

## Air oxidation behavior of Zircaloy-4 at transient condition

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### 1. Introduction

In spent fuel pool accident arising from a loss of water inventory, fuel rods can be exposed to an air environment and temperature increase steadily due to decay heat. Therefore, to analyze the integrity of spent fuel rods, an understanding of the oxidation behavior of zirconium alloys when exposed to air is required.

The importance of air oxidation behavior of zirconium alloys was relatively recently recognized and thus many experiments were conducted in many countries[1]. It is well known that oxidation in air leads to a strong degradation of the cladding material due to formation of zirconium nitride and its re-oxidation at high temperature[2-4].

Oxidizing environments considered are not only air but air/steam mixture[3,4] and most of the tests were conducted isothermally, however, a limited number of thermal transient tests were performed at different heating rates[4]. In addition, new code involving air ingress have been developed, focussed on the severe accident[5,6].

In this study, air oxidation behavior of the bare and pre-oxidized Zircaloy-4 specimen was studied in order to simulate the spent fuel pool accident. Experiments were carried out in transient condition at varying temperature increasing rate(10~40°C/min) up to 800°C from 40°C under atmospheric pressure by in-situ measurements using TGA.

### 2. Experimental

#### 2.1 Specimens

All specimens for experiment were cut off from the commercial Zircaloy-4 cladding tubes. The segments were 10 mm in length and both ends of the specimens were ground carefully up to 2000-grit of SiC paper. Then all the segments were pickled in a solution of 3% HF, 47% HNO<sub>3</sub> and 50% H<sub>2</sub>O. Finally, cleaned in an ultrasonic bath of mixed solution of acetone and ethyl alcohol for 10 minutes.

To determine the effect of pre-oxide in air oxidation, not pre-hydride, the specimens were oxidized in another small chamber with flowing pure oxygen gas at 500°C.

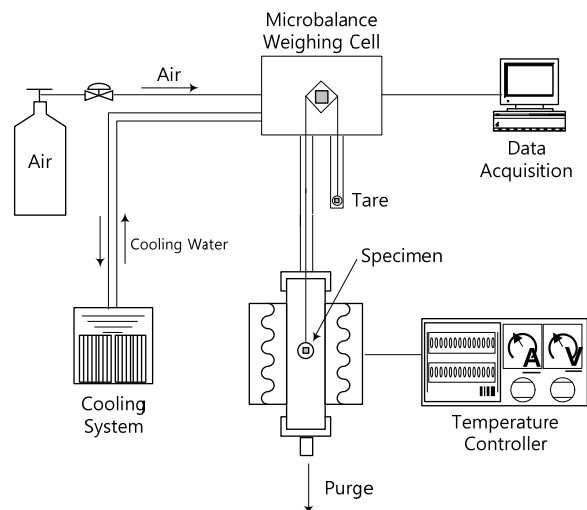


Fig.1. Schematic diagram of TGA.

#### 2.2 Test conduct

Prepared specimens were freely hung from a Pt wire connected to TGA(Thermogravimetric apparatus) whose sensitivity is 1 µg(S3D-P, Satorius). Fig.1 shows a schematic diagram of TGA. An air gas entered the reaction chamber from the upper part of equipment at flow rates of 150 cc/min continuously. When the TGA become stabilized, transient tests were conducted with different temperature increasing rate(10~40°C/min) up to 800°C from 40°C. At the same time, the weight gain and temperature change were measured by an in-situ method and the data was acquired by a data acquisition system connected to a PC. The test was finished when the chamber reached temperature of 800 °C

### 3. Results and Discussions

Fig.2 illustrates the comparison of specific weight gain of bare, 2µm and 20µm pre-oxidized Zircaloy-4 with temperature increasing rate of 10°C/min. The air oxidation of specimen with pre-oxide of 20µm(white oxide) was significantly retarded compared to test without pre-oxide. In case of pre-oxide of 2µm(black oxide), however, the reaction in air was accelerated after 500°C. The result was similar for temperature increasing rate of 20°C/min as well. This means the resistance to air oxidation is depending on pre-existing oxide thickness and it is conflicted with that pre-existing oxide layer may slow down further oxidation[7].

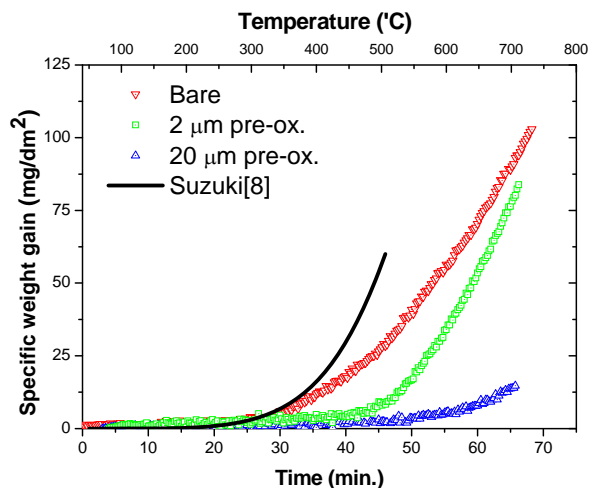


Fig.2. Comparison of specific weight gain of bare, 2 and 20  $\mu\text{m}$  pre-oxidized Zircaloy-4 with temperature increasing rate of  $10^\circ\text{C}/\text{min}$ .

In the pre-transition regime, the oxidation rate is commonly associated with the weight gain per unit surface area as eq. (1). Rate constant  $K$  can be expressed using an Arrhenius-type equation as eq. (2): where  $\Delta W$  is the specific weight gain ( $\text{mg}/\text{dm}^2$ ),  $n$  is the reaction rate exponent,  $t$  is the reaction time (min),  $K_0$  is pre-exponential factor ( $\text{mg}/\text{dm}^2/\text{min}^{1/n}$ ) and  $Q$  is the activation energy ( $\text{J}/\text{mol}$ ).

$$\Delta W = K \cdot t^{1/n} \quad (1)$$

$$K = K_0 \cdot \exp(-Q/RT) \quad (2)$$

From eq. (2), temperature  $T$  can be written as  $\alpha t$  at transient condition: where  $\alpha$  is the temperature increasing rate ( $^\circ\text{C}/\text{min}$ ). Combination of eq. (1) and (2) given as below.

$$\Delta W = K_0 \cdot \exp(-Q/R\alpha t) \cdot t^{1/n} \quad (3)$$

Using the kinetic data of isothermal reaction of Zircaloy-4 with air in temperature range  $350\text{--}500^\circ\text{C}$  from Suzuki[8], eq. (3) determined by the following equation assuming that  $n = 3$ , i.e.,

$$\Delta W = 4.1 \times 10^4 \exp(-50,079/R\alpha t) \cdot t^{1/3} \quad (4)$$

Above  $500^\circ\text{C}$ , result of Hayes[9] was used as below:

$$\Delta W = 2.6 \times 10^4 \exp(-57,196/R\alpha t) \cdot t^{1/2} \quad (5)$$

where  $R = 8.314 \text{ J}/\text{mol K}$

When  $\alpha = 10^\circ\text{C}/\text{min}$ , eq. (4) was plotted in Fig.2. The specific weight gain of model was higher than that of this study. Hayes' model was plotted in Fig.3 with different temperature increasing rate from  $500^\circ\text{C}$  to  $800^\circ\text{C}$ . It was also observed that results of this study was less oxidized in air atmosphere than the model.

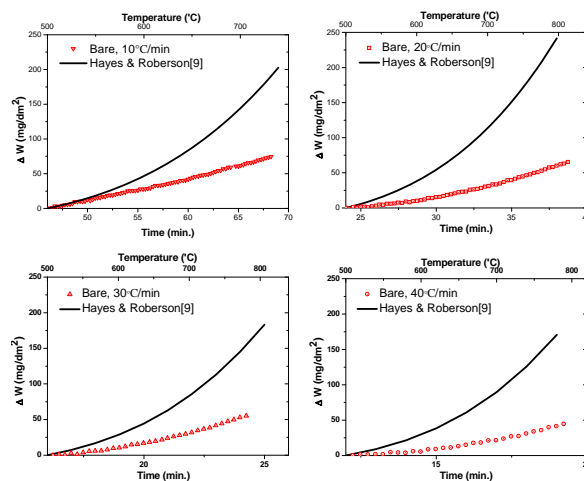


Fig.3. Comparison of  $\Delta W$  with Hayes' model and this study with different temperature increasing rate from  $500^\circ\text{C}$  to  $800^\circ\text{C}$

#### 4. Conclusions

The resistance to air oxidation of Zircaloy-4 was depending on pre-existing oxide thickness. Specific weight gain of two models were higher than those of this study.

To simulate the pre-corrosion of spent fuel at certain burnup, many factors (pre-oxide thickness, hydride concentration) have to be concerned. Then, behavior of cladding material in spent fuel pool accident will be more precisely predicted and criteria for keeping integrity of cladding will be established.

Therefore, in order to estimate the air oxidation behavior at transient condition, experiments will be added with varying hydride concentration, cladding material and oxidizing environment.

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