

Journal of Alloys and Compounds 451 (2008) 673-675

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Thermogravimetric study of the reaction of uranium oxides with fluorine

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Available online 19 April 2007

Abstract

Thermogravimetric study of the reaction of uranium oxides with fluorine was conducted by TG-DTA method using anti-corrosion type differential thermobalance. When UO₂ was heated from R.T. to 500 °C in 5% F₂/He atmosphere, the weight increase appeared at ca. 250 °C with an exothermic peak. Then the weight decreased slightly with a small exothermic peak followed by the complete volatilization with a large exothermic peak at ca. $350 \degree C$. At a flow rate of 15, 30, 60 ml min^{-1} , there seemed to be no significant change for the fluorination of UO₂. With the different heating rates of 1, 2, 5 and $10 \degree C \min^{-1}$, the fluorination peak shifted to higher temperature with increasing heating rates. For the comparison with thermogravimetric results, phase analysis by XRD method was conducted for the products obtained at different temperatures. At 260 °C, the product was UO₂ with a small amount of the intermediate compound, UO₂F. The amount of this compound increased with increasing temperature up to 320 °C. Then another phase of UO₂F₂ appeared at 340 °C but it was immediately fluorinated to the volatile fluoride. When U₃O₈ was used as a starting material, it was found that the steep weight decrease peak appeared at ca. $350 \degree C$ and the uranium volatilized completely. This result suggests that fluorination of U₃O₈ occurs at this temperature forming UF₆. Uranium trioxide showed the similar fluorination behavior to that of U₃O₈.

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Keywords: Uranium; Oxide; Fluoride; Fluorine; Thermogravimetry

1. Introduction

For overcoming the problems associated with the current hydrochemical reprocessing process for spent nuclear fuels, several pyrochemical processes are proposed and examined. Fluoride volatility process is one of such processes, which are in the plant scale development stage. In this process, fluorination of spent UO₂ fuel by fluorine is considered followed by the separation of UF₆ and PuF₆ from fission products by volatilization. Many studies on the formation of uranium fluoride such as UF₄ and UF_6 from oxides have been reported [1,2]. However, formation and fluorination of the U–O–F compounds which may appear in the fluorination of UO₂ are not well studied. Uranyl fluoride, UO₂F₂ is usually formed by the hydrolysis of UF₆ with H₂O either in the gaseous or liquid states. During the hydrolysis, several compounds such as UOF₄ [3,4], U₂O₃F₆ [5] and $U_3O_5F_8$ [5] are formed by controlling the steam pressure precisely. But uranium only takes on a hexavalent state in the above compounds since they are formed from UF₆ in oxidation conditions. On the other hand, UO₂F₂ is also formed by the reaction

0925-8388/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2007.04.099 of UO₃ with HF gas at 350 °C. And this UO₂F₂ is fluorinated to UF₆ by fluorine at 270 °C. UF₆ is obtained by the reaction of UO₂ with fluorine at 500 °C. However, the reaction of UO₂ with fluorine at lower temperature has not been studied yet. In this paper, fluorination behavior of uranium oxides, UO₂, U₃O₈ and UO₃ with fluorine was studied by thermogravimetric method using anti-corrosion type differential thermobalance.

2. Experimental

2.1. Sample preparation

 U_3O_8 was obtained by the oxidation of U metal turnings in air at 800 °C. Stoichiometric UO_2 was prepared by the H_2 reduction of U_3O_8 at 1000 °C. UO_3 was obtained by the dissolution of U_3O_8 in 1-M HNO₃ followed by heating in air at 350 °C. Analytical grade 5% F₂–He gas obtained from CENTRAL GLASS Co., Ltd. and argon gas of 99.9999% purity from Nippon Sanso Co., Ltd. were used as received.

2.2. Thermogravimetric analysis

For the thermogravimetry of the reaction of UO_x with F_2 , the RIGAKU TG-DTA system, Thermoplus 2, which was installed in a high purity argon glove box, was used. About 10 mg of uranium oxide sample was put in a Ni sample pan and set in the sample holder of TG-DTA apparatus. Before heating, the TG-DTA system was evacuated to approximately 100 Pa for 30 min and then refilled with

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Ar up to ambient pressure. After that, 5% F_2 –He gas mixture was introduced. Then the sample was heated from room temperature to 500 °C at constant rates. The heating rates were 1, 2, 5 and 10 °C min⁻¹, and the flow rates 15, 30 and 60 ml min⁻¹.

2.3. Phase analysis

For the phase analysis of the products appeared in the TG-DTA experiments, fluorination experiment with ca. 500 mg sample was carried out with the same reaction condition as those of TG-DTA. 2.4 X-ray diffraction analysis. Then the phase relation of the products was carried out by the X-ray powder diffraction with a Rigaku Type RAD-IC diffractometer using Cu K α radiation(40 kV, 20 mA) monochromatized by curved pyrolytic graphite.

3. Results and discussions

3.1. Thermogravimetry of UO_2

Fig. 1 shows the TG-DTA curves for the reaction of UO₂ with F_2 at a heating rate of 5 °C min⁻¹ with a flow rate of 30 ml min⁻¹. It is seen that the weight increases slightly (ca. 7%) at ca. 200 °C with a middle exothermic peak at 250 °C. Then a slow weight decrease with small exothermic peak between 300 and 350 °C was observed followed by the rapid weight decrease between 350 and 400 °C. At 400 °C, the weight change value is closed to -100%, i.e. the sample volatilized completely. The weight increase at 200 °C is very close to that (7.04%) of formation of UO_2F from UO_2 . As mentioned in Section 1, if UO_2F_2 is formed in F₂ atmosphere, it would be immediately fluorinated to UF₆ and be removed by sublimation. In the temperature region between 200 and 350 °C, formation of intermediate UO_xF_y and fluorination of such UO_xF_y to UO_2F_2 seems to be competitive. So, in this region, the phase relation of the product obtained at different temperatures was analyzed by powder X-ray diffraction method. The results are given in Fig. 2. From 280 to 320 °C, the main phase was UO₂, while small peaks at the high angle side of the UO₂ peaks seemed to appear. From the TG results, the amount of fluorine increased in this region. At 340 °C, the obtained sample was too hygroscopic to conduct the XRD analysis, the sample was handled in the argon glove box, i.e. sample on the XRD plate was covered by the film for avoiding the contact with moisture during the measurements. In the XRD result of 340 °C sample, new peaks at around $2\theta = 43, 46, 50$ and 55° $(\mathbf{\nabla})$ were observed as well as the peaks correspond to the UO₂



Fig. 1. TG curves obtained by the reaction of UO₂ with F_2 at a heating rate of 5 $^\circ C \mbox{ min}^{-1}.$



Fig. 2. XRD results of the products obtained by the reaction of UO₂ with F_2 at different temperatures. (\bullet) UO₂(JCPDS41-1442), (\checkmark) UO₂ F_2 , (\blacksquare) cover film.

phase (\bullet) and the cover film (\blacksquare). The peaks for new phase seem to be anhydrous UO₂F₂ [5]. In the paper of U₃O₅F₈ [6], the d values for this compound were reported. The XRD date of the prepared UO₂F₂ is given in the Fig. 3 compared with the reported values. The strongest peak of UO₂F₂ at around 16° was not observed in the 350 °C product. This suggests that once the UO₂F₂ is formed, fluorination and volatilization seems to be fast.

Since such oxyfluorides were prepared by the reaction of UF₆ with H₂O, the number of fluorine decreases from 6 to 2. In the above UO_xF_y compounds, uranium takes hexavalent and the number of fluorine, *y*, is larger than 2. But in the case of fluorination of UO₂, the obtained UO_xF_y should be x > 2 and y < 2, since UO₂F₂ is formed at ca. 350 °C and it immediately transformed to UF₆. From the above results, the fluorination of UO₂ to UF₆ by F₂ may proceeds via UO₂F, UO₂F₂.

3.2. Effects of conditions on thermogravimetry

Fig. 4 shows the effect of flow rates on the TG curves of the reaction of UO₂ with F_2 with a heating rate of 5 °C min⁻¹. The different flow rates of F_2 were 15, 30 and 60 ml min⁻¹. Since no significant difference was observed in these three TG curves, the amount of F_2 was found to be enough for the TG of the reaction of UO₂ with F_2 even at a low flow rate.

Fig. 5 shows the effect of heating rates on the TG curves of the same reaction as mentioned above. As seen in Fig. 5, these three TG curves are similar, while the curve itself shifted to



Fig. 3. XRD profile of the prepared UO₂F₂ compared with reported value.



Fig. 4. Effect of flow rates on the TG curves of the reaction of UO2 with F2.



Fig. 5. Effect of heating rates on the TG curves of the reaction of UO_2 with F_2 .



Fig. 6. TG curves obtained by the reaction of U_3O_8 and UO_3 with F_2 at a heating rate of 5 $^\circ$ C min⁻¹.

the higher temperate region with increasing heating rate. This suggests that the reaction rate of fluorination is slow compared with the heating rate.

3.3. Thermogravimetry of UO_3 and U_3O_8

Fig. 6 shows the TG curves for the reaction of UO_3 and U_3O_8 by F_2 with a flow rate of 30 ml min⁻¹ at a heating rate

of 5 $^{\circ}$ C min⁻¹. TG curve for UO₂ obtained with the same conditions is also shown for comparison. In the case of UO₃, it is seen that sharp weight decrease appears at ca. 350 °C, and the sample volatilizes completely, i.e. formation and sublimation of UF₆. If oxygen in UO₃ is replaced by fluorine without vaporization, the weight should be increased. However, no significant weight increase was observed before the weight decrease at ca. $350 \,^{\circ}$ C. When the sample was UO₂F₂, similar TG curve was obtained. From these results, it is suggested that the UO₃ reacts with F_2 forming UO₂ F_2 first, but the fluorination of UO₂ F_2 to UF₆ is too fast to keep it as a stable intermediate product. In the case of U_3O_8 , TG curve was found to be similar to that for UO₃. However, the slight weight increase of the TG curve for U₃O₈ at temperatures between 300 and 350 °C suggests the difference in fluorination behavior between U₃O₈ and UO₃. This is caused by the oxidation of tetravalent uranium in U_3O_8 to hexavalent.

4. Conclusion

To investigate the fluorination of UO₂ in spent fuel by fluoride volatility process, fluorination behavior of uranium oxides, such as UO₂, U₃O₈ and UO₃ with fluorine was studied by thermogravimetric method using anti-corrosion type differential thermobalance at temperatures from R.T. to 500 °C in 5% F₂/He atmosphere. The obtained results are as follows;

- (1) Formation of an intermediate oxyfluoride UO_xF_y (x>2, y<2) seemed to occur at ca. 300 °C with an exothermic reaction.
- (2) Complete volatilization with a large exothermic reaction was observed at ca. 350 °C, which corresponds to the formation and sublimation of UF₆.
- (3) The effect of heating rate on thermogravimetry was significant but that of flow rate was not.
- (4) Both U_3O_8 and UO_3 show similar fluorination behaviours which have the formation and sublimation of UF₆ at ca. $350 \,^{\circ}\text{C}$.

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