# The difference in oxidation kinetics of Zr-alloy claddings in air, oxygen and steam

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## 1. Introduction

The Fukushima nuclear reactor accident has made the safety of the nuclear plants as a global issue. In this study, we observed the oxidation behaviors of Zircaloy-4 & Zirlo under accident conditions in pressurized water reactors. Even in the shutdown state of the reactor, the decay heat from the fission products has to be removed. As shown in the Fukushima nuclear reactor accident, the heated fuels by the decay heat react with 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 have been a lot of data regarding the reaction kinetics. Another important phenomenon that occurred in the Fukushima reactor accident was that spent nuclear fuels in the pool were heated due to the loss of cooling. At the extreme case, the fuels are exposed to the mixtures of steam and air and start to make oxidation reactions with ambient gases. To analyze these accidents realistically, we have to know the detail oxidation kinetics of Zr-alloy claddings with steam and air. Also, the kinetics are related with 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℃-1200℃.

## 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

The apparatus for the high-temperature oxidation of Zr-alloys in air and steam used in this study is shown in Fig. 1 and 2. In the case of steam oxidation, Ar gas passed through a bubbler supplying Ar gas with saturated moisture. The weight gain was measured and recorded continuously to a computer connected to the microbalance.

## 3. Results and discussion

The microstructure of specimens oxidized at 1000℃ at various conditions are shown in Fig.1. The specimen oxidized in air shows golden-colored areas that are zirconium nitride phases. Weight gain by oxidation in air, oxygen and steam for each specimen was measured by the microbalance at temperatures 700-1200℃ (Fig.2).


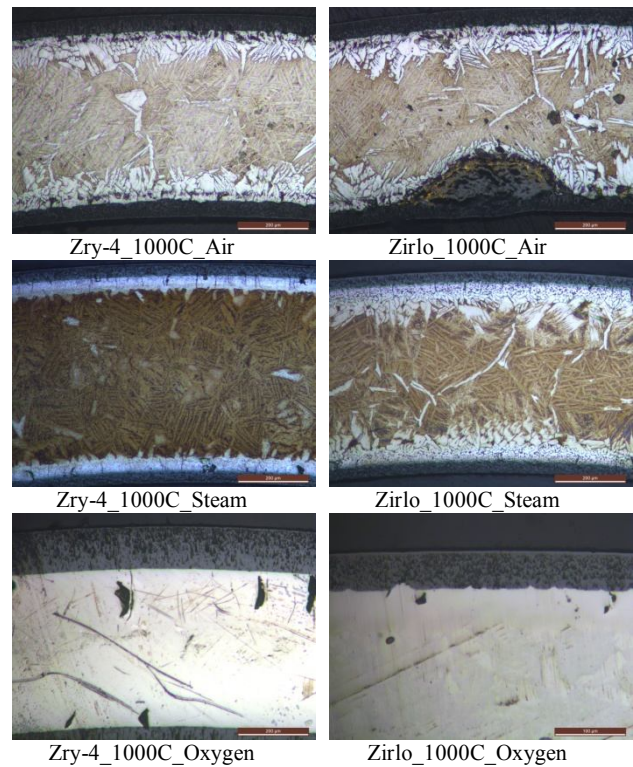
Figure 1. Optical microscopy of Zry-4 and Zirlo specimens oxidized in air, steam, and oxygen at 1000℃ for 30minutes.

Both Zry-4 and Zirlo claddings were oxidized faster in air than in steam. The oxidation rate of both alloys in oxygen was close to that in air. Zry-4 was oxidized slightly faster than Zirlo at 900-1200℃ in air, steam, and oxygen. However, at 700℃, Zirlo was oxidized slightly faster than Zry-4.

We checked the oxidation kinetics at the different ambient gas conditions. The oxidation kinetics can be expressed generally by the form as follows.
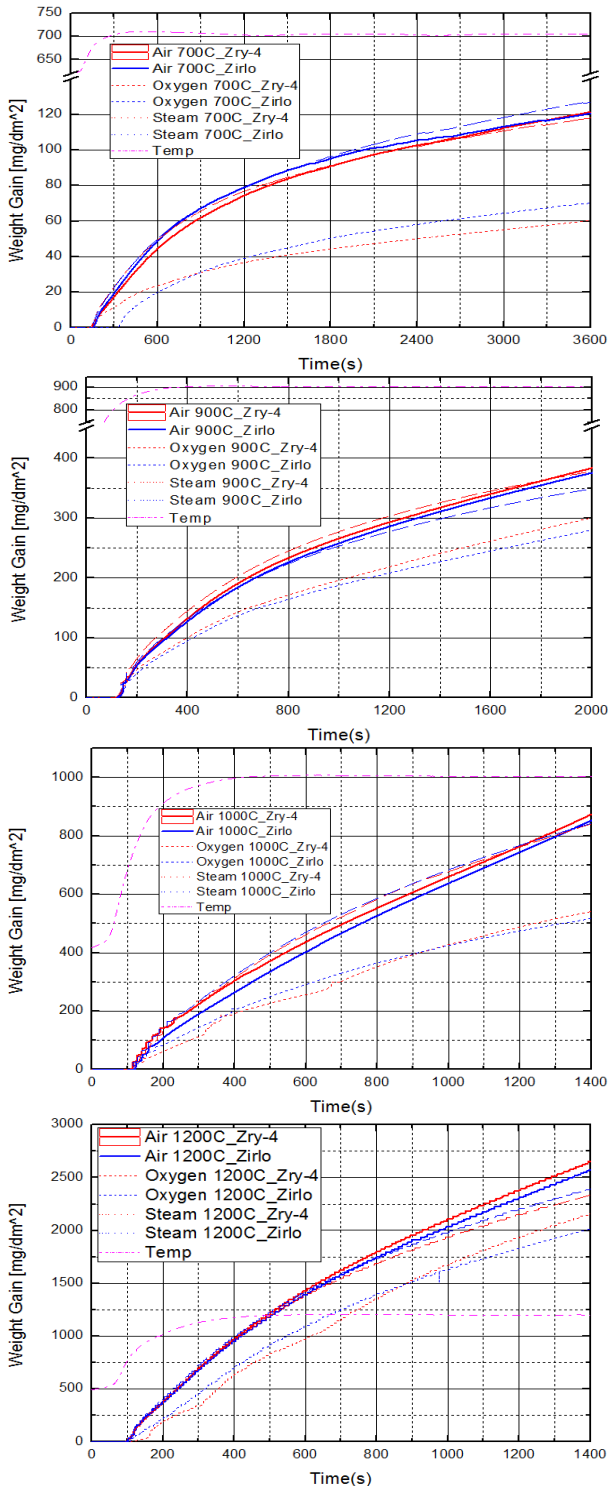
Figure 2. Oxidation behaviors of Zry-4 & Zirlo under Air,Oxygen, Steam at 700℃, 900℃, 1100℃, 1200℃

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

where 'W' is the weight gain (mg/dm$^2$), 'k' is the kinetic constant, t is time (sec). And 'a' indicates the degree (power) of oxidation rate. The constants in the kinetic equation at each temperature were obtained from the measured data (Fig.2), and they are shown in Table 2.

Table 2. The degree (power) of oxidation rate, 'a'.

| Temp | Element | Air | Oxygen | Steam |
|------|---------|-----|--------|-------|
| 700℃ | Zry-4 | 0.381±0.0006 | 0.339±0.0002 | 0.431±0.0004 |
|       | Zirlo | 0.319±0.0005 | 0.362±0.0005 | 0.425±0.0003 |
| 900℃ | Zry-4 | 0.488±0.0003 | 0.380±0.0002 | 0.573±0.0002 |
|       | Zirlo | 0.490±0.0001 | 0.401±0.0002 | 0.539±0.0004 |
| 1000℃ | Zry-4 | 0.703±0.0006 | 0.574±0.0005 | 0.676±0.0016 |
|        | Zirlo | 0.786±0.0004 | 0.565±0.0003 | 0.553±0.0007 |
| 1200℃ | Zry-4 | 0.628±0.0003 | 0.517±0.0005 | 0.738±0.0020 |
|        | Zirlo | 0.629±0.0005 | 0.516±0.0005 | 0.597±0.0008 |

The degree of oxidation, 'a' was in between 0.33 and 0.8. This value was almost the same in Zir-4 and Zirlo. At temperatures between 700 and 900℃, both alloys revealed initial cubic kinetics, and showed parabolic kinetics. However, in air, the reaction degree increased at higher temperatures(>1000℃). The reason might be enhanced oxidation by crack formations across the oxide layer due to the formation of nitrides.

We assumed the overall reaction followed a parabolic rate law. Then, the kinetic constant, 'k' can be expressed by:

$$k = k_0 \cdot exp\left(\frac{-Q}{RT}\right) \qquad (2)$$

where k is rate constant in $mg/dm^2 s^{0.5}$, $k_0$ is pre-exponential factor in $mg/dm^2 s^{0.5}$, Q is activation energy in J/mol, and temperature in K.

Based on the measured data, we evaluated $k_0$ and Q, which are shown in Table 3.

Table 3. Parameters of parabolic rate k constants at temperature [973-1473K]

| Alloy | Parameter | Air | Oxygen | Steam |
|-------|-----------|-----|--------|-------|
| Zry-4 | $k_0[mg/dm^2 s^{0.5}]$ | 57,386 | 46,306 | 100497 |
|       | Q [J/mol] | 83,455 | 81,452 | 93192 |
| Zirlo | $k_0[\frac{mg}{dm^2 s^{0.5}}]$ | 46,911 | 43,214 | 66149 |
|       | Q [J/mol] | 81,585 | 80,745 | 88775 |

## 4. Conclusions

We measured the oxidation kinetics of Zr-alloys in air, steam, and oxygen. The oxidation experiments for the Zry-4 and Zirlo were in the temperature ranges of 700-1200℃. The oxidation rates of Zry-4 and Zirlo in air (and oxygen) were higher than those in steam at 700-1200℃. The main reason for the enhancement of oxidation under the air may be from the formation of nitrides in the metal layer. In steam, the oxidation rates were almost the same as those of early works such as Leistikow and Schanz. Generally oxidation rates of Zry-4 at high temperatures are slightly higher than those of Zirlo at 900-1200℃.

## REFERENCES

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