

Oxidation Behavior of U-0.75 wt% Ti Chips in Air at 250-500°C

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Abstract—A study was conducted on the oxidation behavior of U-0.75 wt% Ti chips (Depleted Uranium, DU chips) using an XRD and a thermogravimetric analyzer in the temperature range from 250 to 500°C in air. At the temperature lower than 400°C, DU chips were converted to UO_2 , U_3O_7 and U_3O_8 whereas at the temperature higher than 400°C, DU chips were completely converted to U_3O_8 , the most stable form of uranium oxide. The activation energy for the oxidation of DU chips is found, 44.9 kJ/mol and the oxidation rate in terms of weight gain (%) can be expressed as;

$$dW/dt = 8.4 \times 10^2 e^{\left(\frac{-44.9 \text{ kJ/mol}}{RT}\right)} \text{ wt\%/min} \quad (250 \leq T(^{\circ}\text{C}) \leq 500)$$

where W=weight gain (%), t=time and T=temperature.

1. Introduction

Depleted Uranium (DU) is a by-product of the process by which the fissionable isotope U-235 is extracted from natural uranium, and thus can be considered a by-product of the nuclear industry. From an engineering standpoint, the most singular property of uranium is its high density - almost twice that of lead, and nearly as high as those of gold and tungsten. Because of this high density, there are three principal non-nuclear uses of DU: radiation shielding; counterweights in airplane, helicopters and missiles; and armor-piercing projectiles for military ordinance¹⁾. These manufactures of DU metal generate chips and scraps. The chips are pyrophoric and oxidize rapidly when exposed to air; therefore, long-term storage of the uranium chips presents a major fire hazard. The pyrophoric nature of the metal chips requires the material to be converted into a stable form which is safe to handle during shipment and subsequent disposal. Lemons *et al.*²⁾ reported in their report on "The Ultimate Disposition of Depleted Uranium" that U_3O_8 , the most inert chemical form of uranium, could be stored safely. But DU chips oxidize rapidly and their heat of oxidation is very high (4.199 kJ/g, U_3O_8). The information of oxidation mechanism is very important for treatment of DU chips.

The knowledge of the oxidation behavior of uranium metals is required to evaluate stability in the long-term storage and the disposal of spent fuels and to stabilize the uranium metal chip waste which is generated during its manufacturing. There have been many studies on the oxidation of uranium metals³⁻¹⁰⁾ and some uranium alloys¹¹⁻¹⁵⁾. Lories³⁾ carried out research on the oxidation of metallic uranium. He reported that the oxidation rate of uranium was nearly parabolic at ordinary temperatures and was linear at burning temperatures. Leibowitz *et al.*^{4,5)} studied the oxidation rates in the temperature range from 125 to 250°C and at oxygen pressures between 20 and 800 mmHg. They revealed some differences in oxidation behavior between the electropolished and the mechanically polished uranium samples. Bennett *et al.*^{7,9)} carried out an experiment to investigate the influence of aluminum content and water vapor on uranium oxidation in air. Also they investigated the influence of swelling on the rate of oxidation of irradiated and unirradiated uranums by comparing with each other. There was no significant influence when the content of aluminum was 500-1550 ppm. Water vapor increased the oxidation rate at 100-200°C by up to a factor of 7.5. However, there were no significant influences of water vapor at 50, 75 and 300°C. Ritchie¹⁰⁾ reviewed the reactions of uranium with oxygen and

water vapor under various conditions. He reported that the rate of reaction was strongly dependent on the nature of the uranium surface i. e. on the thickness, adherence and stoichiometry of the surface oxide-layer and among various techniques to measure the rate of uranium corrosion weight gain measurements were the most common. Antill *et al.*⁽¹¹⁾ reported for the oxidation of uranium alloys in carbon dioxide and in air that additions of titanium, molybdenum, niobium and copper reduced the attack in air at 500°C by factors up to 200, whereas the silicon alloys had a high rate of attack in carbon dioxide at most temperatures. Greenholt *et al.*⁽¹²⁾ carried out the oxidation of uranium-0.75 wt% titanium in environments containing oxygen and/or water vapor at 140°C. He reported that U-0.75Ti reacted with oxygen to form uranium dioxide and the reaction rate which was approximately 3.2×10^{-3} mg/cm²-h, was linear and independent of the oxygen pressure between 0.067 and 133.3 kPa.

In the present paper, the oxidation behavior of DU chips was studied with XRD and a thermogravimetry in the temperature range of 250-500°C in air to stabilize the uranium metal chip waste. The activation energy and the oxidation rate for the DU chips were determined.

2. Experimental

2-1. Apparatus

The experimental apparatus (thermogravimetric analyzing device) for oxidation mainly consists of a furnace, an electric balance, a control and data acquisition system and a conditioning system for the furnace. The schematic diagram of the apparatus is shown in Fig. 1. Temperature of the furnace could be controlled with any mode of heating by a programmable microprocessor. The crucible was made of alumina to avoid reaction of the specimen with the crucible during the experiment.

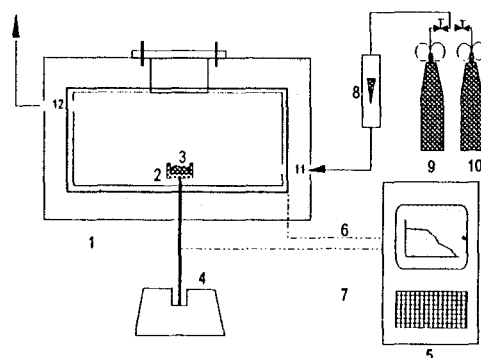
2-2. Specimens

Samples having a dimension of 10.0 mm in length, 1.2 mm in width and 0.3 mm in thickness were cut off from depleted uranium chip waste. About 2 g of chip waste was used on each oxidation experiment.

The shape of the chip before the oxidation experiment was shown in Fig. 2, and the ultimate analysis was conducted on the DU chips (Table 1).

2-3. Experimental Procedure

The samples were contained in alumina crucibles and heated up to the test temperature in a flow of purified argon before the oxidation. For the oxidation



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

Fig. 1. A schematic diagram of the thermogravimetric furnace.

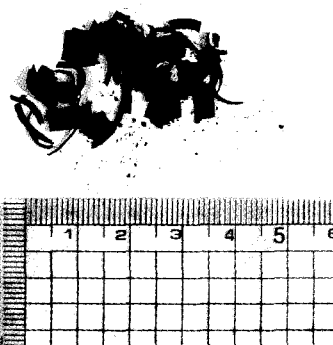


Fig. 2. Shape of sample before oxidation experiment.

Table 1. Ultimate analysis of the DU chips.

No	Ti(%)	Mo (ppm)	Zr (ppm)
1	0.74	< 20	< 20
2	0.75	85	39
3	0.77	< 20	< 20

tests, the oxidant (air) was continuously injected. The weight gains of the samples were measured by microbalance having a load-carrying capacity of 5 g of samples and sensitivity of 1 μ g, and the data were automatically acquired and stored along with the time and the temperature during the oxidation. The flow rate of oxidizing gas was 10 l/min at an atmospheric pressure.

3. Result and discussion

3-1. Reaction and XRD Patterns

There have been many studies on the oxidation of uranium metal, UO_2 , and some uranium alloys. It is generally known that the specimen of uranium and its alloy during oxidation are broken into some pieces of thin plates and blocks and fine powder. Baker *et al.*⁶⁾ reported for metallic uranium that in the low temperature region, below 400°C, there is a thin adherent layer, covered by an oxide which is loose and flaky tending to form well defined plates. For the high temperature runs, above 625°C, the underlying oxide is also very adherent, but appears somewhat sintered, while the surface oxide powders off quite readily.

After complete oxidation, the samples of DU chips broke into some pieces in the low temperature region (250-300°C), powder in the middle temperature region (350-400°C) and fine powder in the high temperature region (450-500°C). Fig. 3 shows the shapes of samples after oxidation at different temperatures, 300, 400 and 500°C.

In the present study, the oxide forms of DU chips after oxidation were conformed by analyzing XRD patterns. After complete oxidation DU chips were converted to UO_2 , U_3O_8 , and U_2O_7 in the temperature range 250-300°C, U_3O_8 and U_2O_7 in the temperature 350°C. At the temperature higher than 400°C DU chips were completely converted to U_2O_7 . Fig. 4 shows XRD results after oxidation at the temperatures of 250, 300, 350 and 400°C, respectively.

3-2. Oxidation Rates

The oxidation rates of uranium and its alloys are various, which could be linear, parabolic and parabolic-linear, depending on oxidation conditions. The factors that affect the oxidation rate are temperature, mois-

ture content, impurity, oxygen potential, roughness of surface, surface area versus volume ratio, irradiation-induced swelling and so on. Bennett *et al.*^{7,9)} reported that temperature had the most pronounced effect and the temperature change from 50 to 300°C increased the rate of oxidation by a factor of over 10⁶. Greenholt *et al.*¹²⁾ reported for uranium-0.75 wt% titanium that the reaction rate is linear and independent of the oxygen pressure between 0.067-133.3 kPa. Fig. 5 shows oxidation data obtained at the temperature range 250-500°C in air.

At 250-300°C the rate of oxidation was nearly

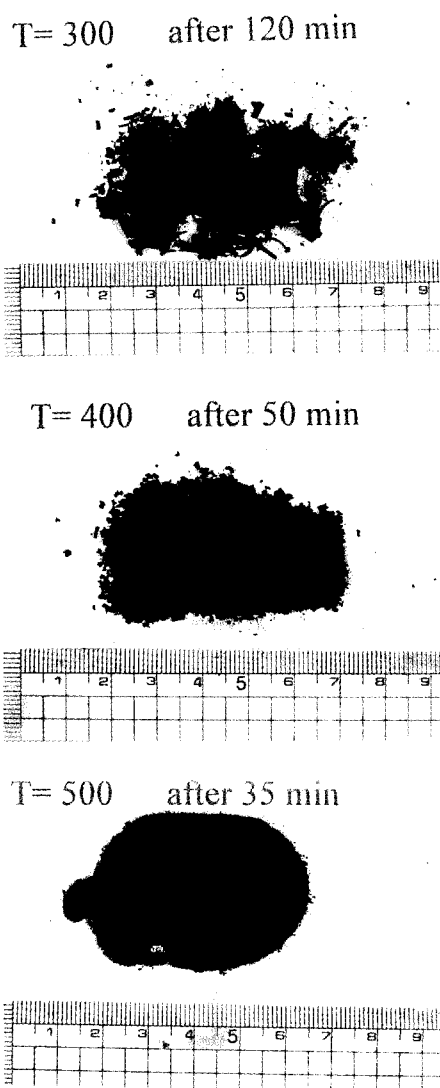


Fig. 3. Shapes of samples after oxidation.

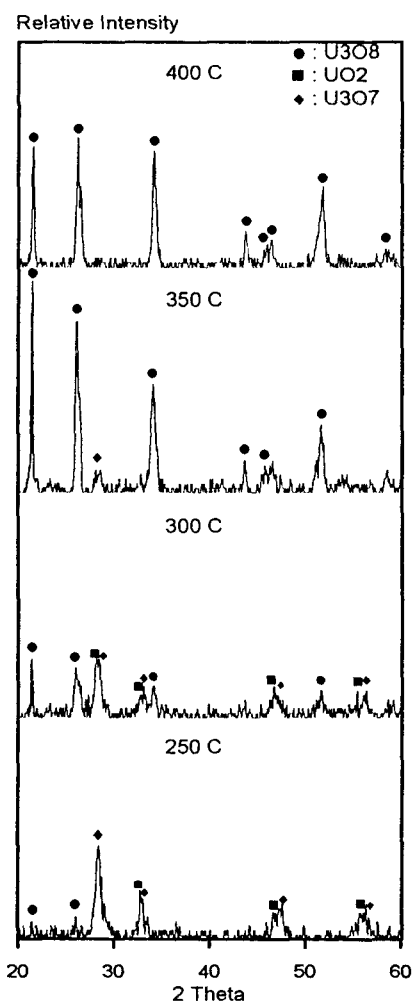


Fig. 4. XRD patterns of products after oxidation.

linear and decreased slightly with time because the product layer formed acts as a protective barrier to the entry of oxygen. Therefore the oxidation process can be said to be controlled by the diffusion of oxygen into the surface of the solid phase rather than chemical reaction kinetics as one of the typical phenomena of the solid-gas reaction at the temperatures used in this study. For the temperature range over 350°C, the oxides formed at the surface of specimens acted as protective layer and were not porous at initial stage. At the middle stage the oxide formed at the surface of specimen was porous and the oxidation rate was increased. At the final stage the protective layer of oxide was blistered and cracked, thus the profile of weight gain percent-time

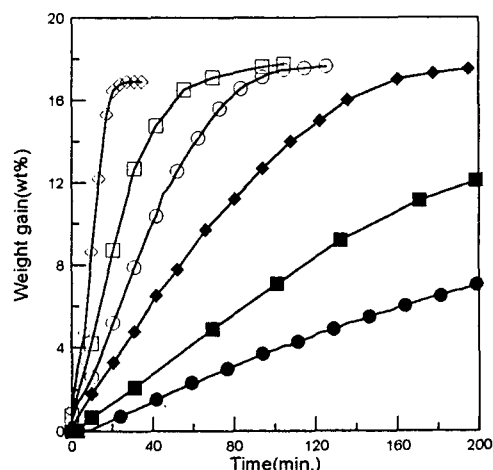


Fig. 5. Weight gain (%) - time curves for the oxidation in air at 250-500°C.

Table 2. Oxidation rates of DU chips with air.

Temp.	rate of oxidation, wt%/min		
	10 wt% weight gain	U ₃ Si	UMo
250	0.0288	0.0002	
300	0.065	0.001	0.394
350	0.15	0.008	0.457
400	0.256	0.023	0.5
450	0.43		0.626
500	0.882		0.68

curve becomes an S-shape.

To observe the reaction rate of DU chips with variation of temperature, the reaction rates, become 10 wt% gains of the DU chips are shown in Table 2.

The weight gain (%) against the inverse of temperature is plotted and shown in Fig. 6. With an Arrhenius type of expression for the rate equation, the frequency factor and activation energy was found. Activation energy for the 10 wt% gain of the DU chips was 44.9 kJ/mol in the temperature range 250-500°C. Ritchie⁽¹⁰⁾ reported for uranium metal in his review of the reaction rates of uranium with oxygen that the activation energy in the temperature range 40-300°C is 75.312 kJ/mol. In our previous study^(13,16) the activation energy of U₃Si in the temperature range 300-400°C was 69.65 kJ/mol and the activation energy of U-Mo chips in the temperature range 300-500°C was 10.08 kJ/mol. The activation energy of DU chips was smaller than that of U₃Si but higher than that of U-

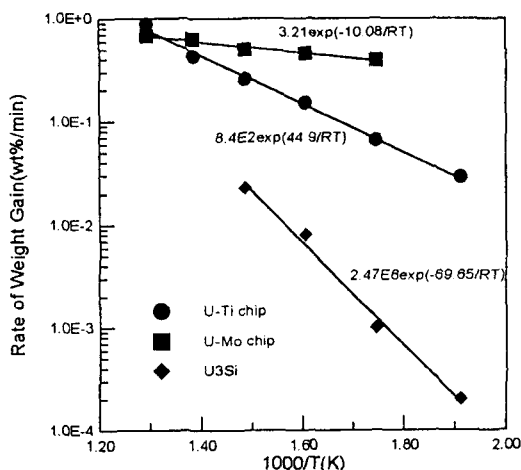


Fig. 6. Rate of Weight gain (%) versus $1000/T$.

Mo chips which was obtained at the same experimental condition. The reaction rate can be expressed as follows:

$$dW/dt = 8.4 \times 10^2 e^{\left(\frac{-44.9 \text{ kJ/mol}}{RT}\right)} \text{ wt\%/min}$$

$$(250 \leq T(^{\circ}\text{C}) \leq 500)$$

where W, t and T are weight gain (%), time and temperature, respectively.

4. Conclusion

Analyses of XRD patterns and thermogravimetry in order to observe the oxidation behavior of DU chips have been carried out and the following conclusions are made.

(1) The samples after complete oxidation break to several pieces, powder and fine powder.

(2) From XRD study, at the temperature lower than 400°C, DU chips were converted to UO_2 , U_3O_8 and U_2O_7 and whereas at the temperature higher than 400°C, DU chips were completely converted to U_3O_8 .

(3) From thermogravimetry analysis, the oxidation kinetics is S-shape.

(4) The activation energy for the oxidation of DU chips is 44.9 kJ/mol.

(5) The oxidation rate can be expressed as;

$$dW/dt = 8.4 \times 10^2 e^{\left(\frac{-44.9 \text{ kJ/mol}}{RT}\right)} \text{ wt\%/min}$$

where W, t and T are weight gain (%), time and temperature, respectively.

References

1. Paul Loewenstein: Industrial Uses of Depleted Uranium, Metal Handbook.
2. T.R. Lemons: The Ultimate Disposition of Depleted Uranium, Martin Marietta Energy System, Inc., Report K/ETO-44 (1990).
3. J. Loria: Oxidation of Metallic Uranium, AEC Research and Development Report HW-61493 (1959).
4. L. Leibowitz, J.G. Schnitzlein, L.W. Mishler and R. C. Vogel: *J. Electrochem. Soc* 108, 1153 (1961).
5. L. Leibowitz, J.G. Schnitzlein, J.D. Bingle, and R.C. Vogel: *J. Electrochem. Soc* 108, 1155 (1961).
6. L. Baker, J.R. and J.D. Bingle: *J. Nucl. Mater.* 20, 11 (1966).
7. M.J. Bennett, B.L. Myatt and J.E. Antill: *J. Nucl. Mater.* 50, 2 (1974).
8. M.J. Bennett, B.L. Myatt, D.R.V. Silvester and J.E. Antill: *J. Nucl. Mater.* 50, 2 (1974).
9. M.J. Bennett and B.L. Myatt: *J. Nucl. Mater.* 66, 37 (1977).
10. A.G. Ritchie: *J. Nucl. Mater.* 102, 170 (1981).
11. J.E. Antill and K.A. Peakall: *J. Less-Common Metals*, 3, 239 (1961).
12. C.J. Greenholt and L.J. Weirick: *J. Nucl. Mater.* 144, 110 (1987).
13. K.H. Kang, K.S. Kim, K.J. Kim, Y.C. Seo and Y.M. Park: *J. Nucl. Mater.* 228, 220 (1996).
14. G.A. Rama Rao, V. Venugopal and D.D. Sood: *J. Nucl. Mater.* 209, 161 (1994).
15. K.H. Kang, K.J. Kim, H.K. Shin, C. Kim and Y.M. Park, "Oxidation Behavior of U-10 wt% Zr Alloy in Air at 300-500°C", *J. Nucl. Mater.* (submitted).
16. K.H. Kang, K.J. Kim, H.K. Shin, C. Kim and Y.M. Park, "A Preliminary Study for the Design of Air-Controlled Oxidizer for Treatment of Depleted Uranium Chip Waste", *J. Nucl. Mater.* (submitted).