

# Air Oxidation Behaviors and Kinetics of UO<sub>2</sub> and Zircaloy-4 cladding under Spent Fuel Pool Accident Condition

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## 1. Introduction

The paradigm of nuclear plant operations has changed to 'safety is first' since the Fukushima nuclear power plant accident in 2011, and the study on nuclear fuel is required when an accident occurs in the SFP (Spent Fuel Pool). However, if the cooling function of the spent fuel pool is lost or destroyed by a massive earthquake or terror, the spent fuel may be exposed to the coolant water surface. At this time, the spent fuel cladding undergoes a rapid oxidation reaction with high temperature air, and if the spent fuel cladding breaks, the UO<sub>2</sub> pellet also undergoes a rapid oxidation reaction with high temperature air. Oxidation of UO<sub>2</sub> pellets and Zircaloy-4 cladding with steam accelerates rapid hydrogen generation and release of radioactive materials, a precise understanding of oxidation behavior required. Of course, since UO<sub>2</sub> pellets and Zircaloy-4 cladding has been used as fuel materials for light water reactors, there has been a variety of researches [1-5], but there is a lack of accurate information on air oxidation behaviors that accelerates degradation of UO<sub>2</sub> pellets and Zircaloy-4 cladding faster than steam. Therefore, in this study, the air oxidation behavior and reaction rate of UO<sub>2</sub> pellets and Zircaloy-4 cladding are evaluated under of severe accident conditions in the SFP.

## 2. Experiment

In this work, A TGA was utilized, which is capable of measuring real-time reaction of UO<sub>2</sub> pellets and Zircaloy-4 cladding with air. The test temperature was set from 600 °C to 1,400 °C, and the weight change of the specimen was measured in real time at each temperature.

## 3. Results & Discussion

### 3.1 Air oxidation behavior of UO<sub>2</sub> pellet during SFP severe accident condition

First, the air oxidation behavior of UO<sub>2</sub> sintering in the intermediate temperature zone (650 °C to 800 °C) was presented in Figure 1. In the case of UO<sub>2</sub>, unlike oxidation behavior at low temperature intervals, the oxidation rate was reduced as temperatures increased. Next, the air oxidation behavior of UO<sub>2</sub> at high temperature (1,000 °C~1,200 °C) is presented in Figure 2. In high temperature areas, the UO<sub>2</sub> showed a tendency

to increase the rate of oxidation again as the temperature increased, and unlike in low temperature areas, the initial air oxidation reaction occurred rapidly up to about 2 wt.%.

### 3.2 Air oxidation behavior of Zircaloy-4 cladding during SFP severe accident condition

First, Figure 1 shows the results of air oxidation experiments under isothermal conditions. As seen in Figure 1, the behavior at the initial interval of the total oxidation time was presented to see the initial oxidation behavior. As a result, the oxidation rate slowed down somewhat with the time of the accident. The initial oxidation behavior for air oxidation at high temperatures has been shown to follow the parabolic kinetic law, where the oxidation rate exponent is approximately 2. In other words, under accident conditions in a SFP, the weight increase with oxidation reaction time showed a decrease in reaction rate with time exposed to air, and the degree of oxidation showed about twice as much when the oxidation time was four times.

Next, the results of the experiments on air oxidation of the transient conditions are presented in Figure 2. In the case of transient oxidation testing, oxidation is also caused by air exposure in the process of reaching the final target temperature. This results in oxidation already occurring before the final target temperature is reached. In other words, a high-temperature air oxidation reaction occurs when an oxide layer is formed. In this case, the amount of oxidation formed before the final target temperature was assessed to be in the range of approximately 10 to 20 μ m, depending on the temperature. In other words, it has a similar effect on the oxidation behavior of cladding with a 10~20 μ m oxide layer. As with isothermal's initial oxidation test results, the weight increase behavior of the oxidation reaction time with air initially decreased with the accident progression time, and followed the parabolic kinetic law as described earlier, where the oxidation rate exponent was approximately 2. Compared to the isothermal test results, it was found to be somewhat slow in reaction rate, but no significant differences were found.

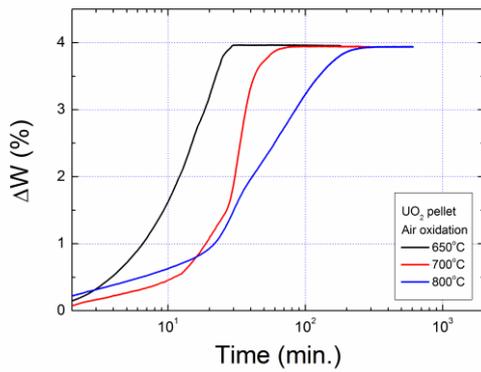


Fig. 1. Air oxidation behavior of  $UO_2$  pellet in middle temperature range during SFP severe accident condition

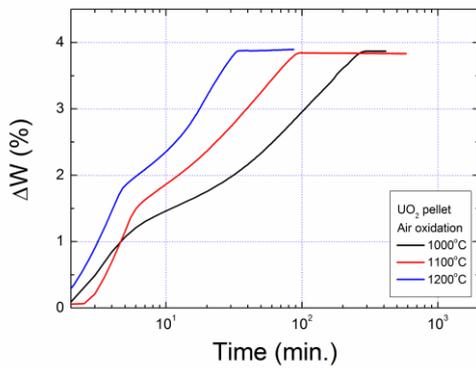


Fig. 2. Air oxidation behavior of  $UO_2$  pellet in high temperature range during SFP severe accident condition

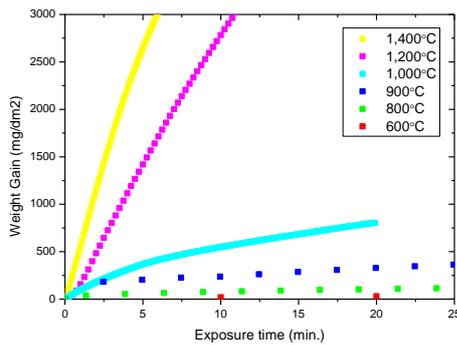


Fig. 3. Air oxidation behavior of Zircaloy-4 cladding during SFP severe accident condition (Transient)

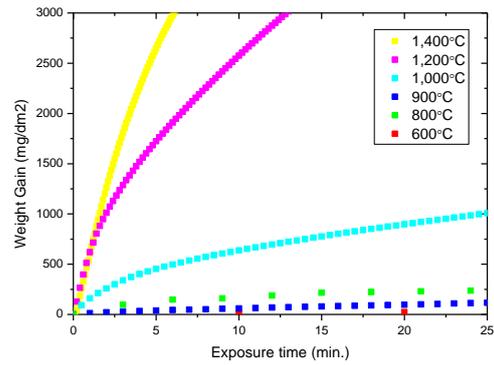


Fig. 4. Air oxidation behavior of Zircaloy-4 cladding during SFP severe accident condition (Isothermal)

#### 4. Conclusions

This study aimed to predict the behavior of the air oxidation reaction of  $UO_2$  and Zircaloy-4 cladding, assuming that under the severe accident caused by the loss of cooling function and/or coolant accident occurred in the SFP.

The main results are as follows:

First,  $UO_2$  tends to increase the rate of oxidation again as the temperature increases in the high temperature region, and unlike the low temperature region, the initial air oxidation reaction occurs rapidly up to about 2 wt.%.

Second, the weight increase behavior with oxidation reaction time with air initially showed a decrease in reaction rate with accident progression time, and followed the parabolic kinetic law, where the oxidation rate exponent was approximately 2.

#### REFERENCES

- [1] J.Y. Colle, J.P. Hiernaut, D. Papaioannou, C. Ronchi, A. Sasahara, Fission product release in high-burn-up  $UO_2$  oxidized to  $U_3O_8$ , Journal of Nuclear Materials 348 (2006) 229.
- [2] J.P. Hiernaut, T. Wiss, D. Papaioannou, R.J.M. Konings, V.V. Rondinella, Volatile fission product behaviour during thermal annealing of irradiated  $UO_2$  fuel oxidised up to  $U_3O_8$ , Journal of Nuclear Materials 372 (2008) 215.
- [3] F. Valdivieso, V. Francon, F. Byasson, M. Pijolat, A. Feugier, V. Peres, Oxidation behaviour of unirradiated sintered  $UO_2$  pellets and powder at different oxygen partial pressures, above 350 °C, Journal of Nuclear Materials 354 (2006) 85.
- [4] B.J. Lewis, W.T. Thompson, F. Akbari, D.M. Thompson, C. Thurgood, J. Higgs, Thermodynamic and kinetic modelling of fuel oxidation behaviour in operating defective fuel, Journal of Nuclear Materials 328 (2004) 180.
- [5] E.R. Gilbert, C.A. Knox, G.D. White, Behavior of spent LWR fuel in nitrogen and air, in Proc. of third International Spent Fuel Storage Tech. Symposium/Workshop, Seattle, Washington, U.S.DOE, CONF-860417, S-263 (1986).