

The high-temperature oxidation kinetics of Zr-alloy claddings in air and steam

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1. Introduction

Nuclear plant safety is currently a major issue around the world. Nuclear safety problems could result in fuel cladding breaks. Therefore, it is very important to analyze the mechanical properties of fuel cladding. As shown in the Fukushima nuclear reactor accident, the fuels heated by the decay heat were reacted with the steam transformed from the coolant by the reduced pressure inside the reactor. The reaction kinetics of Zr-alloy claddings with steam is very important, and there has been a lot of data regarding the reaction kinetics.

In this study, we observed the oxidation behaviors of Zircaloy-4 and Zirlo under accident conditions. In an extreme case, the fuels could be exposed to mixtures of steam and air, which could start oxidation reactions with ambient gases. To analyze these accidents realistically, we have to know the details of the oxidation kinetics of Zr-alloy claddings with steam and air. Also, the kinetics are related to the oxidation mechanism. We also examined the oxidation of Zr-alloy claddings with oxygen to observe the oxidation mechanism. In this study, we measured the oxidation kinetics of Zry-4 and Zirlo claddings at 700°C–1200°C.

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.

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	-

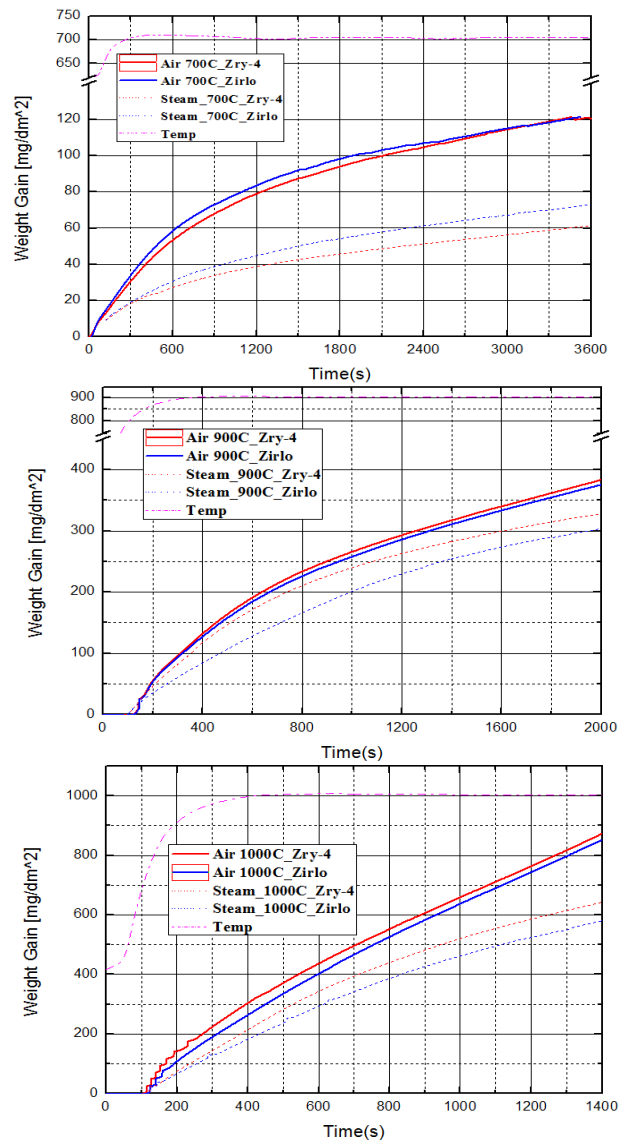
2.2. Experimental Procedures

In the case of steam oxidation, Ar gas is passed through a bubbler, which supplies the Ar gas with saturated moisture. The weight gain was continuously measured and recorded by a computer connected to the micro-balance.

3. Result & Conclusion

The weight change for each specimen due to the oxidation in the air and the steam was measured using a microbalance at 700–1200°C. The weight gain per area for each specimen is shown in Fig. 1. Both the Zry-4 and Zirlo specimens showed parabolic oxidation kinetics at temperatures between 700 and 800°C. However, initially a linear oxidation kinetic behavior was observed 1000 and 1200°C in air and steam.

Zirlo seems more resistant to oxidation in both air and steam at temperatures between 900 and 1200°C (Figure 1).



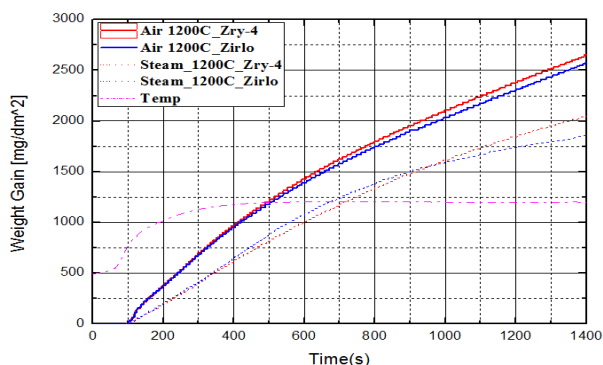


Figure 1. Oxidation behaviors of Zry-4 & Zirlo under Air, Steam at 700 °C-1200 °C

The XRD patterns for fresh samples with different Zry-4 loading are given in Figure 2. These observations show XRD patterns for the changed Zry-4 sample in the air. Three phases were identified in each diffraction pattern of Figure 2(a-d). The original metal sample peak was indexed to be α -Zr. After 5–15 min of oxidation, it can be concluded that most of the α -Zr peaks shifted to lower 2θ . Figure 1(b-c) indicates the Zr oxide particulate phase ZrO_2 (Tetragonal) peak. Figure 2(d) is the XRD pattern for ZrO_2 (Monoclinic) with no α -Zr.

The four selected XRD patterns for air samples are shown. During the experiment, tetragonal phases were detected, and small amount of α -Zr pattern was measured due to the phase transformations of the base metal and its oxide. However, after finishing the oxidation experiment under atmosphere temperature, a new phase appeared in the samples with a higher monoclinic phase. If ZrN layers are produced, this will support the rapid creation of an oxidation layer.

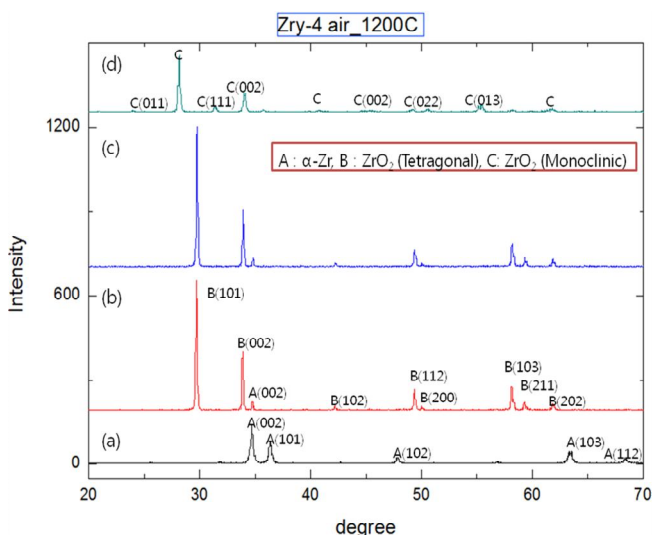


Figure 2. XRD patterns for the changed Zircaloy-4 sample in the air: (a) Zry-4 before the oxidation; (b) 5 min of oxidation; (c) 15 min of oxidation; (d) after the oxidation under atmosphere temperature.

4. Conclusions

The scale surfaces developed on the Zry-4 under the different conditions are compared in Figure 3. In Figure 3, a crack can be observed under the air condition, and it may be that the nitride effect caused the crack in the protective layer. Therefore, rapid and substantial oxygen material diffusion occurred in the preformed oxide layer at 1200 °C. In the steam condition, the oxide layer formed substantial protective oxide material at 700–1200 °C (Figure 3). As the EDAX results show, under the air oxide layer there was measured a small amount of carbon and oxygen. This is clear evidence of the results. Further examination of the oxidation kinetics of Zry-4 and Zirlo is needed for the safety evaluation of accidents occurring in air-steam mixtures.

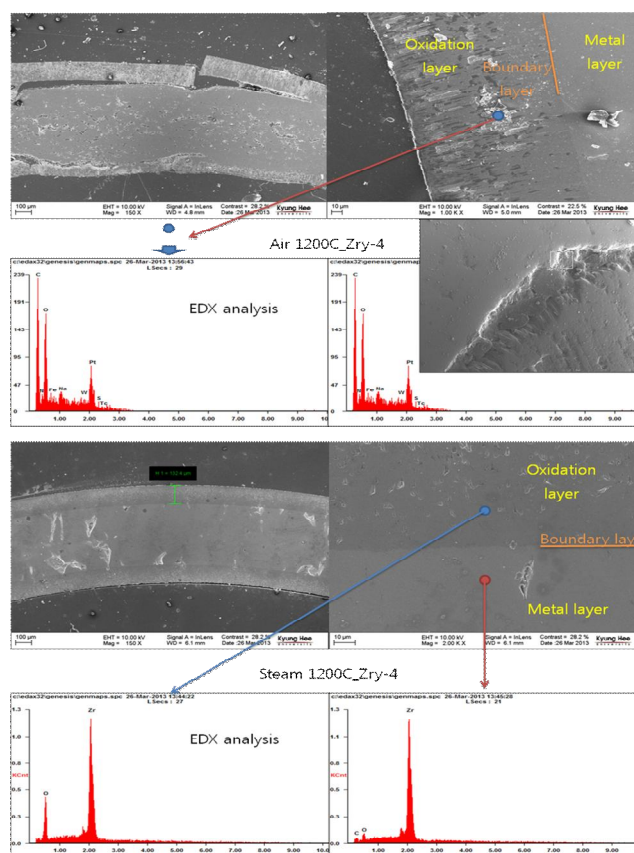


Figure 3. SEM and EDX views of the surface region of Zry-4 specimens oxidized at 1200 °C for 20 min in air and steam.

REFERENCES

- [1] F. J. Erbacher and S. Leistikow, Zircaloy fuel cladding behavior in a loss-of-coolant accident: A review, Zirconium in the Nuclear Industry, ASTM STP, vol. 939, p. 451, 19872.
- [2] C. Duriez, T. Dupont, B. Schmet, F. Enoch, Zircaloy-4 and M5 high temperature oxidation and nitriding in air, Journal of Nuclear Materials, vol. 380, pp. 30-45(2008)
- [3] T. Maekawa and B. Ishii, Oxidation of zirconium in air, Material Transaction JIM, vol. 3(1962)
- [4] S. Leistikow and G. Schanz, The oxidation behavior of Zircaloy-4 in steam between 600 and 1600 °C, Werkstoffe und Korrosion, vol. 36, pp. 105-116(1985)