High-temperature steam oxidation and oxide crack effects of Zr-1Nb-1Sn-0.1Fe fuel cladding

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ABSTRACT

In this study, high-temperature steam oxidation experiments were performed at 1012–1207 °C on Zr-1Nb-1Sn-0.1Fe fuel cladding tubes to study their weight gains and microstructural characteristics. Many specimens were tested at each test temperature, and the results were reproducible and reliable. It is often debated whether the Zr-1Nb-1Sn-0.1Fe alloy follows the weight gain correlation developed by Cathcart and Pawel (C-P correlation) at around 1000 °C. According to our results, the C-P correlation overpredicts the weight gain at around 1000 °C, and this observation agrees well with the data reported by Westinghouse. In addition, the microstructures of the specimens were analyzed using scanning electron microscopy, and it was found that circumferential cracks are formed at the oxide-metal interface only at around 1000 °C. In previous studies, it has been postulated that cracks in the oxide promote the oxidation process, but it appears that the circumferential cracks at the oxide-metal interface decrease the oxidation rate before the breakaway oxidation occurs by disturbing the diffusion of oxygen. The oxidation rate reduction due to the circumferential cracks appears to be the reason for the overprediction of the C-P correlation at around 1000 °C.

1. Introduction

Zirconium alloys have been used as fuel cladding materials in light water reactors (LWR) since the 1960s due to their low neutron absorption cross section, acceptable corrosion resistance, and good mechanical strength. However, it has been suggested that zirconium alloys are disadvantageous in emergencies such as loss of coolant accident (LOCA). During a LOCA, the temperature of the cladding can rise up to 1080 °C [1], and it can rapidly become brittle due to the increased concentration of oxygen in the metal substrate and the increased thickness of the brittle phases such as zirconium dioxide and oxygen stabilized alpha zirconium [2]. In this regard, the Nuclear Regulatory Commission (NRC) issued a regulation, 10 Code of Federal Regulations (CFR) 50.46 [3], which indicates that the peak cladding temperature of 1204 °C and 17% equivalent cladding reacted (ECR) should not be exceeded during a LOCA. In addition, the regulation from the NRC is continuously being revised, and according to a recent draft revision (10 CFR 50.46c) [4], a new regulation for the breakaway oxidation is likely to be adopted soon. Breakaway oxidation is known to cause rapid absorption of hydrogen to the metal substrate, and the cladding rapidly becomes brittle since the absorbed hydrogen increases the concentration of oxygen in the metal substrate [5].

To ensure that a fuel rod remains safe in an accident, it is important to know the precise amount of oxygen absorbed by the zirconium alloys at a specific temperature and time. Considerable work has been carried out to accurately estimate the weight gain of the zirconium alloys under LOCA simulated conditions [6–20], and most of these studies were carried out using Zircaloy-4. However, the weight gain data of the recently developed alloys such as ZIRLO, M5, E110, and HANA-6 are still insufficient, and a slight inconsistency exists. For example, the weight gain results of ZIRLO at around 1000 °C reported by Argonne National Laboratory (ANL) and Westinghouse are inconsistent with each other [6,8].

Furthermore, it is necessary to study how the breakaway oxidation occurs during the accident. So far, many studies have been performed to analyze how the breakaway oxidation occurs [6,15,20–27], and efforts are underway to elucidate the exact mechanism [18,28–39]. Many previous studies suggest that the phase transformation of the oxide during the oxidation causes

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cracks to be formed within the oxide [15,20], and both the oxidation rate and hydrogen absorption rate increase abruptly since the cracks are assumed to deteriorate the oxidation resistance [23]. However, it has not been fully explained how the cracks cause the onset of the breakaway oxidation and what kind of cracks are necessary for the breakaway oxidation to occur. These processes should be studied to fully understand the breakaway oxidation.

This study presents the weight gain results of a Zr-1Nb-1Sn-0.1Fe alloy cladding tube that was oxidized at 1012, 1057, 1112, 1160, and 1207 °C under steam conditions. Before obtaining the weight gain results, the exact temperature of the specimen was meticulously measured. Then the weight gain data were produced at each temperature, and the results appeared to be consistent. The obtained weight gain data were compared with the results reported in other studies; in particular, the consistency with the weight gain correlation developed by Cathcart and Pawel (C-P correlation) [7], which is one of the most widely accepted correlations, was analyzed in detail. In addition, the microstructures of the oxide layers were analyzed using optical microscopy (OM) and scanning electron microscopy (SEM).

2. Materials and methods

2.1. Specimen preparation

A Zr-1Nb-1Sn-0.1Fe cladding tube was used in this study; the chemical composition of the alloy is shown in Table 1. The specimens were cut using a diamond wafer cutter (ISOMET 5000, BUEHLER). The length of each specimen was 40 mm, the outer diameter was 9.5 mm, and the thickness was 0.57 mm. After cutting, the edges of the specimen were carefully ground using silicon carbide paper (320 grit), and then, the specimen was cleaned ultrasonically using a chemical detergent (Alconox) and organic solvents (ethanol and acetone).

2.2. High-temperature steam oxidation system

Fig. 1 shows the schematic of the high-temperature steam oxidation equipment used in this study. The specimen was placed between the two alumina holders to prevent the eutectic reaction between the specimen holder and the specimen. Steam generated from the bottom of the equipment moved through the inner and outer surfaces of the specimen so that both sides of the specimen were oxidized. The steam flow rate per cross-sectional area of the quartz tube was about 3.5 mg/cm^2/s. After the steam flow was stabilized, the specimen was heated using a radiant heating furnace with an axial uniform heating zone of 180 mm. The radiant heating furnace used in this study had six heating bulbs arranged in a circumferential manner to ensure uniform temperature distribution.

Before performing the actual experiments, the thermal benchmark tests were conducted. The primary purpose of the thermal benchmark test is to define the exact temperature of the specimen. The temperature of the specimen was measured by placing a sheathed R-type thermocouple in contact with the specimen; the thermocouple was fixed in place using a molybdenum wire. Fig. 2 illustrates the temperature controls during three equivalent thermal benchmark tests, which were conducted to check the
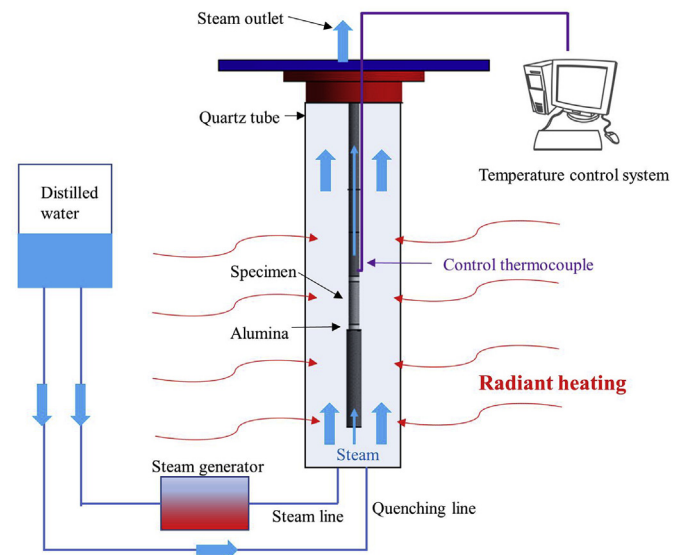

Fig. 1. Schematic of the high-temperature steam oxidation equipment used in this study.

reproducibility of our thermal benchmark method. During this test, the temperature of a specimen at a specific location was measured three times, and the temperature of each run was defined by averaging the value in the last 100 s before the cooling. The maximum difference between the three cases was 1.4 °C, which means that our thermal benchmark method is reproducible. The temperature control method shown in Fig. 2 was designed in accordance with the NRC guidelines [40]. The specimen was rapidly heated from 300 °C to the target temperature at the rate of about 40 °C/s to reproduce the accident conditions. For the isothermal oxidation test, the temperature overshoot was minimized so that the maximum temperature overshoot was about 11.6 °C. After rapid heating, the temperature of the specimen was stabilized to a constant temperature. As shown in Fig. 2 (b), the temperature of the specimen during the isothermal oxidation period was controlled to within ± 1 °C.

After confirming that our thermal benchmark method is reproducible, the temperature was measured at 9 different locations on the specimen, including three circumferential locations (0°, 180°, and 270°) and three axial locations (10 mm, 20 mm, and 30 mm). The 90° circumferential direction was not included because the control thermocouple was located at that angle. All the measured data are displayed in Fig. 3. As mentioned previously, the temperature of each thermal benchmark was defined by averaging the value in the last 100 s before cooling, and the representative temperature of the specimen was defined as the average of the temperatures at the nine different locations. In addition, the maximum temperature difference within the specimen was lower than 20 °C, which is considered as homogeneous temperature distribution [40]. Furthermore, after the thermal benchmark, the heating and cooling times were converted into the effective isothermal oxidation time [7], which was used to calculate the total oxidation time.

In addition to the thermal benchmark, other tests were performed to check the reliability of our system. To ensure that the measured temperature during the thermal benchmark test was accurate, it was calibrated against the melting point of a gold wire (99.99% pure). Furthermore, the reproducibility of our experiments was checked by performing three equivalent oxidation experiments. The weight gain results are shown in Table 2. The maximum weight gain difference between the three equivalent experiments

Table 1
Chemical composition of the zirconium alloy used in this study.

Element	Zr	Nb	Sn	Fe
Composition (wt.%)	Balance	0.96	0.99	0.12