a calculated increase in the corrosion data of around 30% due to Li increasing in coolant (Billot et al., 1994). In the present study, a simple procedure, a decrease in corrosion rate at 2.2 ppm Li than those in pure water was found as our previous work (Abdel–Hakim Kandil et al., 2014). The steep decrease in the electrochemical corrosion rate at 2.2 than those in H_2O in case of zirconium specimen was also reported (unpublished results in master thesis study, it was found 0.796×10^{-3} and 1.400×10^{-6} mmpy for H_2O and 2.2 ppm Li, respectively). From the corrosion point of view, there are some consequences of the use elevated 3.5 ppm Li concentration.

As presented in Table 1, the corrosion of Zircaloy-2 in aqueous lithiated solutions is sensitive to the concentration of alkali. The corrosion rate is increased by 100 ppm Li ion in the water with respect to pure water (it is about 6.4 times). This effect of the lithium hydroxide on the rate is due to a pH effect. With increase of alkali lithium hydroxide, the hydroxyl ions could retard the normal recrystallization and growth of oxide crystallites and thus maintain an increasing of the corrosion rate (Ramasubramanian et al., 1989). Scanning electron microscope (SEM) examinations revealed that the oxide had some pores in definite sites (Fig. 2),

Table 1
Effect of LiOH and H_3BO_3 on the electrochemical corrosion rate.

Medium	PH (at room temp.)	I_{corr} (µA/cm^2)	Corrosion rate (mmpy)
Pure deionized water	6.8	0.1473	1.693×10^{-3}
2.2 ppm Li	10.44	0.1111	1.277×10^{-3}
3.5 ppm Li	10.69	0.1586	1.823×10^{-3}
5 ppm Li	10.85	0.4974	5.716×10^{-3}
10 ppm Li	11.0	0.04401	0.506×10^{-3}
30 ppm Li	11.53	0.09370	1.077×10^{-3}
50 ppm Li	11.85	0.5581	6.413×10^{-3}
70 ppm Li	12.0	0.2027	2.329×10^{-3}
100 ppm Li	12.2	0.9377	$\mathbf{10.776 \times 10^{-3}}$
350 ppm Li	12.59	4.235	48.667×10^{-3}
7000 ppm Li	14.0	55.16	633.867×10^{-3}
100 ppm Li + 50 ppm B	11.71	0.7680	$\mathbf{8.825 \times 10^{-3}}$
100 ppm Li + 100 ppm B	11.53	0.3157	$\mathbf{3.628 \times 10^{-3}}$
100 ppm Li + 1000 ppm B	8.22	0.2188	$\mathbf{2.514 \times 10^{-3}}$
100 ppm Li + 4000 ppm B	7.54	0.1349	$\mathbf{1.550 \times 10^{-3}}$