

The Comparison of microstructures between air and steam oxidation of Zr alloys at high-temperatures

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1. Introduction

In the field of nuclear plant safety analysis, various low probable accidental situations may result in fuel rod exposure to air-containing atmospheres. Oxidation of zirconium alloys at high temperature for severe accident analysis has been widely studied in steam. However, the air oxidation studies are scarce than steam oxidation studies. Air oxidation and steam oxidation have difference in the microstructure. In order to have better understanding of the oxidation of zirconium in air, we compared the microstructures of oxides formed in air to those formed in steam. It turned out that the role of nitrogen in the presence of oxygen affected the oxide microstructure and also the oxidation 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~12mm. They had been cleaned and etched.

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 air testing of the Zirconium alloys used in this study is shown in Fig 1. In the tube furnace, there is an Alumina tube in the center and the heater is surrounding the tube. The furnace maintained a fixed temperature i.e., 1200C, and we put the specimens at the center of the tube. After a certain time passed, the specimens were pulled out. The weight of each specimen was measured before and after the experiment, and the weight gain was recorded. The part of the specimen was cut, grounded and polished. The microstructures of the polished surface of the specimen were observed by an optical microscope.



Figure 1. Apparatus (tube furnace) for high temperature oxidation of Zr alloys in air

3. Results

The weight gain results were shown in the figure 2. The weight gain by the oxidation in air was much higher than that in steam. Zry-4 claddings were somewhat more oxidized than Zirlo claddings. Below 1000C, it was observed that Zirlo claddings were oxidized more than Zry-4 claddings in air.

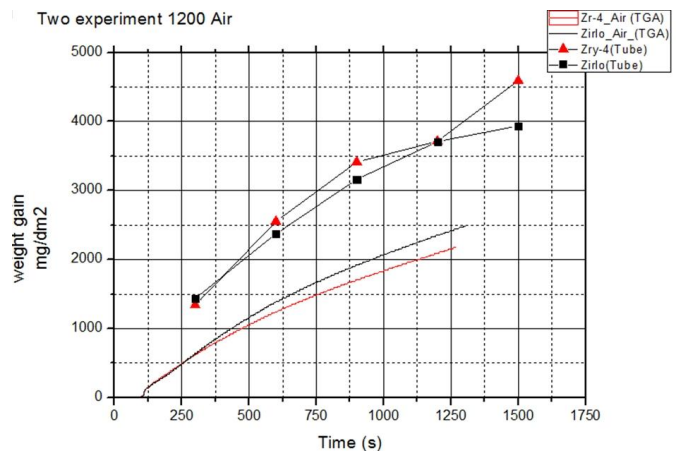


Figure 2. The weight gain of Zry-4 and Zirlo specimens oxidized in air. The weight gain curve oxidized in the steam was also shown for the comparison [1].

In the oxide formed in the steam, columnar grains were observed. Columnar oxide grains are known to be very effective against corrosion, since the columnar structure is stable under the compressive stress working at the side direction of the column. The oxidation in steam follows the parabolic rate law indicating the oxide layer is protective mainly due to these columnar grains.

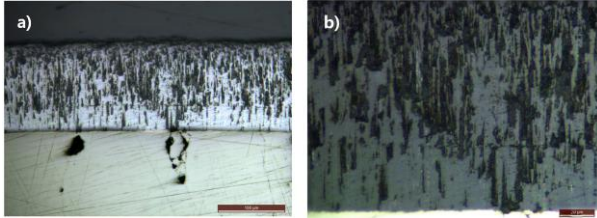


Figure 3. The microstructure of a Zry-4 cladding oxidized in steam. a) oxide on the metal layer, b) oxide layer magnified.

When Zr alloys were oxidized in air, most of oxide looked normal and took the form of columnar structure. However, some portions in the oxide layer looked abnormally grown. Figure 4 shows the abnormally grown oxide layer. In the abnormally grown area, there always were golden color compounds, i.e., zirconium nitride (ZrN). The oxides in between these ZrN's looked very different from the normal oxides originally formed on the surface initially.



Figure 4. The microstructure of a Zirlo cladding oxidized in air at 1200C for 5 minutes.

Thermodynamically ZrO_2 is absolutely more stable at 1200C than ZrN in the air based on HSC calculation. This means the compound formed in the mixture of N_2 and O_2 (i.e., air) should be ZrO_2 . The formation of ZrN at the inner side of the oxide layer needs some explanation. Duriez et al., explained that N_2 diffuses through oxide layer and forms ZrN beneath the oxide layer [2]. However, how nitrogen can reach to the metal beneath the oxide layer should be explained.

Once the nitride formed beneath the oxide layer, the oxide took different form from the columnar structure. And ZrN continuously formed with the growth of the abnormal oxide. Figure 5 shows the microstructure of the abnormally grown oxide layer. Throughout the

abnormal oxide, ZrN were observed. Near nitrides, cracks were also found. The cracks looked to normal to radial direction indicating the existence of tension in this direction.

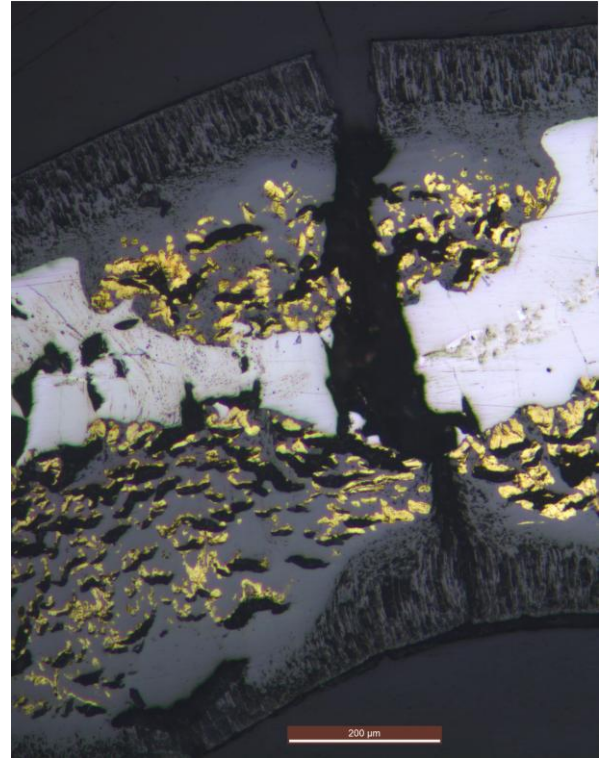


Figure 5. The microstructure of abnormally grown oxide layer in a Zr-4 cladding oxidized in air at 1200C for 20 minutes.

3. Conclusions

Zr alloys were oxidized more in air than in steam at high temperature around 1200C. Oxides formed in steam took the form of columnar structure which is believed to be protective against oxidation. Zr-alloys oxidized in air contained partly abnormally grown oxide layer. In the abnormally grown oxide, golden (yellow) spots were noticed, and they were zirconium nitride. These nitrides seem the reason for the abnormal oxide growth; however, how the nitride was formed, and how the nitride affected the oxide formation need more explanation.

REFERENCES

- [1] S. Leistikow and G. Schanz, The oxidation behavior of Zircaloy-4 in steam between 600 and 1600 °C, *Werkstoffe und Korrosion* 36, 105-116(1985)
- [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, p. 30-45(2008)
- [3] Tatsuo Maekawa and Bunpei Ishii, Oxidation of Zirconium in Air, *Material Transaction JIM*, vol. 3(1962)