

Adsorbate effects on the Zr-Nb alloy oxidation in air

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1. Introduction

In commercial pressurized water reactors (PWRs), boric acid is used as a soluble neutron poison and LiOH is used to control the PH in the coolant of PWR.

Spent nuclear fuels are stored in both wet and dry storage conditions. Recently, dry storage facilities are more favored because of lower maintenance expenses and easier selection of available sites [1]. In the dry storage facility, the spent fuel can be oxidized in air conditions because the spent fuel temperature is higher than that in wet storage. In addition, the surface of some spent fuels is covered by adsorbates and the effects of these adsorbates have not been clarified yet. In this study, the effects of these adsorbates on the oxidation of Zirlo at the high temperature in air were investigated.

2. Methods and Results

2.1 Specimen

The Zirlo tube was used in the condition, as received from the supplier. Table 1 shows the elemental composition (w/o) of Zirlo. The cladding tube was cut to the height of 20 mm, then grounded, polished and cleaned and used for the specimens.

Table 1. Chemical composition of the specimen

	Zr	Sn	Nb	Fe	Cr	O
Zirlo	base	1.0	1.0	0.1	.	0.12

2.2 Experiments

The effects of adsorbates on Zirlo oxidation in air were determined by measuring the weight gain of the specimens during oxidation. Continuous measurements were used in this study.

Four types of adsorbates were used in the air oxidation experiments. Specimens adsorbed with LiOH, H₃BO₃, and a mixture of H₃BO₃ and LiOH, and simulated CRUD on the cladding surface were tested.

Adsorption of these adsorbates was conducted by drying, after the insertion of specimens in 1 M solution for a few minutes. The mixture of H₃BO₃ and LiOH was made from a solution containing equal molar amounts of these compounds. Table 2 shows the surface concentration of adsorbates on the specimens.

Table 2. The surface concentration of adsorbates on the specimens

Adsorbate	Oxidation Temperature (°C)	Surface concentration (mg/m ²)
LiOH	700	0.297505
	800	2.742602
H ₃ BO ₃	700	0.136005
	800	0.192482
LiOH+H ₃ BO ₃	700	0.306598
	800	1.624315
CRUD	700	0.237984
	800	0.280541

The apparatus for high temperature oxidation was constructed as shown in Figure 1. An electronic heater moved up and down. The heater was moved up to the position of the specimen after the oxidation temperature was reached. Helium gas was supplied to the microbalance for protection from possible damage. The weight gain was measured and recorded continuously to a PC connected to the microbalance. The accuracy of the measurement was about 10 µg. The target temperature range was from 700 °C and 800 °C, and the oxidation time was about 3 hours.

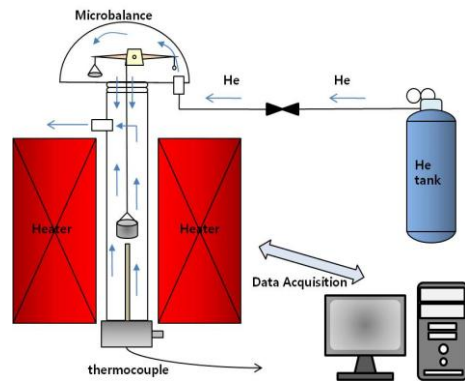


Fig. 1. Apparatus for high temperature oxidation in the air

2.3 Results and Discussion

To see the effects of the chemicals used in the primary system on air oxidation of Zirlo at high temperature, specimens adsorbed by the LiOH, H₃BO₃, mixture, and CRUD were oxidized in air. Experiments were performed at temperatures from 700 °C and 800 °C. Figure 2 shows the oxidation results at 700 °C and Figure 3 shows the results at 800 °C. As indicated by the figure, LiOH retarded the air oxidation of Zirlo at high temperature. In addition, the mixture of H₃BO₃ and LiOH did have a noticeable effect at 800 °C.

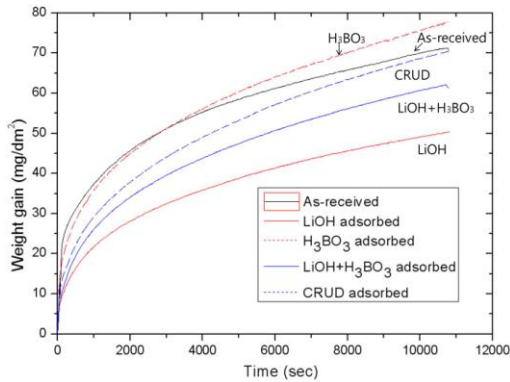


Fig. 2. Kinetics of adsorbates on air oxidation of Zirlo at 700 °C.

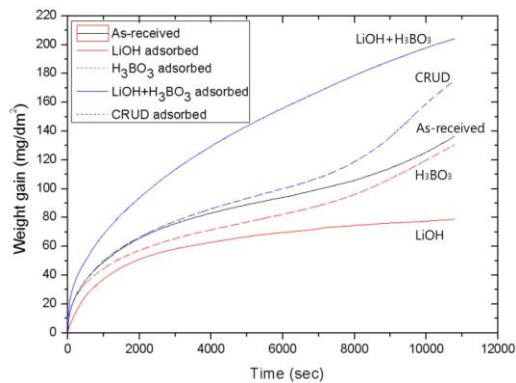


Fig. 3. Kinetics of adsorbates on air oxidation of Zirlo at 800 °C.

In a related study, Park and Cho analyzed the oxide layers formed on Zircaloy adsorbated in air and steam [1]. In the air condition, LiOH enhanced oxidation at the low temperature (<500 °C). However, LiOH decreased the oxidation rate at the high temperature (>700 °C) in the steam condition.

In this study, LiOH retarded the air oxidation of Zirlo at 700 °C and 800 °C. LiOH-adsorbed Zirlo was found to have 42% lower amount of the weight increase than as-received Zirlo at 800 °C. H₃BO₃- or CRUD-adsorbed Zirlo affects negligibly the oxidation in air at 700 °C and 800 °C. However, the transition occurred earlier in the case of both H₃BO₄- and CRUD-adsorbed Zirlo specimen at 800 °C.

Interestingly, the mixture of H₃BO₃ and LiOH does make a different effect in different temperatures. The mixture (LiOH+H₃BO₃) does make a noticeable effect at 800 °C and the mixture-adsorbed Zirlo was found to have 50 % higher amount of the weight increase than as-received Zirlo at 800 °C. The reason for the different oxidation kinetics has not been clarified and still under the analysis.

Figure 4 shows the oxide thickness of Zirlo specimens at 800 °C for 3 hours in air. The oxide layer formed under LiOH looks thinner than that of the normal cladding. Mixture (LiOH+H₃BO₃) adsorbates enhanced the oxidation clearly.

Figure 5 shows the surface of the specimens tested at 800 °C. The surface of LiOH-adsorbed Zirlo consists of

clusters of small particles. The oxide surface of the Zirlo tube, without adsorption, shows a normal surface with micro cracks originated from thermal shock.

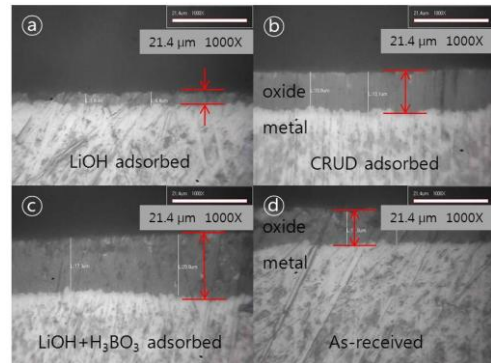


Fig. 4. The oxide thickness of Zirlo specimens at 800 °C for 3 hours in air; (a) LiOH adsorption, (b) CRUD adsorption, (c) adsorption of the mixture of H₃BO₃ and LiOH, (d) without adsorption.

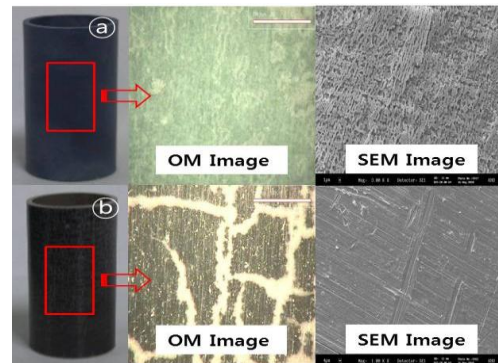


Fig. 5. The oxide surface of Zirlo specimens at 800 °C for 3 hours in air; (a) LiOH adsorption, (b) without adsorption.

3. Conclusions

In order to see the effects of adsorbates on Zirlo oxidation in dry storage conditions, Zirlo tube specimens with adsorbates on the surface were oxidized in air. The effects were quite different, according to the type of adsorbate.

H₃BO₃- or CRUD-adsorbed Zirlo specimen affects negligibly the oxidation in air at 700 °C and 800 °C. However, transition occurred earlier in the case of both H₃BO₄- and CRUD-adsorbed Zirlo specimen at 800 °C. Mixture (LiOH+H₃BO₃) does make a noticeable effect at 800 °C. LiOH retarded the air oxidation of Zirlo at 700 °C and 800 °C. It is thought that LiOH plays an important role in the growth of good quality monoclinic oxides.

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