Kinetics of Zr-alloy cladding oxidation in the mixture of air and steam at high temperatures

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1. Introduction

In Fukushima Daiichi Nuclear Power Plant accident, No.4 plant was exploded by hydrogen explosion. There was a strong speculation about the possibility of the reaction between the overheated fuels and the steam-air mixture in the storage pool. Later, it turned out to be due to the hydrogen leaked from No.3 plant. However, the reaction of the hot fuels with the steam-air mixture became an important issue. There have been a lot of data accumulated about Zr-alloy interaction with steam. However, Zr-alloy interactions with air and steam-air mixtures have not been studied relatively much. In this study, we measured the oxidation kinetics of Zry-4 and Zirlo claddings in air, and steam-air mixtures, and analyzed the kinetics.

2. Experimental

2.1. Specimen Preparation

The specimens used in this study were 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~12mm and had 2 holes at near the top. The hole size was about 2.1mm. They were cleaned and etched before the test.

Table 1. Chemical composition of Zirconium alloys

	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 Experimental Procedures

The apparatus for the high-temperature oxidation of Zr-alloys in air and steam used in this study is shown in figure 1. It consists of a furnace containing an alumina furnace tube. In the case of steam oxidation, Ar gas passed through a bubbler supplying Ar gas with a heavy moisture. The specimen was hung by a platinum wire to the microbalance. The platinum wire was separated from the Zr-alloy specimen by 2mm diameter alumina tube located through the holes in the specimen. This alumina tube prevented a possible eutectic reaction between zirconium and platinum. An electronic heater was able to move up and down. The heater was moved up to the position of the specimen after the oxidation temperature was reached. Argon gas was supplied to the microbalance for the protection of possible damage. The weight gain was measured and recorded continuously to a computer connected to the microbalance. The accuracy of the measurement was about 10ug. The target temperature range was up to 1200℃(Steam-Air mixture).

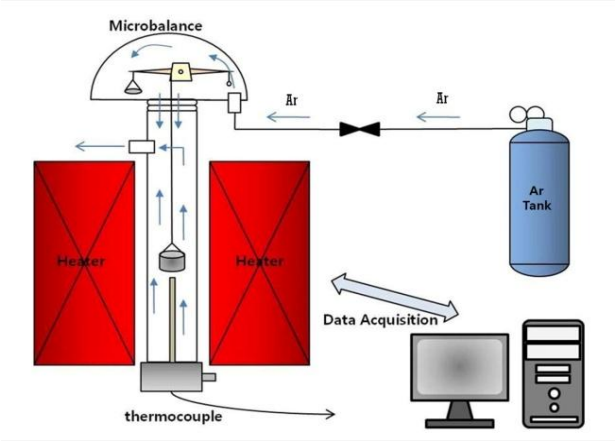


Figure 1. Apparatus for high temperature oxidation.

3. Results

Weight change by the oxidation in air, steam and the mixture of air and steam for each specimen was measured by the microbalance at 1000 -1200℃. The weight gain per area for each specimen is shown in Fig. 2. At temperatures 1000-1200℃, both Zry-4 and Zirlo specimens show parabolic oxidation kinetics in all atmospheres.

Zirlo seems more resistant to oxidation both in air and steam at high temperatures. Sudden changes of weight gain were observed by the spall of oxide film.

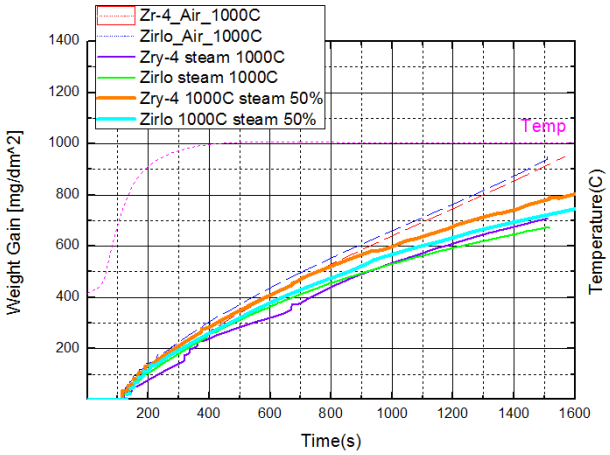
$$\mathbf{W = k \cdot t^{a}} \qquad (1)$$

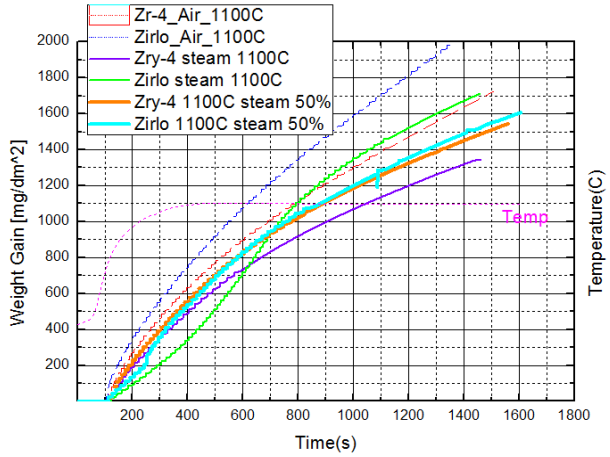
W is the weight gain (mg/dm^2), k is the constant, t is time (sec). The constants in transition regions at each temperature were obtained from the measured data points (Fig.2), and they are shown in Table 2.

With the comparison of the rate exponents in Zry-4 and Zirlo, the rate exponent of Zirlo is higher than Zry-4 except for 1000℃(steam 50%). At high temperature (1000-1200℃), the oxidation kinetics follows a parabolic rate law. Especially at 1200℃, the rate exponent of Zry-4 & Zirlo rapidly increases.

Table 2. Constant calculated from the each specimen in Air

Temp	Element	a	k
1000℃	Zry-4	0.7976	2.57106
	Zirlo	0.73324	4.20423
1100℃	Zry-4	0.62048	18.96601
	Zirlo	0.66911	16.05859
1200℃	Zry-4	0.69613	17.30732
	Zirlo	0.71659	16.88513





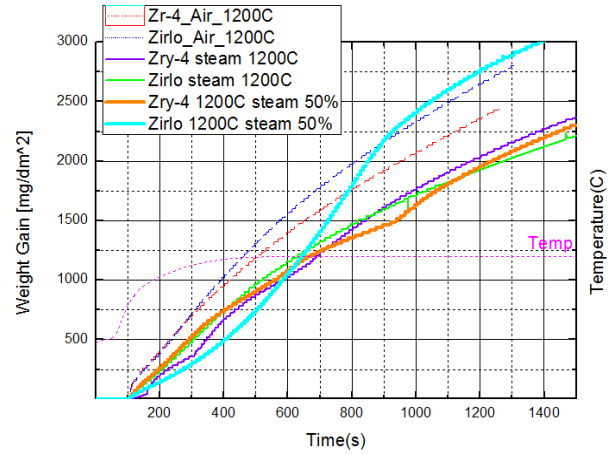


Figure 2. Oxidation behaviors of Zry-4 & Zirlo under steam-air mixture at 1000℃, 1100℃, 1200℃

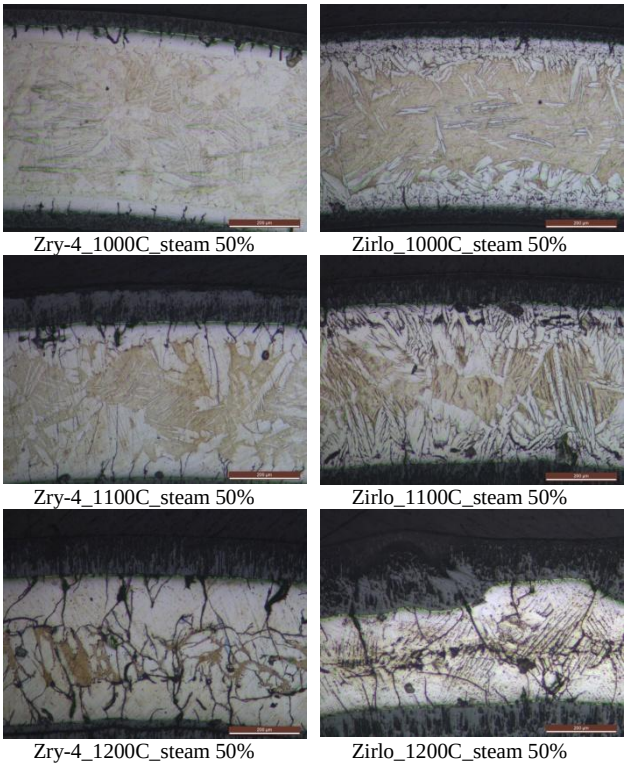


Figure 2. Optical microscopy of a Zry-4 & Zirlo sample oxidation in steam 50% at 1000-1200℃ during 20mins (200 ㎛)

4. Discussion and Conclusions

The characteristics of oxidation for the Zry-4 and Zirlo were measured in the temperature ranges of 1000-1200℃ under air, steam, and the mixture of air and steam. In steam oxidation, The oxidation rates of Zry-4 and Zirlo in air are higher than those in steam at 1000-1200℃. 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 Zry-4 at high temperatures are similar or slightly more than those of Zirlo under the steam. However, Zirlo oxidized faster than Zry-4 in air at these high temperatures. 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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