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Air Oxidation of Zirconium-alloys

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1. Introduction

In the nuclear plant safety analysis, various probable accidental situations may result in fuel rod exposure to the air. In this accidental situation, the first exposed material is the cladding. A recent example is Fukushima accident. The spent fuel rod was exposed to air by the lost water of spent fuel pool at the Station No.4. Then the cladding was oxidized in air and serious problems followed. Nowadays Zirlo is used for a cladding material in Korean nuclear power plants rather than Zr-4. It is of concern that the oxidation resistance of Zirlo may be different from that of Zry-4. We measured the oxidation kinetics of both Zirlo and Zry-4, and compared their kinetics.

2. **Experimental**

2.1 Specimen preparation

The specimens used in this study are Zry-4 and Zirlo tubes used in commercial nuclear power plants. Table 1 shows the chemical composition of the specimen. Cladding tubes were cut to the height of 10mm~11mm and had 2 drilled holes at the top. They were polished, pickled, and cleaned.

Table Ⅰ. Chemical composition of specimen

	Zr (wt%)	Nb (wt%)	Sn (wt%)	Fe (wt%)	Cr (wt%)
Zry-4	bal.	-	1.35	0.2	0.1
Zirlo	bal.	1.0	1.0	0.1	-

2.2 Apparatus and Experimental Method

The apparatus used in this study is shown in Fig. 2. It consists of a furnace containing an alumina furnace tube. The specimen is connected to a platinum wire through holes in it, and is hung to a microbalance mounted above the furnace tube. An electronic heater was able to move up and down. The heater was moved up to the position of the specimen after oxidation temperature was reached. Argon was supplied to the microbalance for the protection of possible damage. The weight gain was measured and recorded continuously to a PC connected to the microbalance. The accuracy of the measurement was about 10ug. The target temperature range was from 800-1100℃.

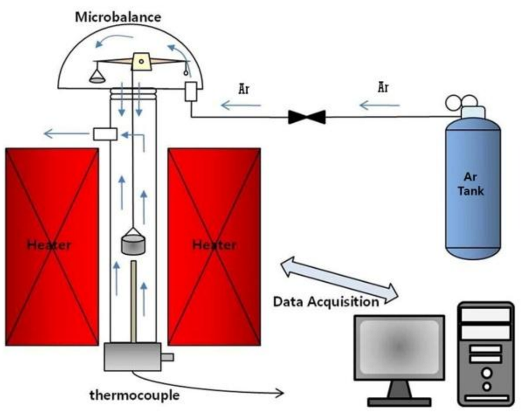


Figure 1. Apparatus for high temperature oxidation in the air

3. **Results**

Weight change by the oxidation in air for each specimen was measured by the microbalance at 800-1000℃. And from the measurements, the weight gain per unit area for each specimen was calculated (Fig.2). Sudden changes of weight gain were observed by the spall of oxide film. The specimens oxidized at 800 and 900 ℃ showed any spall during oxidation. However, spalling of oxide films were observed in both Zirlo and Zry-4 above 1000℃. Interestingly, Zirlo was oxidized faster than Zry-4 at temperatures 800-1100℃ in the air. OM pictures of the specimens is shown in Fig.3. Oxide film of the Zirlo cladding is also thicker than that of Zr-4.

We can divide the weight gain curve in two regions-parabolic and linear. At temperatures below 900℃, the transition from parabolic to linear rate was noticeable. However, only linear growth law was shown in the measurements at temperatures higher than 1000℃. The transition point of each specimen was set and kintic constants were calculated by the following oxidation kinetics. Above 1000℃, we assumed there is no transition point.

$$\mathbf{W = k \cdot t^{a}} \qquad (1)$$

W is the weight gain (mg/dm^2), k is the constant, t is time (sec). The constants in pre- and post-transition regions at each temperature were obtained from the measured data points (Fig.2), and they are shown in Table 2. At 800℃, the weight gain follows a parabolic rate law. As temperature increases, the oxidation kinetics follows a linear rate law.

Table Ⅱ. Constant calculated from the each specimen

Temp	Element	Pre-transition		Transition	Post-transition
		a	k_p	Time [s]	k_l
800℃	Zry-4	0.471	1.454	1000	0.034
	Zirlo	0.533	1.491		0.070
900℃	Zry-4	0.664	0.986	100	0.058
	Zirlo	0.696	0.962		0.150
Temp	Element	a		k	
1000℃	Zry-4	0.960		0.340	
	Zirlo	0.759		1.390	
1100℃	Zry-4	0.754		2.262	
	Zirlo	0.855		2.337	

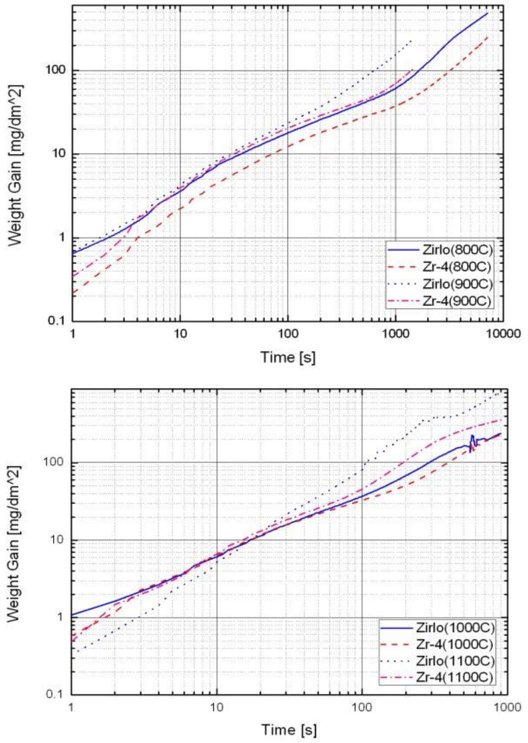
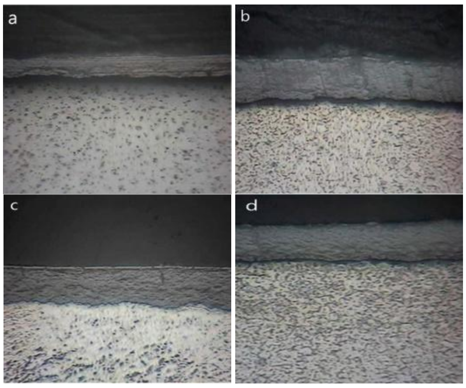


Figure 2. Result of air oxidation at 800℃, 900℃, 1000℃, 1100℃



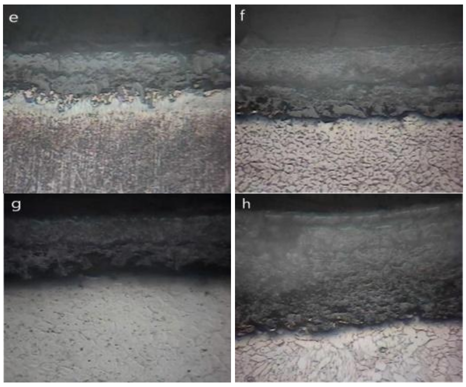


Figure 3. OM image of the each specimen (a) Zr-4 at 800℃, (b) Zirlo at 800℃, (c) Zr-4 at 900℃, (d) Zirlo at 900℃, (e) Zr-4 at 1000℃, (f) Zirlo at 1000℃, (g) Zr-4 at 1100℃, (h) Zirlo at 1100℃

4. Discussion and Conclusions

The kinetics of oxidation of Zr-alloys in air was somewhat different from that in steam. In steam oxidation, both Zirlo and Zry-4 follows a parabolic rate law above 800℃. However, oxidation rates of both alloys in air are higher than the rates in steam. The main reason for the enhancement of oxidation under the air may be from the formation of nitrides in the metal layer. Generally oxidation rates of Zirlo at high temperatures (above 800℃) are similar or slightly less than those of Zry-4 under the steam. However, Zirlo oxidized faster than Zry-4 in air at these high temperatures. The micro-structure of the oxide layer formed on Zirlo cladding shows more fine microcracks near the metal interface (Fig.3). These microcracks seem fast paths and help for oxygen or oxygen vacancies to move through the oxide layer, resulting in thicker oxide layer. The oxide formed on Zirlo seems to be more fragile or more sensitive to the nitrides than Zry-4, when oxide layer grows into the metal layer. Nowadays Zirlo is more widely used as a cladding material than Zry-4. More examination on the oxidation kinetics of Zirlo is needed for the safety evaluation on the accidents occurs in open air.

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