The Researches of UO_2 Powder Oxidation in air by TG/DSC

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1. Introduction

For nuclear fuel industry, it is important to figure out the status and the kinetic properties of UO_2 powder oxidation. When the nuclear fuels are fabricated with UO_2 powder, there would be lots of sludge of UO_2 powder and defective pellets to be recovered. This leads to the low production efficiency and high cost. The oxidation of wastes should be conducted at recovery process for reuse economically. In order to manage the wastes in fuel manufacturing process well, it is important to know the phenomena and the thermodynamic properties of UO_2 oxidation [1,2].

The aim of this research is to confirm the phases and to obtain the activation energies of oxidation of natural UO_2 powder in dry air. Two kinds of experiments were performed in the dry air at the constant heating rate and the isothermal conditions using TG/DSC [3]. The constant heating rate experiment from 25 to 500 °C and the isothermal experiment at 300, 350, 400 and 450 °C were conducted. And in order to know the phases of UO_2 powder oxidation, XRD measurement was taken with the samples obtained by the time step oxidation at 350 °C.

2. Experimental

2.1. Sample preparation

The natural UO_2 powder sample was selected for the oxidation experiments. After being measured by XRD (D2 PHASER, BRUKER), the sample was identified as $UO_{2.13}$. So it should have been oxidized to U_3O_8 using muffle furnace because the sample had wettability and it was supposed to be reduced for making pure UO_2 samples. After the oxidation of the original sample, the obtained U_3O_8 was reduced to UO_2 by using electric box furnace in Ar+4%H_2 gas with a flow rate of 100 ml/min for 4 hours. After the reduction, the product was identified as a stoichiometric UO_2 by XRD analysis as given in Fig. 1. The color of samples was changed from black to brown and the particle size of the UO_2 sample was found to be around 5 to 7 μm by SEM observation.

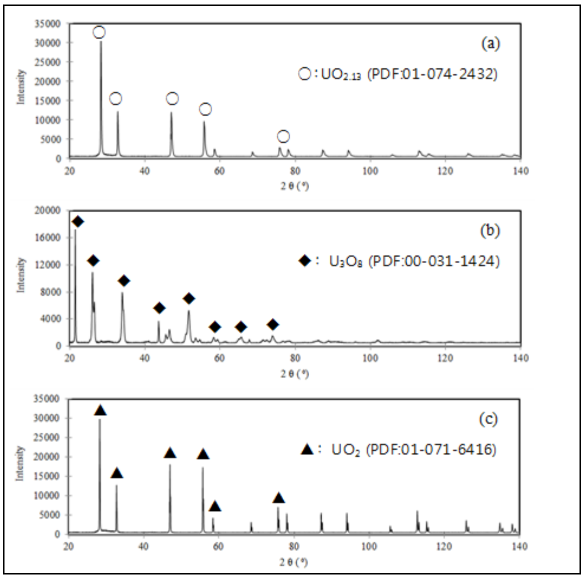

Fig. 1. The powder XRD patterns for (a) starting material, (b) after oxidation and (c) after reduction.

2.2. TG/DSC measurement

The oxidation behavior of UO_2 powder samples was investigated by TG/DSC method (SETSYS Evolution TG-DSC, SETARAM). Two kinds of experiments were conducted in the dry at the constant heating rate and the isothermal conditions. In the constant heating rate experiment, the temperature was increased from 25 °C to 500 °C at 20 °C/min. And the flow rate of the dry air was 25 ml/min [4]. The sample weight was 29.45 mg in an alumina crucible. Also the blank test was performed using only the alumina crucible for the correction of TG/DSC data.

In the isothermal experiments, the temperatures of 300, 350, 400, and 450 °C were chosen for the oxidation experiments. The heating rates from room temperature to 300, 350, 400, and 450 °C were 30, 35, 40, and 45 °C /min, respectively. Unlike for the constant heating rate experiment, the flow rate of the dry air was 167 ml/min. Pre-processing was done before the dry air was flowed into the TG/DSC system for the oxidation of UO_2 powder. The average of sample weights was about 29.49 mg in an alumina crucible and the standard deviation was 5.25 mg. The blank tests were also performed using the alumina pans without the samples at each of temperatures. After the experiments, the weight of the samples was measured with the electronic balance and XRD.

2.3. Time interval oxidation of UO_2

The oxidation experiment of UO_2 powder in muffle furnace was conducted at 350 °C to figure out the state of UO_2 product. Two types of oxidation behavior were clearly observed in TG/DSC curves obtained at 350 °C such that the temperature was selected for the oxidation experiment. The UO_2 powder around 50 mg was put into the quartz boats. The number of the prepared boats was eight. The seven points were chosen at intervals of 100 seconds by referring the oxidation of TG curve at 350 °C. After taking out the samples, the weight change of the samples was checked with the electronic balance. And the phases in the UO_2 samples were also analyzed with the XRD measurement [5].

3. Results and Discussion

3.1. Constant heating rate experiment

Fig. 2 shows the curves of TG/DSC with UO_2 powder at constant heating rate condition in the dry air [4]. Two types of oxidation were observed in TG curve. The first one is mild oxidation around 250 °C and the second one is rapid oxidation around 350 °C. Two exothermic peaks in DSC curve were observed following the TG curve. The first peak is lower than the second peak in the DSC curve.

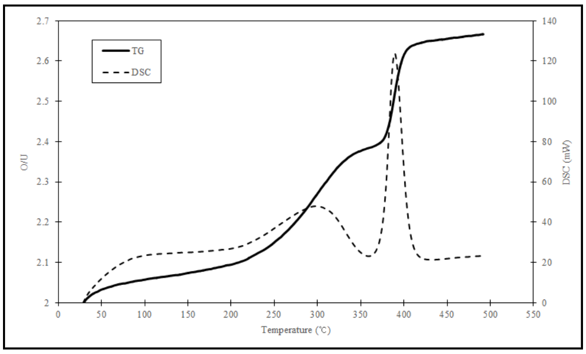

Fig. 2. The curves of TG/DSC with the oxidation of UO_2 powder in dry air.

Table I indicates the values of activation energies by increasing temperature. The values of activation energies at each of oxidations were integrated following the base line of DSC curve. Even though the region of first oxidation at DSC curve is broader than the region of second oxidation, the value of the activation energies for the first oxidation is a little bit lower than for the second oxidation. Because the second peak in DSC curve is much higher than the first peak.

Table I: The values of activation energies at each of oxidations

△H	First oxidation	Second oxidation	Total
kJ/mole	49.7040	51.4099	101.1139

3.2. Isothermal experiment

Fig. 3 shows the TG/DSC curves for the oxidation of UO_2 powder in dry air at 300 °C. Two types of oxidation were also observed in TG curve. The first oxidation is more rapid than the second one. Even though the time of oxidation was almost 2 hours, the TG curve couldn't reach the U/O of 2.66, U_3O_8, which is the fully oxidation point. That means time is needed more to be oxidized to U_3O_8. Two exothermic peaks in DSC curve were also observed during the sample was oxidized. However the second peak in DSC is unclear comparing to the first peak.

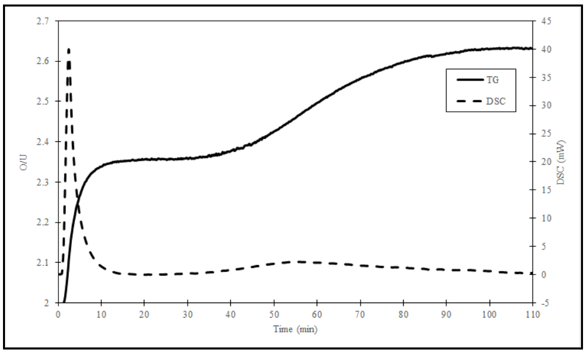

Fig. 3. The TG/DSC curves for the oxidation of UO_2 powder in dry air at 300 °C.

Table II shows the values of activation energies at 300 °C. The region of first oxidation at DSC curve could be precisely integrated to obtain the value of activation energy comparing with the region of second oxidation. Because the region of the second oxidation was not clear. The value of activation energy for the first oxidation is much higher than the value of the activation energy for the second oxidation.

Table II: The values of activation energies at each of oxidations, 300 °C

△H	First oxidation	Second oxidation	Total
kJ/mole	61.2927	27.0729	88.3656

Fig. 4 shows the curves of TG/DSC with UO_2 powder at 350 °C. Two types of oxidation were clearly observed in TG curve. Time, 900 secs, was enough for fully oxidation. The experiment at 350 °C has the distinct TG curve to see the two types of oxidation more than the experiments of other temperatures. So 350 °C was selected as a representative temperature for the experiment of phase analysis to observe the evolution of

UO_2 product discussed in section 3.3. Two exothermic peaks in DSC curve were also observed clearly during the oxidations happened. The first peak is higher than the second peak in the DSC curve.

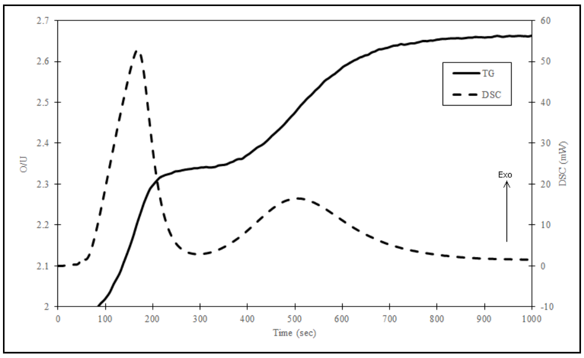

Fig. 4. The TG/DSC curves for the oxidation of UO_2 powder in dry air at 350 °C.

Table III shows the values of the activation energies at 350 °C. The values were obtained using the method which was used at the previous experiment. The value of the activation energy for the first oxidation is also higher than the second oxidation.

Table III: The values of activation energies at each of oxidations, 350 °C

△H	First oxidation	Second oxidation	Total
kJ/mole	57.3318	39.4524	96.7842

Fig. 5 shows TG/DSC curves of UO_2 powder at 400 °C. Unlike for the experiments at 300 and 350 °C, a simple weight increase of oxidation was observed in TG curve. It is supposed that two types of oxidation would become one. Because the temperature of 400 °C is too high to make two types of oxidation separately. Two exothermic peaks in DSC curve were observed. And the peaks seem to become closer than the previous experiments.

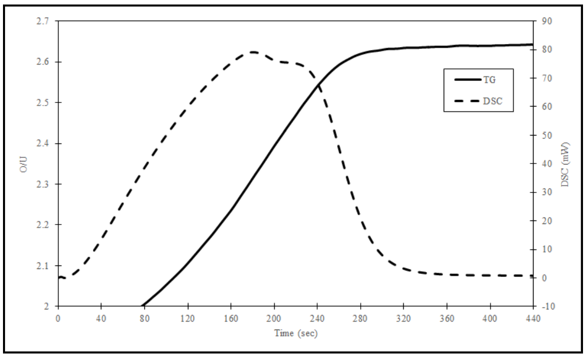

Fig. 5. The TG/DSC curves for the oxidation of UO_2 powder in dry air at 400 °C.

Table Ⅳ indicates the value of the activation energy at 400 °C. Unlike for the experiments at 300 and 350 °C, it is impossible to separate the regions between the first and the second oxidation. It is supposed that the first and second oxidation would occur together.

Table Ⅳ: The values of activation energies at each of oxidations, 400 °C

△H	First & Second oxidation	Total
kJ/mole	109.6443	109.6443

Fig. 6 shows the TG/DSC curves of UO_2 powder at 450 °C. Comparing with the result at 400 °C, a similar type of oxidation was observed in TG curve. And the time needed for the fully oxidation was similar to the experiment at 400 °C even though the temperature of 50 °C was increased. Unlike for other experiments, an exothermic peak in DSC curve was observed. It is considered that two exothermic peaks became one because the temperature was higher than others.

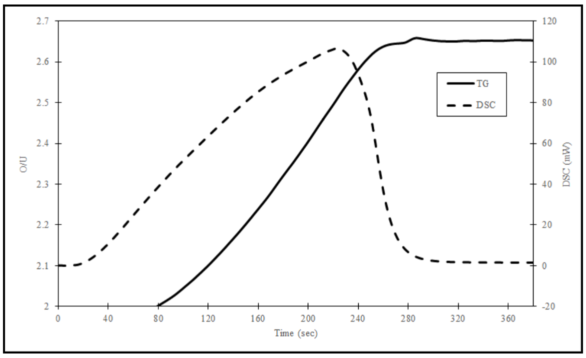

Fig. 6. The TG/DSC curves for the oxidation of UO_2 powder in dry air at 450 °C.

Table Ⅴ shows the value of the activation energy at 450 °C. The regions of the first and second oxidation seem to be one region. That means the first and second oxidation would happen almost at the same time. The value of the activation energy at 450 °C increased slightly comparing with the value of the activation energy at 400 °C.

Table Ⅴ: The values of activation energies at each of oxidations, 450 °C

△H	First & Second oxidation	Total
kJ/mole	118.2573	118.2573

3.3. Phase analysis of the products at 350 °C with increasing oxidation time

The phase change of UO_2 powder in air at 350 °C with increasing time was shown in Fig. 7. In order to compare the evolution states of the products, the XRD pattern for starting material was also given for comparison, identifying the phase as pure UO_2. In 100 seconds, there was still UO_2. U_3O_7 was observed with UO_2 in 200 seconds. In 300 seconds, UO_2 was not identified by XRD analysis. And U_3O_7 was observed in the sample as mono-phase. From 400 seconds, small peaks of U_3O_8 were observed. And the fraction of U_3O_8 phase increased with increasing time. In 800 seconds, U_3O_8 became the dominant phase in the product of UO_2 powder. As a result, it is obvious that U_3O_7 is transformed from the UO_2 and U_3O_8 is formed from U_3O_7 during the oxidation of UO_2 powder in the dry air.

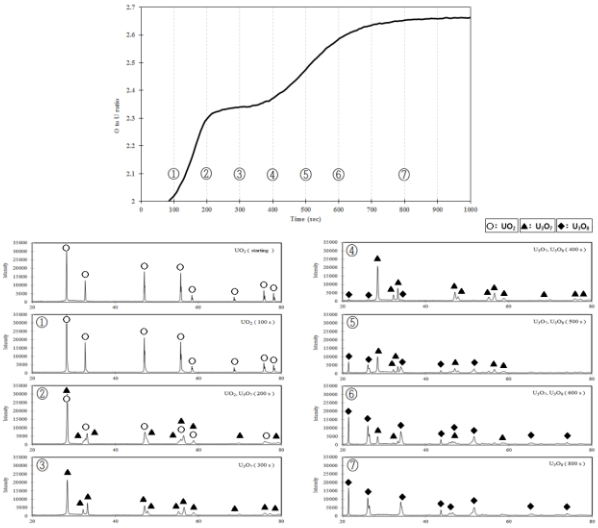

Fig. 7. Change of XRD patterns for the products of UO_2 powder heated at 350 °C in air with increasing time.

4. Conclusions

The oxidation of un-irradiated UO_2 powder in the dry air was studied according to the three kinds of experiments. The constant heating rate and the isothermal experiments were conducted using TG/DSC. And in order to analyze the phase of UO_2 products, the experiment was performed at 350 °C with the samples by using muffle furnace and XRD.

In the constant heating rate experiment, two types of oxidation; mild and rapid oxidation were observed in TG curve and two peaks in DSC curve were also presented following the two oxidations.

In the isothermal experiments were conducted at 300, 350, 400 and 450 °C. Two types of oxidations in TG curves and two regions of oxidations in DSC curves appeared at 300 and 350 °C. In contrast, a type of oxidation in TG curves and a region of oxidation in DSC curves appeared at 400 and 450 °C.

In the phase analysis of UO_2 product experiment, U_3O_7 and U_3O_8 were observed following the time. It was confirmed that U_3O_7 is formed from UO_2 and U_3O_8 is transformed from U_3O_7 in the un-irradiated UO_2 powder.

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