The Effects of the temperature and the density on the Oxidation Behavior of Uranium Dioxide in Air at 573~873 K

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1. Introduction

The knowledge of the oxidation behavior of UO_2 is necessary for evaluation of its stability during irradiation in the reactor because O/U ratio affects the thermal properties such as melting point, specific heat, thermal expansion and thermal conductivity. It is also needed to establish the OREOX (Oxidation and Reduction of Oxide Fuel) process during the fabrication of DUPIC (Direct Use of fuel Spent PWR Fuel in CANDU Reactor) fuel [1] and to evaluate the stability in long-term storage and disposal of spent fuel. For theses reasons the oxidation behavior of UO_2 has been studied extensively for 50 years. In this study the oxidation behavior of UO_2 sintered pellet was studied using an XRD and a thermo-gravimetric analyzer to obtain the more exact data of oxidation behavior of UO_2 pellets and to confirm the effects of the oxidation temperature and the density of specimen.

2. Experimental

The blank test was performed to confirm the buoyance effect occurred by natural convection due to temperature difference and by air flow rate. The temperature range was from 573 to 973 K and air flow-rate was 1 *l*/hr and 10 *l*/hr in the blank test.

The oxidation experiments to confirm the effects of the temperature on the oxidation behavior of the UO_2 pellet were performed under isothermal mode in the temperature range from 573 to 873 K in air. To confirm the effects of the density of the UO_2 pellet, specimens whose density range was from 94.64 to 99.1 % of theoretical density and the average grain size was 14.7 μm were used in this experiment.

Specimens having a dimension of 8.06~8.41 mm in diameter and 1.4 mm in thickness were cut from the UO_2 pellet by the diamond saw. Before tested, specimens were abraded with 600 grit silicon carbide paper, washed in acetone in an ultrasonic cleaner, and rinsed with ethyl alcohol. An experimental apparatus used in this study was TGA 92-12 (SETARAM, France). Its working temperature range is from room temperature to 1273 K and the maximum heating rate is 99.9 K per minute. The alumina crucible was used to avoid the reaction between UO_2 and crucible.

3. Results and Discussion

3.1 Blank test

Fig. 1 shows the effects of the air pressure, air flow-rate and the temperature affected on weight gain under the isothermal condition in the blank test. Weight gains due to increasing temperature are 0.84, 1.06, 1.29, 1.50 and 1.72 mg at 573, 673, 773, 873 and 973 K, respectively. Weight gain is about 0.6 mg in the air flow-rate of 1 *l*/hr and 1.5 mg in 10 *l*/hr at 600 K. Weight gain in the blank test increases with increasing temperature and air flow rate.

These results are used in correction of data obtained from the oxidation experiment of UO_2.

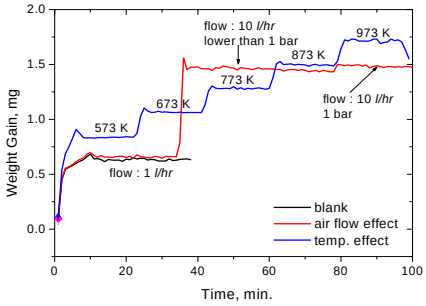

Fig. 1. The effects of the air pressure, air flow rate and the temperature during the isothermal experiment in the blank test.

3.2 Density effect

Fig. 2 shows the effects of the density of UO_2 pellet.

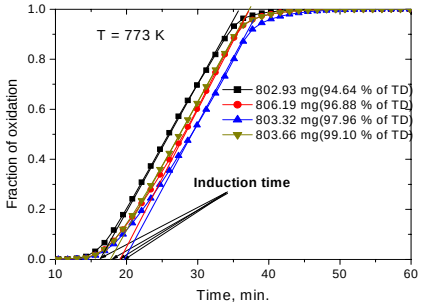

Fig. 2. The effect of the density of UO_2 pellet.

Oxidation rate decreases as the density increases from 94.64 to 99.1 % of TD. The difference of oxidation rate among the specimens with over 96.88 % of TD is very small. However, it is clear between the specimens with density of 94.64% and 96.88 % of TD. Na et al. [2] reported that there is no open pore in the surface of UO_2 pellet having density over 96 % of TD. Specimen having the density below 96 % of TD has wide specific area because of open pore. So the oxidation rate per surface area increases compared to that of no open pore specimen.

The induction time for the oxidation of UO_2 is delayed with an increasing density.

3.3 Temperature effect

Fig. 3 shows the effects of the temperature on the oxidation behavior of UO_2 pellet. It is well known that the reaction between UO_2 and oxygen is stepwise oxidation in air to form U_3O_7 and U_3O_8. [3]

$$UO_2 \rightarrow U_3O_7/U_4O_9 \rightarrow U_3O_8$$

The formation of U_3O_8 follows a nucleation and growth mechanism and displays sigmoidal reaction kinetics. In the figure, the initial rate of oxidation is very low (induction period) followed by a gradually increasing oxidation rate up to a maximum and then followed by a gradually decreasing to constant.

The activation energy for the oxidation of UO_2 is determined to be 89.54 kJ/mol and 34.40 kJ/mol in the temperature range from 573 to 723 K and from 723 to 873 K, respectively.

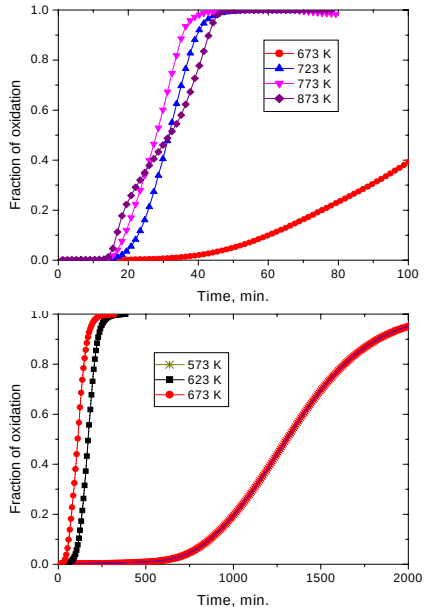

Fig. 3. Fraction of the oxidation of UO_2 in air

Acknowledgements

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