

Oxidation Behavior of Unirradiated and Irradiated UO₂ in Air at 150-375°C

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(Received March 29, 1996)

Abstract

Air-oxidation experiments on unirradiated and irradiated UO₂ were performed at temperature from 150 to 375 °C for investigating the long-term storage behavior of spent PWR fuel. The rate of oxidation was monitored by a thermogravimetric analyzer(TGA) and an X-ray diffraction(XRD). The correlation between the onset-time for U₃O₈ formation and temperature was given as follows ;

$\log t(\text{hr}) = -12.89 + 7650/T(\text{K}), 423 < T(\text{K}) < 573$. The activation energy of this process was found to be 145kJ/mole. In comparison with that of unirradiated UO₂ pellet, the oxidation rate of irradiated UO₂ increase more rapidly at the initial stage and shows a lower saturation point at the later stage. The oxidation rate of high burnup UO₂ and gadolinia-doped UO₂(Gd₂O₃-UO₂) were observed to be much slower than that of unirradiated UO₂ pellets.

1. Introduction

In many countries, dry storage has been regarded as a safe and economical method for the interim storage of spent nuclear fuel after several years of water-cooled storage and before final disposal in a geological repository. A major concern of dry storage is the oxidation of fuel in defected rods. The sequential oxidation of UO₂ in air to form oxygen-rich uraninite derivatives (up to compositions near U₃O₇), then U₃O₈, has been known for 30 years [1-3]. Nevertheless, this reaction still attracts investigation, mainly because of its importance to dry storage or disposal of irradiated UO₂ fuel [4-6]. The about 30% net volume expansion on forming U₃O₈ from UO₂ can damage previously defected fuel rods [8,9]; If this occurs during dry storage of fuel, it could complicate subsequent handling and storage of the fuel. Therefore,

it is important to understand UO₂ fuel oxidation in sufficient detail to define appropriate allowable conditions for the safe handling and storage of spent fuel. Many studies on the air oxidation of UO₂ have been focused on the formation of U₃O₈ [10-13]; However, some important aspects of this reaction are still not fully understood. Much of the information on UO₂ oxidation comes from studies with unirradiated UO₂ [9-13], but there are significant differences between oxidation behavior of unirradiated and irradiated fuel.

In this paper a study of UO₂ oxidation in air was conducted for analyses of the long-term storage behavior and accident analysis of fuel rod during both wet and dry storage-conditions. The oxidation behavior of irradiated UO₂ was compared with that of unirradiated UO₂.

2. Experimental

Unirradiated UO_2 specimens were cut from the commercial PWR type UO_2 pellet. Continuous weighing method was used to obtain more accurate data. Figure 1(a) shows the oxidation test equipment and automatic data acquisition system. Oxidation test was performed in a cylindrical type furnace with a programmable controller. Weight gain was measured continuously by Cahn-30 balance with an interface and a data acquisition system. The maximum precision of the balance is $0.1\mu\text{g}$.

Oxidation test on irradiated UO_2 was performed on the fragment specimens taken from Kori Unit-1 and Unit-2 PWR fuel using an intermittent weighing method. The Kori Unit-1 fuel had a final discharge burnup of 35 GWD/MTU. It had been cooled for 6 years in storage pool. To know the burnup effect on oxidation of UO_2 , some different specimens with 13.9 and 39.2 GWD/MTU burnup were used. 15-month ambient air aging specimen was also examined to determine the aging effect. To investigate the effect

of fuel composition on the oxidation behavior, the Kori Unit-2 fuel specimens were used. Two spent fuel rods from Kori Unit-2 reactor, which have different fuel types (rod K12: Urania fuel, rod L12: Gadolinia-doped fuel), were taken for these tests. Figure 1(b) shows the hot cell test equipment test for oxidation of irradiated UO_2 .

3. Results and Discussion

The oxidation experiments of unirradiated UO_2 fuel for PWR were performed at the temperature from 150°C to 300°C in air. X-ray diffraction (XRD) method used to detect the formation of U_3O_8 in the early stage of oxidation. Representative XRD traces of PWR fuel specimens oxidized for different oxidation time at 150 and 250°C are shown in Figure 2.

At 150°C XRD peaks indicate no U_3O_8 formation in all five specimens, which are essentially two-phase, consisting of only UO_2 and U_5O_7 without U_3O_8 upto 10,000 hours' oxidation (Fig. 2a). Figure 2(b) shows

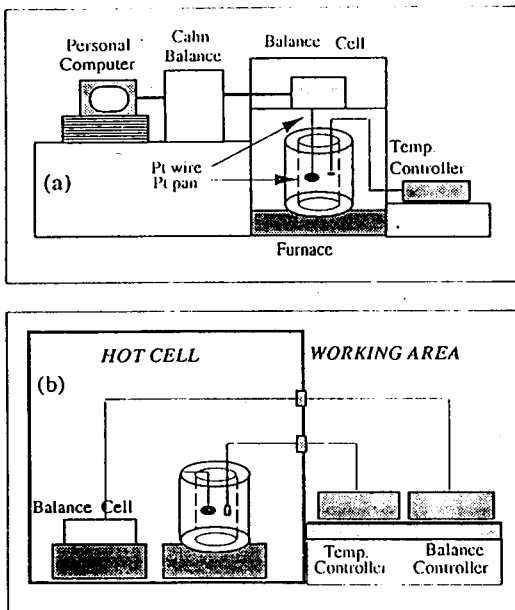


Fig. 1. Oxidation Test Apparatus of (a) Unirradiated UO_2 and (b) Irradiated UO_2

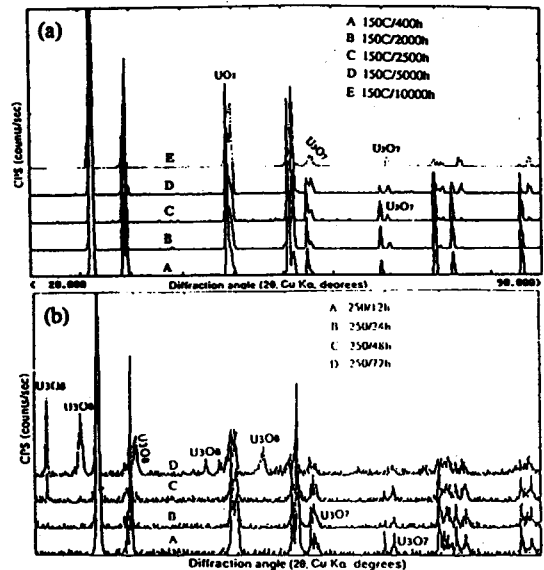


Fig. 2. X-ray Diffraction Traces for Unirradiated UO_2 Oxidized at (a) 150°C and (b) 250°C in Air

XRD traces for four UO₂ specimens oxidized at 250°C in air for 12, 24, 48 and 72 hours. The initial formation of U₃O₈ phase was observed after 48 hours' oxidation. Figure 3 shows the correlation between the U₃O₈ formation onset-time and the test temperature. The Arrhenius relationship of the U₃O₈ formation onset-time for unirradiated specimen was given as in the following equation.;

$$\text{logt}(\text{hr}) = -12.89 + 7650/T(\text{K}), \quad 423 < T(\text{K}) < 573.$$

The activation energy of this process was found to be 145kJ/mole.

Comparison of the oxidation behavior of the irradiated specimens with that of the unirradiated specimens at 300-375°C in air were shown in figure 4.

The weight gain curves of irradiated UO₂ oxidation in this figure were quite different from that of unirradiated UO₂ oxidation. In the early stage of the oxidation, the irradiated UO₂ was oxidized faster than unirradiated UO₂. However, at the later stage of oxidation, a oxidation of the irradiated UO₂ slower than unirradiated one. The following factors, such as oxidation condition, structural changes, fission products, changes of chemical composition and oxygen poten-

tial etc., thought to be the causes of the differences. Some investigators [14] reported that the fabrication history and shape of test specimen did not affect the weight gain characteristics. The difference of the oxidation curve shapes between unirradiated and irradiated UO₂ might be considered due to the microstructural change by irradiation. During irradiation, the sintering and fission gas pores distributed in UO₂ grain can migrate into the grain boundaries, and form fission gas bubbles. These bubbles in the grain boundary may accelerate the oxidation rate due to increase in the diffusion paths and surface area for oxygen. Thomas and Woodley [15,16] observed the fission gas bubbles of 2-10nm diameter in grain boundaries of irradiated UO₂. They explained that the fast oxidation in the initial stage was due to the fast diffusion of oxygen through the microchemical interconnected grain boundary formed by bubbles. Therefore the fast and slow oxidation features at the initial and

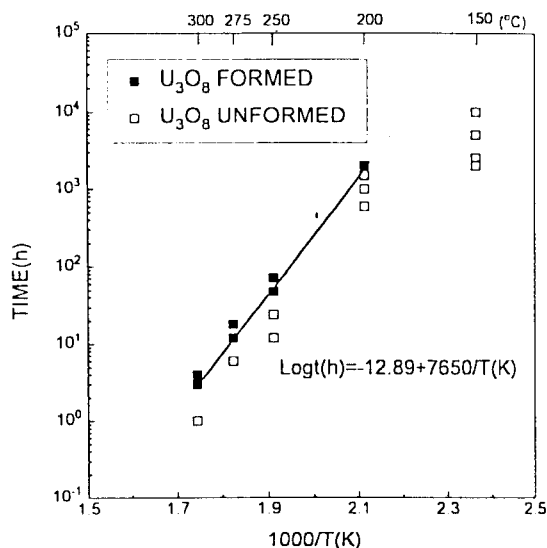


Fig. 3. Relationship Between the U₃O₈ Formation Onset-Time and Test Temperatures(150~300°C)

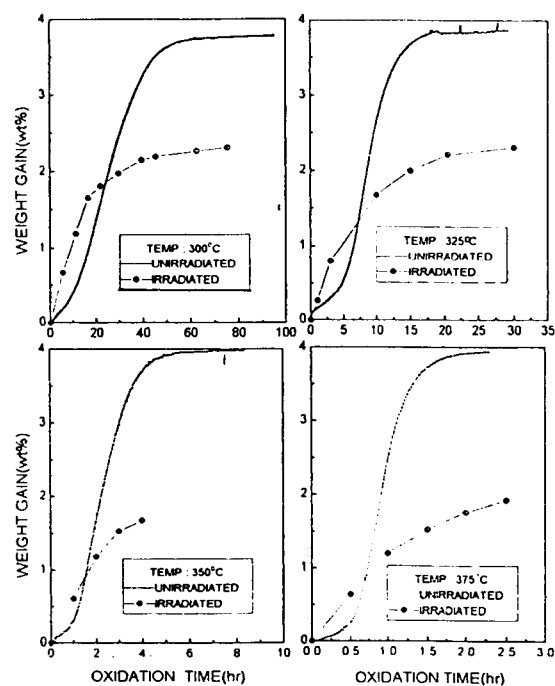


Fig. 4. Comparison of Oxidation Behaviors of Irradiated and Unirradiated UO₂ from 300°C to 375°C

later stages might be explained as follows; At the initial stage the irradiated UO_2 is oxidized faster by easy diffusion of oxygen through the micro-channel inter-linked grain boundaries formed by bubbles. In the later stage, however the possibility of some other phase formation, for example U_4O_9 , ect., may explain the delaying of U_3O_8 formation as well as Thomas' suggestion[13]. For the detail mechanism study of delaying oxidation phenomena at the later stage, more experiments are needed.

The effects of burnup and aging on irradiated UO_2 from Kori-1 are also studied at 350°C in air and the results are shown in Fig. 5. The effect due to the burnup difference between 13.9 GWD/MTU and 39.2 GWD/MTU seems not to be clear as shown in this figure.

Campbell[5] says the aging of UO_2 can make some protection layer on UO_2 surface and the layer can delay the oxidation rate. In this work, however, the aging effect, as also shown in Fig. 5, was not clearly appeared. The absence of aging effect might be explained from the fact that the relatively high oxidation temperature could destroy the protection layer produced under relatively low temperature.

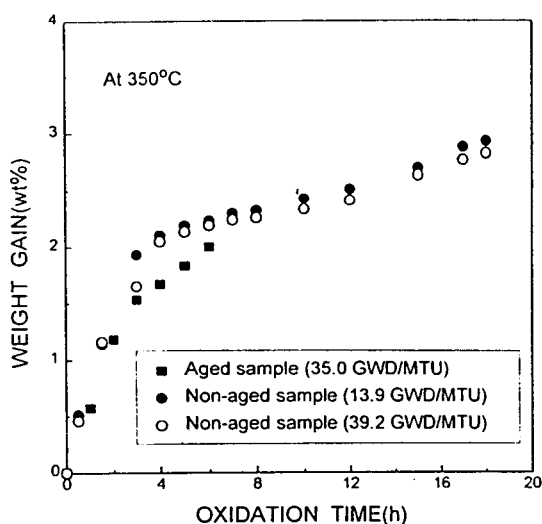


Fig. 5. Burnup and Aging Effects on Oxidation of Irradiated UO_2

Figure 6 shows the 275°C oxidation experiment results of the irradiated urania fuel (UO_2) with 16 GWD/MTU burnup, the irradiated gadolinia-doped fuel ($\text{Gd}_2\text{O}_3\text{-UO}_2$) with 10 GWD/MTU burnup, and the unirradiated UO_2 fuel.

The unirradiated UO_2 shows the oxidation behavior of a Sigmoid curve. It become fragmented roughly after weight gain of 1.2%. The local powdering happens after weight gain of 1.5%. The UO_2 specimen is completely powderized after weight gain of 1.9%. However, the irradiated urania and gadolinia-doped fuels show more rapid increase of oxidation rate at the initial stage. Oxidation rate of urania fuel becomes slow at 2wt% weight gain and increases rapidly again accompanying by local powdering phenomena after 150 hours' oxidation. Oxidation rate of the gadolinia-doped fuel decrease after reaching to 2wt%. If this result can be analysed based on the stability of U_4O_9 phase, which was proven by PNL study[13], gadolinia-doped fuel might have a longer delaying time of the oxidation increase rate after 2wt% weight gain. The result is in agreement with the experiment result using Gd_2O_3 doped

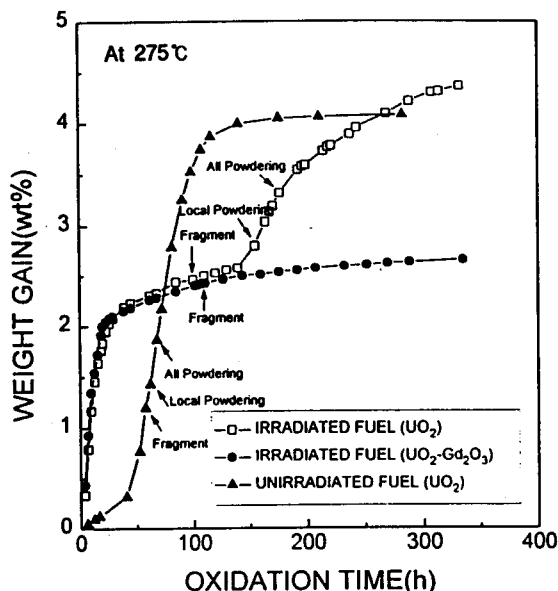


Fig. 6. Comparison of Oxidation Behaviors of Irradiated and Unirradiated UO_2 at 275°C

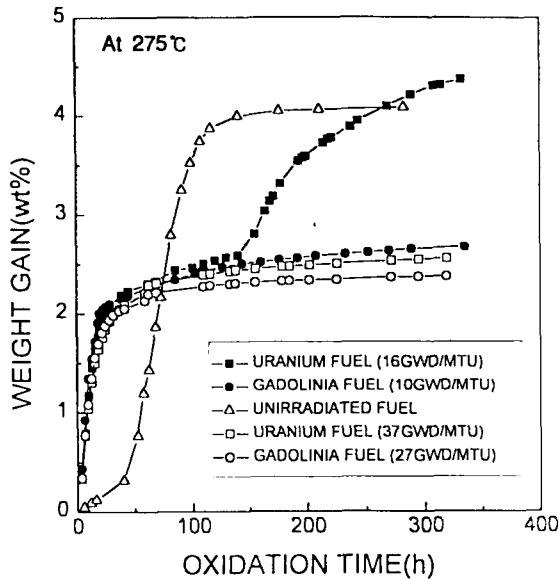


Fig. 7. The Effect of Burnup on Oxidation of Irradiated Urania and Gadolinia Fuels

specimens of the PNL study. Figure 7 shows the oxidation results of the uranium and gadolinia-doped fuel tested at 275°C.

The burnup doesn't affect significantly on the initial oxidation rate. But the delaying time of the oxidation increase rate is found to be extended at relatively high burnup. This test results are in agreement with SIMFUEL oxidation test results obtained by Taylor considering the burnup effect that the U_3O_8 formation time is delayed as burnup is increased.

4. Conclusions

From this study on the unirradiated and irradiated UO_2 oxidation behavior, the following conclusions can be drawn :

1. The Arrhenius relationship for the onset-time of U_3O_8 formation and temperature are given as follows;
 $\log t(\text{hr}) = -12.89 + 7650/T(K)$, $423 < T(K) < 573$.
 The activation energy of this process was 145kJ/mole.

2. In comparison with that of the unirradiated UO_2 , the oxidation rate irradiated UO_2 increases more rapidly at the initial stage and shows a lower saturation point at the later stage. The aging history of UO_2 specimens has no effect on their oxidation behavior.
3. Oxidation rates of relatively high burnup UO_2 and gadolinia-doped specimens were observed to be much slower than that of normal discharge burnup UO_2 .

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