Investigation of High-temperature Oxidation Kinetics and Residual Ductility of Oxidized Samples of Sponge-based E110 Alloy Cladding Tubes

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ABSTRACT

Two-sided oxidation experiments were recently conducted at 1000-1200°C in flowing steam with samples of sponge-based Zr-1Nb alloy E110. Although the old electrolytic E110 tubing exhibited a high degree of susceptibility to nodular corrosion and experienced breakaway oxidation rates in relatively short time, the new sponge-based E110 has demonstrated steam oxidation behavior comparable to Zircaloy-4. The sponge-based E110 followed the parabolic law, and the derived oxidation rate constant is in good agreement with the Cathcart-Pawel (CP) correlation at 1100-1200°C. For 1000°C oxidation, the weight-gain of sponge-based E110 is much lower than Zircaloy-4. No breakaway oxidation was observed at 1000°C up to 8000 s. Ring compression tests were conducted to evaluate the residual ductility of oxidized samples at room temperature and at 135°C. All sponge-based E110 specimens were still ductile at 135°C after being oxidized up to 20% equivalent cladding reacted at 1000-1200°C. Metallographic examinations were performed on oxidized E110 specimens to correlate material performance with microstructure.

I. INTRODUCTION

Fuel rod cladding is the first barrier for retention of fission products and the gross structural integrity of the cladding ensures coolable core geometry. To ensure adequate cladding performance during Emergency Core Cooling System re-flooding and during loss-of-coolant-accidents (LOCA), the current U. S. Nuclear Regulatory Commission (NRC) licensing criteria limits the peak cladding temperature and the maximum cladding oxidation during the accident. The purpose of these limits is to prevent cladding embrittlement during a LOCA to mitigate the potential for subsequent catastrophic widespread cladding fracture. The objective of this work is to experimentally verify the kinetics of high-temperature oxidation and residual ductility of sponge-based E110 cladding under conditions relevant to LOCAs, and to provide information for comparison with Zircaloy-4 and Cathcart-Pawel (CP) predictions [1]. The methodology used is consistent with the conditions and methodology of prior work performed for the NRC [2, 3].

II. EXPERIMENTAL

The sponge-based E110 cladding tested in this program was provided by the Stock Company AA Bochvar High-Technology Research Institute of Inorganic Materials (SC VNIINM). The cladding has an outer diameter of 9.50 mm and a wall thickness of 0.582 mm. Oxidation kinetics

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studies of E110 were performed with a resistance-heating furnace, which is acceptable by the NRC for generating post-quench ductility (PQD) specimens for ductility determination. The resistance furnace used in this program is a 122 cm long resistance furnace with a uniform temperature zone > 10 cm in length. Controlled movements of the 25.00 mm long test specimens into and out of the furnace were used to achieve desired heating and cooling rates. Before the oxidation testing, the diameter of each sample was measured with a caliper to an accuracy of ± 0.03 mm. Sample weight measurements were conducted before and after each test using a calibrated balance with an accuracy of ± 0.0001 gram. After oxidation, 8 mm rings were sectioned from the oxidized samples for ring compression testing (RCT) to evaluate the post-quench ductility. The samples were compressed radially using an Instron 6589 at a crosshead speed of 0.033 mm/s. Load-displacement data were recorded by the companion software. Tests were conducted at room temperature and at elevated temperature (135°C).

III. RESULTS

Oxidation Kinetics Study

Cathcart et al. gave related rate equations for the total oxygen consumed in terms of weight gain in grams per square centimeter of surface area. It obeyed parabolic kinetics. The rate equation for weight gain is $W_g^2 = k^2$ t, where k is a temperature-dependent coefficient, W_g is the sample weight gain, and t is the test time. A related parameter often used for steam oxidation study of Zr alloy is ECR. ECR is defined as the percentage of the cladding thickness that would be oxidized if all the oxygen pickup stayed in the oxide layer as ZrO_2.). The conversion between W_g and ECR for two-sided oxidation is ECR = 87.8 W_g/h, where ECR is in %, W_g is in g/cm^2, and h is cladding thickness in cm [2].

Steam oxidation tests were conducted at 1000-1200ºC. Figure 1 shows the temperature histories for six tests with sponge-based E110 at 1000°C (three tests were conducted at ECR=17%) recorded using a type-S monitor thermocouple. The oxidation times were determined using the CP equation described in Ref. 1. This weight gain model was integrated over the actual temperature history, including the ramp, to generate a best-estimate model prediction of the weight gain during tests.

To determine an accurate posttest sample weight, it is important that the sample be free of moisture. In these experiments all test articles were dried in stagnant air for 4 hours or more. The drying time was verified by weight measurements where the sample weight was observed to decrease during the drying process until it reached a minimum and remained at that minimum. The posttest sample weight was measured to the nearest 0.1 mg. The weight gain was determined by subtracting the pretest weight from the posttest weight and normalizing this value to the steam-exposed surface area of the sample.

Comparison of measured and CP-predicted weight gains for oxidized E110 is shown in Figure 2. The measured sample weight gain of the E110 is in excellent agreement with the CP-predicted weight gains at 1200°C, and slightly lower than the CP-predicted weight gains at 1100°C. In particular, the oxidation rate at 1000°C was extremely low, compared to CP-predicted weight gain at 1000°C. Although the breakaway oxidation was observed in standard E110 at 1000°C [4], no breakaway was found for the sponge-based E110 examined in this work.

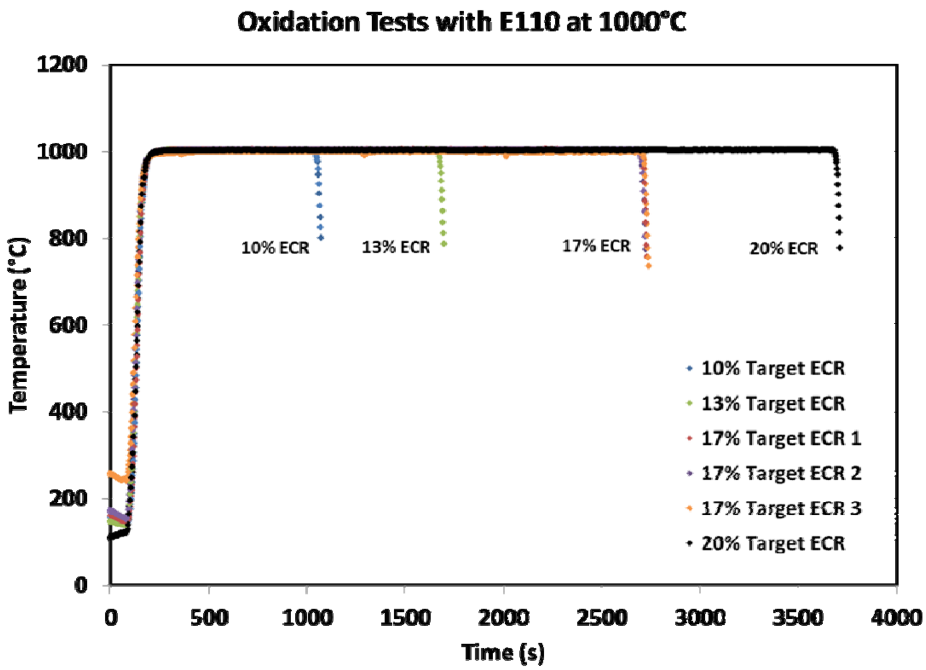


Fig. 1. Summary of the temperature histories for the steam oxidation tests at 1000°C.

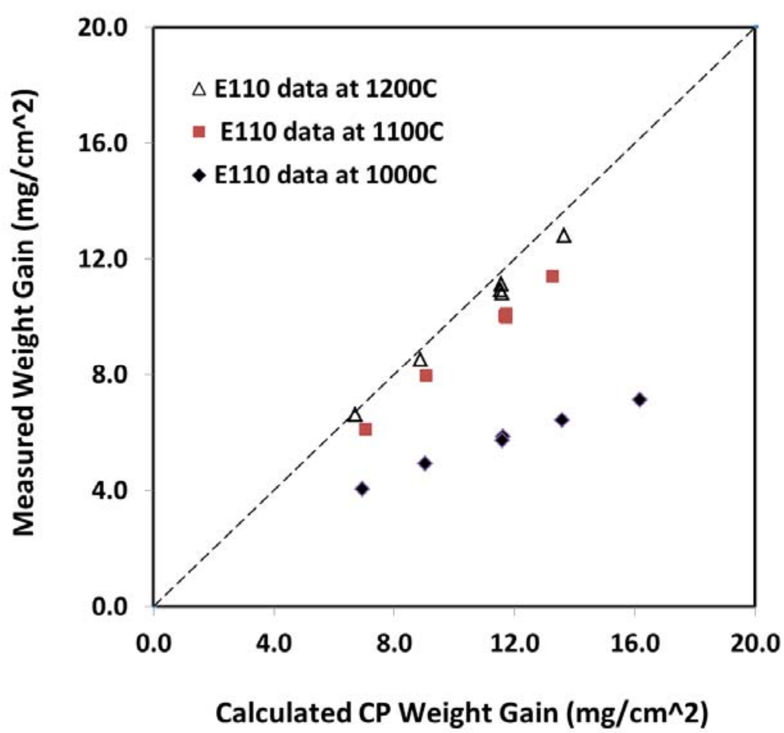


Fig. 2. Comparison of measured and CP-predicted weight gains for sponge-based E110.

Post Quench Ductility Tests

In order to evaluate the ductility of post quenched E110 oxidation samples, RCT was performed. 8-mm rings were cut from the oxidation samples following oxidation and quench. A uniaxial compression of the hydrided samples by the RCT apparatus yielded a load-displacement curve used to evaluate the ductility of the rings. The load-displacement curves were analyzed by the traditional offset-displacement method used in analyzing tensile-test data [5-6]. The offset strain, determined from load-displacement data, was normalized to the as-fabricated outer diameter (9.50 mm) to give a nominal plastic hoop strain. Testing was stopped when considerable load drop was seen, which was taken as an indication of cracking. Table 1 summarizes the results of the post-quench ductility testing for the samples oxidized at 1000-1200ºC.

The RCT results indicate that offset hoop strain (displacement) gradually decreases as the ECR increased. Meanwhile the samples oxidized at 1200°C are more brittle than those oxidized at 1000°C, even though they have the same ECR values. The ductility (offset hoop strain) increased when the RCT was performed at elevated temperature.

Table 1. Post-test ductility results for E110 cladding oxidized at 1000-1200°C, cooled with water quench at 800°C, and ring-compressed at room temperature (RT) and 135°C

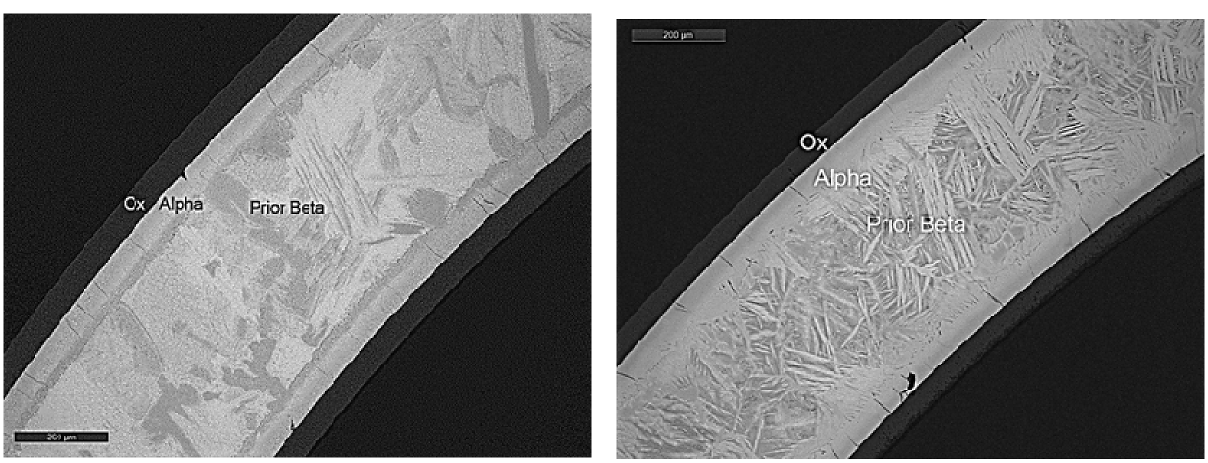
Oxidation Temperature (°C)	Measured WG (mg/cm^2)	CP-WG (mg/cm^2)	Measured ECR (%)	CP-ECR (%)	Offset Hoop Strain (%) RT	Offset Hoop Strain (%) 135°C
1000	4.0	7.0	6.2	10.6	18.2	19.9
1000	4.9	9.0	7.7	14.0	14.4	19.5
1000	5.9	11.6	8.9	17.6	16.5	21.2
1000	5.7	11.6	8.7	17.5	15.9	18.9
1000	6.0	11.4	9.1	17.2	16.4	19.0
1000	6.4	13.6	10.0	21.0	3.1	20.7
1100	6.1	7.1	9.4	10.9	11.1	17.5
1100	8.0	9.1	12.3	14.0	7.7	14.3
1100	10.0	11.7	15.5	18.1	5.4	18.5
1100	10.0	11.7	15.3	17.7	7.5	18.9
1100	10.1	11.7	15.3	17.7	6.9	18.1
1100	11.4	13.3	17.3	20.1	3.4	17.2
1200	6.6	6.7	10.1	10.2	3.7	16.5
1200	8.5	8.9	13.0	13.5	2.5	14.3
1200	10.9	11.5	16.8	17.8	1.1	10.4
1200	10.8	11.6	16.6	17.7	2.0	13.3
1200	11.1	11.6	17.1	17.8	1.6	9.5
1200	12.8	13.6	19.7	21.0	2.1	5.4

Metallographic Examinations

The microstructure of the steam-oxidized E110 specimens was examined using optical microscopy to image the oxide, alpha, and prior-beta layers and their interfaces. Micrographs of Zircaloy-4 and E110 oxidized to 17% CP-ECR at 1100°C (see Fig. 3) reveal that the E110 alpha and prior-beta layers are not as uniform as the one formed in Zircaloy-4. Metallographic examinations on Zr alloys by have been widely investigated for the US Zircaloy-4 [1,2] and Russian Zr-Nb alloy E110 [2, 4 and 7]. Transmission electron microscopy study showed an inhomogeneous distribution of Nb in E110 ally [4 and 7], which was not the case for Zircaloy-4. As indicated by Billon et al [2], Nb causes local regions of beta stabilization even at higher oxygen content. These cause an irregular interface between the alpha and prior beta layers, which was also observed in other Zr-Nb alloys M5 [2, 8] and ZIRLO [2, 4]. Table 2 provides the oxide layer thicknesses measured using the micrographs. The oxide layer thicknesses of E110 sample oxidized at 1000°C are much lower than CP-predicted value, consistent with the weight gain data.

Table 2. Oxide layer thicknesses of E110 samples oxidized for ECR=10, 13, 17 and 20%

Temperature (°C)	Calculated CP-ECR (%)	Measured ECR (%)	Calculated Oxide Thickness (μm)	Measured Oxide Thickness (μm)
1000	10.6	6.2	38.5	16.5
1000	14	7.7	50.0	18.0
1000	17.6	8.9	64.4	22.0
1000	21	10	75.3	22.5
1100	10.9	9.4	36.8	28.0
1100	14	12.3	47.3	37.0
1100	18.1	15.5	61.3	47.5
1100	20.1	17.3	69.3	54.5
1200	10.2	10.1	33.3	26.5
1200	13.5	13	44.0	36.0
1200	17.8	16.8	57.4	48.5
1200	21	19.7	67.8	57.0



(a) (b)

Fig. 3. Micrographs of Zircaloy-4 (a) and E110 (b) oxidized at 1100°C to 17% ECR.

IV. SUMMARY

Two-sided oxidation studies have been conducted on sponge-based E110 cladding exposed to steam at 1000-1200°C for ECR up to 20%. The results from the tests have been analyzed and compared to the CP correlation predictions for weight gain. The parabolic rate constant is in excellent agreement with the CP model predictions at 1200°C, slightly lower at 1100°C, and much lower at 1000°C.

The ductility of post quenched samples was evaluated by RCT. Generally speaking, the ductility, represented by the offset strain offset strain gradually decreases as the oxygen pickup increases. Meanwhile, the samples oxidized at 1200°C are more brittle than those oxidized at 1000°C at the same ECR value. The ductility increased when the RCT was performed at elevated temperature.

Metallographic examinations reveal that the E110 alpha and prior-beta layers are quite different in appearance from those of Zircaloy-4. An irregular interface between the alpha and prior beta layers was observed. The oxide layer thicknesses of the E110 samples are in excellent agreement with CP-prediction at 1200°C, but much lower than CP-predicted value at 1000°C. The microstructural data reveals that the thicker the oxide layer, the more oxygen in E110 cladding. The ductility of oxidized E110 decreases as the oxygen content increases.

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