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Oxidation Behavior of UO_2 in Air at 300~550°C

Kweon-Ho Kang, Suk-Youl Hwang* and Kil-Jeong Kim
*Korea Atomic Energy Research Institute, *Pyeong Taek Technical College*

Abstract — The oxidation behavior of UO_2 pellets was studied using a thermogravimetric analyzer and an XRD in the temperature range of 300 to 550°C in air. From XRD studies it is found that UO_2 is converted to U_3O_8 and the weight gains of UO_2 specimen are characterized by S-shape curves. After complete oxidation the specimens broke into fine powder and the average weight gain was about 3.93 wt%. The activation energy of 50% conversion of UO_2 to U_3O_8 is 81.6 kJ/mol and the oxidation rate per unit time was found to be as follows $dw/dt=6.54\times10^6\, e^{(\frac{-81.6\ kJ/mol}{RT})}$, wt%/h : at 50% conversion of UO_2 into U_3O_8 where w, t and T were wt% gain, conversion time and temperature, respectively.

1. Introduction

A knowledge of the oxidation behavior of UO_2 is necessary for evaluation of its stability in long-term storage and the disposal of spent fuels. There have been many studies on the oxidation of UO_2[1-8]. Aronson *et al.*[1] reported on the oxidation of UO_2 powder that at temperatures below 260°C, UO_2 was oxidized up to $UO_{2.4}$, while above 260°C UO_2 was oxidized up to U_3O_8 by a two-step reaction through the phase U_3O_7. Peakall *et al.*[2] carried out the oxidation experiment for UO_2 pellets in air at 350~1000°C. Scott *et al.*[3] carried out the oxidation for various uranium dioxide preparations in air at temperatures up to 800°C. Matae Iwasaki *et al.*[4] studied the oxidation of UO_2 pellets in air at 800 and 900°C. They reported that there were three types of oxidation in the oxidation-time curve in temperature ranges from 400 to 700°C, 800 to 900°C and 900 to 1000°C. Matae Iwasaki *et al.*[5] carried out oxidation experiments for UO_2 pellets in air at 400~700°C to investigate the effect of different heat treatment conditions of pellets on the particle size of the product of pulverization. Peter *et al.*[6] studied the early stages of U_3O_8 formation on unirradiated CANDU UO_2 fuel oxidized in air 200~300°C by using XRD. They reported that the XRD measurements permitted detection of U_3O_8 formation earlier than the visual detection of the powder and U_3O_8 was formed more rapidly on a rough UO_2 surface than a polished one. Bae *et al.*[7] studied the oxidation behavior of unirradiated UO_2 pellets at 400 to characterize the oxidised powder and to establish a new spallation model. You *et al.*[8] studied the oxidation behavior of UO_2 in the range of 250~400°C. They carried out the experiment on irradiated and non-irradiated UO_2 and compared the two. Ritchie[9] reviewed reactions of uranium with oxygen and water vapor under various conditions.

In this paper the oxidation behavior of UO_2 was studied and presented by XRD and thermogravimetry in the temperature range of 300~550°C in air for evaluating the stability of spent fuel in long-term storage and its disposal. The oxidation behavior of UO_2 is compared with those of UO_2 and metallic uranium previously reported by other studies.

2. Experimental Procedures

2-1. Materials

Specimens having a dimension of 10.75 mm in diameter and 1.45~1.55 mm in thickness were cut from the commercial PWR type UO_2 pellet whose nominal density is around 97% of theoretical density and grain size is about 10 μm. It was made by sintering at 1,700°C in H_2 after compacted under 12 bar pressure and its density was changed from 3.5 g/cm^3 to 10.7 g/cm^3. The initial average weight and

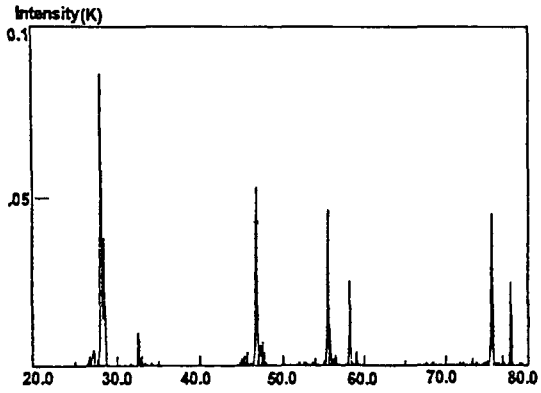


Fig. 1. XRD pattern of initial specimen.

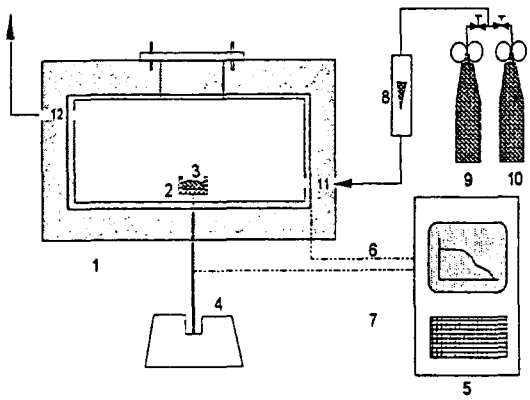
surface area of a specimen was 1,492 mg and 232.2 mm^2, respectively. Before tested, specimens were abraded with 600 grit silicon-carbide paper, washed in acetone in an ultrasonic cleaner, and rinsed with ethyl alcohol. All the specimens were stored in a dry environment and were tested with their surfaces covered with oxide films formed in air at room temperature. Fig. 1 shows a XRD pattern of the specimen before the oxidation experiment.

2-2. Apparatus

The experimental apparatus (thermogravimetric analyzing device) mainly consists of a furnace, a control and data acquisition system and a controlling system for the furnace. A schematic diagram of the thermogravimetric furnace is shown in Fig. 2. Temperature of the furnace can be controlled with any mode of heating by a programmable microprocessor. In order to avoid any reaction between the specimen and the crucible, an crucible was used.

2-3. Experimental Procedure

The specimens were contained in the alumina crucibles to retain the non-adherent products and were brought to the test temperature in a flow of purified argon before the oxidant was introduced. The oxidation tests were performed by continuously weighing the samples in a stream of oxidizing gas. The weight gains of specimens were measured during the oxidation test by microbalance with a load-carrying capacity of 5 g and sensitivity of 1 μg. Data



1. Furnace 2. Crucible 3. Sample
4. Balance 5. Computer 6. Temp. Control
7. Wt. Record 8. Flow Regulator 9. Argon Canister
10. Oxygen Canister 11. Gas Inlet 12. Gas Outlet

Fig. 2. A schematic diagram of thermogravimetric furnace.

were automatically acquired and stored with the time and temperature. The flow rate of the oxidizing gas was 4.5 *l*/min at an atmospheric pressure.

3. Results and Discussion

3-1. Oxidation Reaction and XRD Patterns

Fig. 3, 4 show the shape of specimens and XRD results after oxidation, respectively. When UO_2 is oxidized in air, it can be transformed into various meta-stable oxides, such as U_4O_9, U_3O_7 and U_3O_8. It is known that specimens of uranium dioxide after

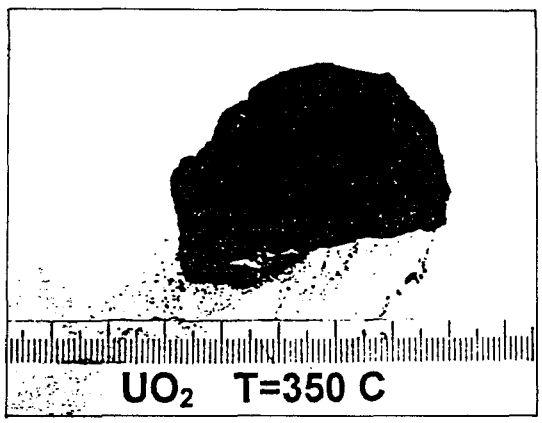


Fig. 3. Shape of the specimen after oxidation at 350°C for 500 min.

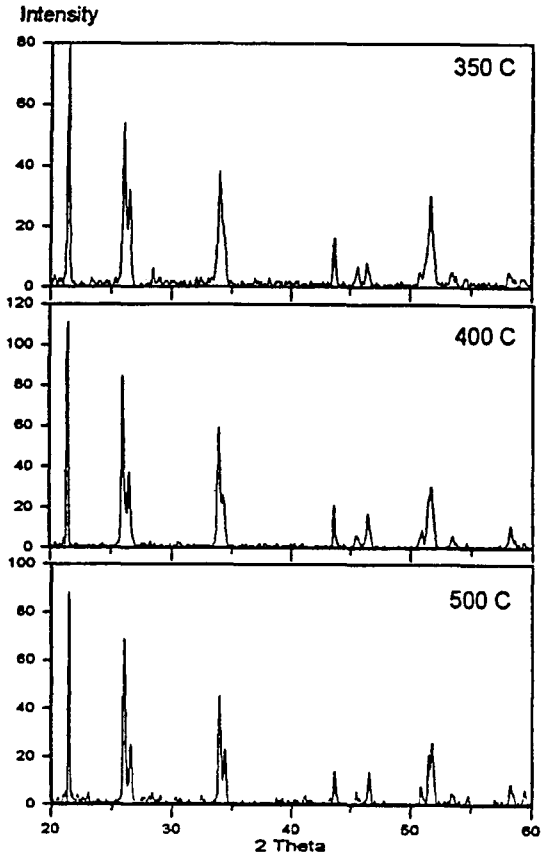


Fig. 4. XRD patterns of products after oxidation.

oxidation are fragmented and pulverized to powder due to the volume change resulting from phase transformation of UO_2 to intermediate phases and finally U_3O_8. Aronson *et al.*[1] carried out the oxidation experiment with UO_2 powder in air and oxygen at the temperature range of 160 to 350°C. They reported that the oxidation process could be divided into two steps. In the first step, the tetragonal oxide, $UO_{2.34+0.03}$ is formed. In the second step, this tetragonal phase is converted to orthorhombic U_3O_8. In the oxidation of pelletized UO_2, Peakall *et al.*[2] reported that, at temperature range of 350 to 600°C, pellets were oxidized rather quickly to U_3O_8 and were broken into fine particles. Scott *et al.*[3] reported that fine uranium dioxide powders were oxidized in the characteristicaly two step processes, first, to a tetragonal phase of the composition $UO_{2.35+0.02}$ and then to U_3O_8. They also reported that uranium dioxide of low surface area was oxidized by only single stage oxidation from UO_2 to U_3O_8. Matae Iwasaki *et al.*[4] reported in their study for air-oxidation of UO_2 pellets at 800 and 900°C that the oxidation of UO_2 pellets proceeded by two steps: the first step, $UO_2 \rightarrow (UO_{2+x}) \rightarrow U_4O_9$ and the second step, $U_4O_9 \rightarrow U_3O_8$. The first step reaction proceeded from the surface into the inner layers of the pellets, and the reaction rate appeared to be controlled by the diffusion of oxygen through the U_4O_9 phase. The second step reaction which proceeded rapidly with fragmentation of the pellet into small pieces, seems to be initiated by nucleation of U_3O_8 in the U_4O_9 phase. Bae *et al.*[7] reported that, as oxidation started at 400°C, the grain boundary was cracked because of the volume contraction and partial spallation of intermediate phases. During the oxidation intergranular cracks propagated towards the inside of the pellet and the formation of U_3O_8 accelerated the spallation. In this study, the specimens were fragmented into fine powders followed by converting to U_3O_8 in the range of temperature from 300 to 550°C. This result is different from the form of a well defined plate that is found in the oxidation of metallic uranium[10].

3-2. Oxidation Rates

The oxidation rates of uranium and its alloys are various. They could be linear, parabolic or paralinear depending on the oxidation conditions. The factors that effect oxidation rate include temperature, moisture content, impurity, oxygen potential, roughness of surface, surface area vs. volume ratio, irradiation induced swelling, etc. Fig. 5 shows oxidation data obtained in this study over the temperature range of 300~550°C.

Aronson *et al.*[1] reported on the oxidation of UO_2 powder that the rate controlling process in the first stage was the diffusion of oxygen through the uranium dioxide lattice. The value found as the diffusion coefficient D was expressed by, $D=5.5\times10^{-1}\exp[(109{,}960\pm6{,}276)/RT]$, where the activation energy was 109.96 ± 6.276 kJ/mole. You *et al.*[8], reporting on the oxidation behavior of UO_2 in air, stated that the weight gain of the non-irradiated UO_2 was characterized by the S-shape curve. In this study, the oxidation of UO_2 proceeds slowly at the

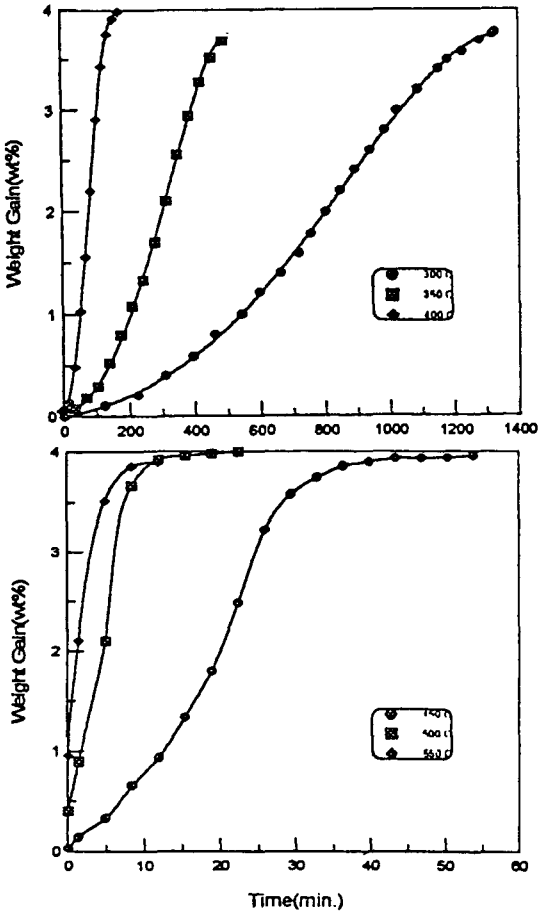


Fig. 5. Weight gain-time curves for the oxidation in air at 300~550°C.

initial stage of reaction and increases more sharply after a certain time until decreasing again due to slow reaction at the end of experiment. Therefore, the profile of the weight gain-time curve for this temperature range becomes S-shape, which is similar to the results of other studies. The S-shape profile of the weight gain-time curve is different from that obtained by a linear or paralinear reaction in the oxidation of metallic uranium[9-11]. The surface reaction could be controlled by the diffusion of oxygen into the internal structure of the specimen in the temperature range. Since the fragmentation of the specimen is caused by the volume expansion and the resulting powder increases the surface area for reaction, the reaction rate increases at higher orders at a certain period of time as explained previously. This observation supports the fact that the oxidation reaction process is controlled by diffusion of oxygen into the surface of the solid phase rather than the chemical reaction kinetics as one of the typical phenomena of the solid-gas reaction.

Table 1. Oxidation rates of UO_2 with air.

Temp.	rate of oxidation, wt%/h		
	25% conversion	50% conversion	You *et al.* study
300	0.07	0.12	0.06
325			0.24
350	0.28	0.39	1.09
375			2.17
400	1.23	1.47	5.263
450	4.54	5.75	
500	8.41	25.8	
550	19.7	90.4	

From the stoichiometric calculation of complete oxidation to U_3O_8, the weight gain of the final product would to be 3.95 wt%. In this study, the weight gain of the final product is about 3.93 wt%. To observe the reaction rate of UO_2 with variation, the reaction rates at the gains of 25% and 50% are shown in Table 1.

The weight gain per unit time for 50% transformation vs. the reciprocal of the temperature is plotted and shown in Fig. 6. From an Arrhenius type expression for the rate equation, the activation energy were for weight gain of 50% were calculated

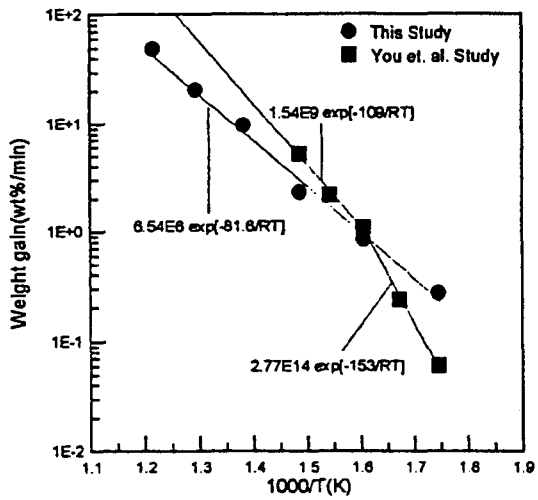


Fig. 6. Rate of weight gain versus 1000/T.

to be 81.6 kJ/mol in the range of 300~550°C, which is smaller than the value obtained by You *et al.*. You *et al.*[8] obtained the activation energies of 153 kJ/mol in 250~350°C and 110 kJ/mol in the range of 350~400°C. They also suggested the existence of a transition point at 350°C. In this study, however, the transition point did not appear. The activation energy is 81.6 kJ/mol . Because the oxidation was carried out in blowing air in this study but in You's study was carried out in stationary air, the oxygen potential was higher in this study than in You's study. In this study, from the plot, the reaction rate per unit time could be expressed as follows:

$$dw/dt = 6.54 \times 10^6 e^{\left(\frac{-81.6\,kJ/mol}{RT}\right)}, \text{ wt\%/h}$$

: at 50% transformation into U_3O_8

where the activation energy is 110.79 kJ/mol.

4. Conclusions

Analyses of XRD patterns and thermogravimetry to observe the oxidation behavior of UO_2 pellet were carried out and the following conclusions could be made.

1) From XRD study, UO_2 pellet converted to U_3O_8 in the temperature range of 300~550°C.

2) From thermogravimetry analysis, the weight gains of UO_2 specimens were characterized by S-shape curves.

3) The activation energy for 50% conversion of UO_2 to U_3O_8 was 81.6 kJ/mol and the oxidation rate per unit time was found to be:

$dw/dt = 6.54 \times 10^6 e^{\left(\frac{-81.6\,kJ/mol}{RT}\right)}$, wt%/h : at 50% conversion of UO_2 into U_3O_8 where w, t and T were wt% gain, conversion time and temperature

4) After complete oxidation, the specimens were fragmented into fine powder.

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