ELSEVIER

Journal of Nuclear Materials 305 (2002) 106–111

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Processing of uranium oxide powders in a fluidized-bed reactor. I. Experimental

W.D. Cho [a,*], Man-Hee Han [a], Mark C. Bronson [b], Yury Zundelevich [b]

[a] Department of Metallurgical Engineering, University of Utah, Salt Lake City, UT 84112, USA
[b] Lawrence Livermore National Laboratory, University of California, Livermore, CA 94551, USA

Received 12 March 2002; accepted 24 July 2002

Abstract

The oxidation of UN powders was carried out in a spout-type fluidized-bed reactor in gas mixtures of oxygen and argon, and over the temperature range of 200–500 °C. The rate of the conversion from UN to U_3O_8 powders was measured using gas chromatography and found to be dependent on temperature, partial pressure of oxygen and gas flowrate. The solid reactants and products were analyzed using SEM and XRD. Based on the experimental results, the conversion process was explained by the crackling core model.

© 2002 Elsevier Science B.V. All rights reserved.

PACS: 28.41.Kw; 81.65.Mq; 82.80.B

1. Introduction

Options have been sought to convert uranium and plutonium metal to oxide in a safe, speedy and controllable manner. One option begins with uranium or plutonium that is converted to hydride in order to separate the metal from other materials. The hydride is then converted to a nitride to allow for safe oxidation. Conversion of the nitrides to oxides has been performed in fixed bed reactors but conversion rates are slowed due to poor heat transfer in the oxide bed and the desire to maintain a flowable oxide product. Fluidized bed reactors have been proposed to enhance heat transfer and maintain flowable oxide product with high conversion rates. This paper describes the experimental details of the work performed on the conversion of uranium nitride into uranium oxide in a fluidized bed reactor.

There have been very few studies for the oxidation and nitrogenation of uranium. The kinetics of uranium oxidation in CO_2 [1], and in dry air and moist air [2] were investigated over a wide range of temperature. The formation of uranium nitride by the reaction of uranium hydride with nitrogen and ammonia has been studied using the thermogravimetry technique [3]. The oxidation of UN and UC was investigated using the thermogravimetry method in the temperature range of 230–270 °C under various oxygen partial pressures. It was observed that the oxidation kinetics were independent of oxygen pressure and the final product was UO_3. It was also found that U_2N_3 and UO_2 were formed as intermediate species during the oxidation of UN [4]. An experimental study was completed on the thermal ignition of UN and UC in oxygen and air. The product was found to be U_3O_8 [5].

The purpose of this research is to investigate various aspects of fluidized-bed oxidation of uranium nitride powder. This paper covers the kinetics of the conversion of uranium nitride to uranium oxide as a function of temperature, gas flowrate and oxygen concentration in the fluidizing gas.

2. Experimental

Several pieces of pure uranium metal were provided by the Lawrence Livermore National Laboratory

---

[*] Corresponding author. Tel.: +1-801 581 6278/6386; fax: +1-801 581 4937.

E-mail address: w.cho@m.cc.utah.edu (W.D. Cho).

0022-3115/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(02)01135-2

(LLNL). These uranium pieces were sectioned into smaller pieces, which were used to prepare uranium nitride powder (UN). The processing of uranium nitride powder consists of three steps: (1) reaction of uranium with hydrogen at 250 °C to form uranium hydride, (2) reaction of uranium hydride with nitrogen at 400 °C to form uranium nitride ($UN_{1.73}$), and (3) conversion of $UN_{1.73}$ to UN at 1350 °C under argon atmosphere. The three steps can be represented by the following chemical reactions:

(1) $U(s) + \frac{3}{2}H_2(g) \rightarrow UH_3(s)$,
(2) $UH_3(s) + \frac{1.73}{2}N_2(g) \rightarrow UN_{1.73}(s) + \frac{3}{2}H_2(g)$,
(3) $UN_{1.73}(s) \rightarrow UN(s) + \frac{0.73}{2}N_2(g)$.

It was confirmed by XRD analysis shown in Fig. 1 that the final product was fine uranium nitride (UN) powder. The particle size of the UN powders was analyzed using Microtrac particle size analyzer model 7995-30 and the average particle size was found to be 7 μm. Fig. 2 is a SEM micrograph showing the UN powder. The UN powders were kept in a vacuum-sealed desicator. The UN powder is stable in air at room temperature without ignition. However, it ignited around 70 °C in air. It was also observed that the intermediate product uranium nitride ($UN_{1.73}$) was ignited in air at room temperature.

Experiments for the conversion of uranium nitride to uranium oxide were carried out using a fluidized bed. Fig. 3 illustrates the experimental apparatus, which consists of a high-temperature fluidized-bed reactor, a system for controlling the composition of gaseous reactant mixtures, and a gas chromatograph (GC) to analyze the output gases. The fluidized-bed reactor is made of a quartz tube with an inner diameter of 4.5 cm and length of 120 cm and a porous quartz frit (pore size 40–60 μm) as a gas distributor plate.

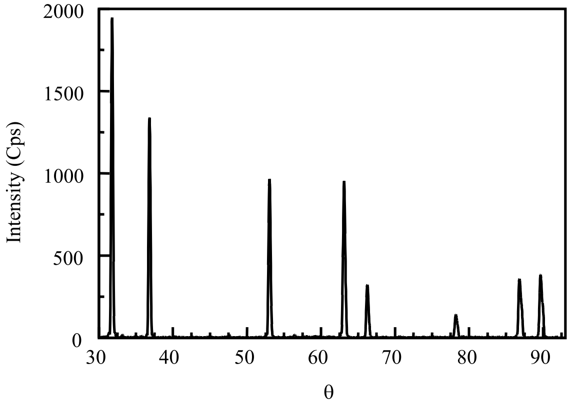

Fig. 1. X-ray diffraction pattern of UN powders.

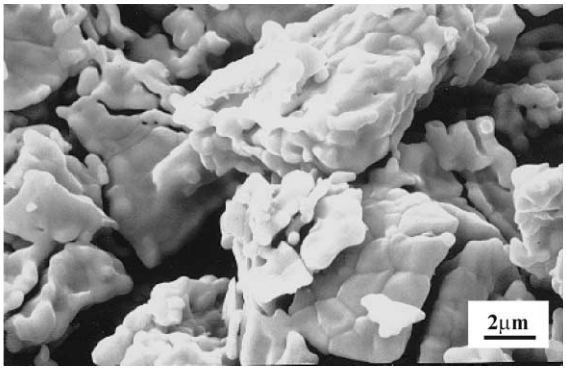

Fig. 2. SEM micrograph of UN powders.

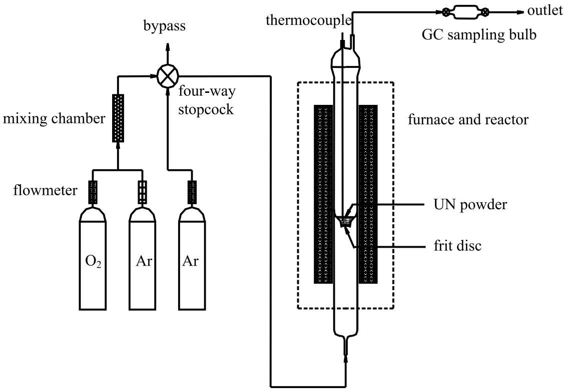

Fig. 3. Experimental apparatus for a fluidized-bed reactor system.

The reactor was charged with about 20 g of UN powder and argon gas was passed for sufficient time to flush out all the air from the quartz tube reactor. The nitride powder was fluidized when the argon gas flow rate reached 0.44 l/min. The furnace power was turned on and argon gas flow was maintained until the desired temperature was reached. When the nitride bed was at the desired temperature the Ar gas was replaced by an Ar–O_2 gas mixture and oxidation of the uranium nitride was initiated. A K-type thermocouple was embedded into the sample powders for temperature measurements. The outlet from the reactor was connected to a water trap to remove very fine entrained solids. The experimental variables included temperature, gas flow rate and oxygen partial pressure. The final product was analyzed using XRD and SEM.

The flue gas from the fluidized-bed reactor during the conversion of UN powder was analyzed by a GC using a molecular sieve column. The GC was calibrated using several known gas mixtures including air and various mixtures of oxygen and nitrogen. Helium was used as a carrier gas for the GC. The gas samples were collected from the sampling bulb using a syringe of 1 ml volume and were injected to the GC. The GC was connected to a

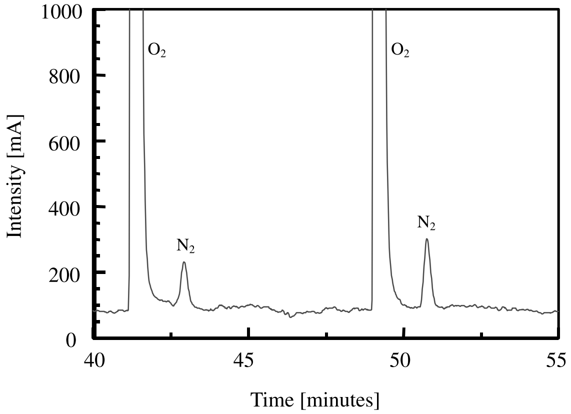

Fig. 4. Oxygen and nitrogen peaks obtained from GC.

personal computer (PC) to monitor the change of gas composition with time. Fig. 4 shows a typical example of oxygen and nitrogen peaks obtained from GC analysis. The peaks were obtained continuously and the areas under the peaks were calculated using the Peaksimple Software program.

3. Results and discussion

3.1. Characterization of product

The final product was found to be mostly U_3O_8 at all experimental conditions studied in this project. Fig. 5 is an example of XRD patterns for the product powders containing principally U_3O_8, with small amounts of U_3O_7 and unreacted UN. Fig. 6 presents a SEM image of uranium oxide particles converted from UN at 200 °C with 2.5% O_2. It was noticed that the volume of the powder bed significantly increased after the conversion. Indicating that the bulk powder density of the uranium oxide was less than that of the uranium nitride powder.

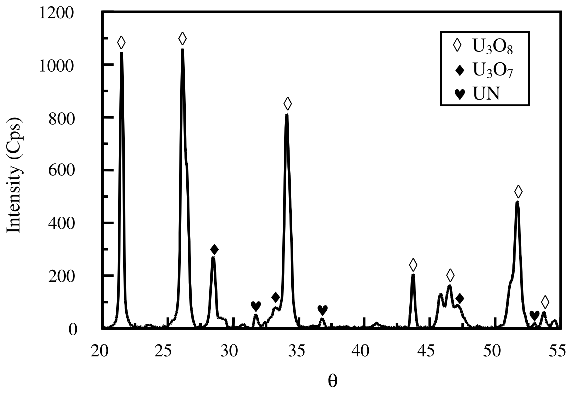

Fig. 5. XRD pattern of powders after conversion of UN into U_3O_8.

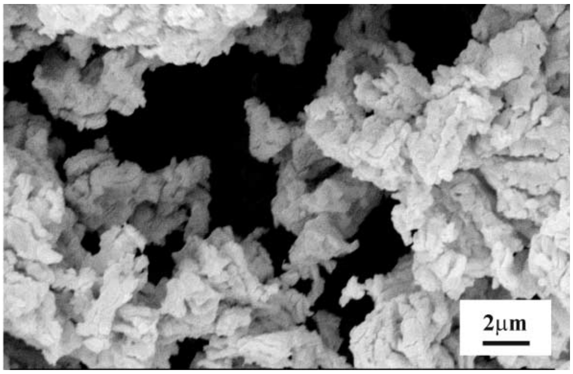

Fig. 6. SEM micrograph of U_3O_8 powders.

3.2. Calculation of conversion rate

As described in the experimental section, nitrogen and oxygen peaks during the conversion are obtained as a function of time using gas chromatography. The amounts of nitrogen and oxygen in the output gas were determined by measuring the area under the peaks. The extent of conversion of uranium nitride to uranium oxide was calculated based on the amounts of oxygen consumed and nitrogen produced, and the following stoichiometric equation for the conversion.

$$\mathrm{UN(s)} + \tfrac{4}{3}\mathrm{O_2(g)} = \tfrac{1}{3}\mathrm{U_3O_8(s)} + \tfrac{1}{2}\mathrm{N_2(g)}. \tag{1}$$

The mole fraction of nitrogen, X_{N_2}, in the output gas can be expressed by

$$X_{N_2} = \frac{n_{N_2(f)}}{n_{O_2(f)} + n_{N_2(f)} + n_{Ar(f)}} \tag{2}$$

and can be obtained from GC analysis. The values $n_{O_2(f)}$, $n_{N_2(f)}$ and $n_{Ar(f)}$ are the molar volume concentrations of nitrogen, oxygen and argon in the output gas, respectively.

Using the stoichiometric constants in Eq. (1), $n_{O_2(f)}$ and $n_{Ar(f)}$ can be related to the molar volume concentrations of oxygen and argon in the input gas, $n_{O_2(i),}$ and $\mathrm{n}_{Ar(i)}$.

$$n_{O_2(f)} = n_{O_2(i)} - \tfrac{8}{3}n_{N_2(f)}, \tag{3}$$

$$n_{Ar(f)} = n_{Ar(i)}. \tag{4}$$

Substituting Eqs. (3) and (4) into Eq. (1), the following equations are obtained:

$$X_{N_2} = \frac{n_{N_2(f)}}{n_{O_2(i)} - \tfrac{5}{3}n_{N_2(f)} + n_{Ar(i)}}, \tag{5}$$

$$n_{N_2(f)} = \frac{X_{N_2}(n_{O_2(i)} + n_{Ar(i)})}{1 + \frac{5}{3}X_{N_2}}. \tag{6}$$

Accordingly, the molar volume concentration of nitrogen in the output gas can be calculated from the determined mole fraction of nitrogen in the output gas using Eq. (6). Since the gas flowrate is a known constant value, once molar volume concentration of nitrogen in the output gas is determined as a function of time, the moles of U_3O_8 produced and the moles of UN reacted can be obtained as a function of time. Thus, the percent of conversion of UN to U_3O_8 can be calculated using the following equation.

$$\%\text{Conversion} = \frac{\text{moles of UN reacted}}{\text{initial moles of UN}} \times 100. \tag{7}$$

3.3. Effect of temperature

The effect of temperature on the rate of conversion of UN powders is presented in Fig. 7. The rates of the nitride conversions were measured at three different temperatures using a mixture of 2.5% O_2 in argon. It is clearly observed that the rate of the conversion increases with increasing temperature. Typically, these conversion versus time curves exhibit a sigmoidal (S) shape and consist of three stages: initial slow conversion, rapid conversion in the middle stage, and slow conversion at the end. It is evident that higher temperature results in a higher conversion rate. The sigmoidal shaped conversion–time behavior may not be represented by the shrinking core model, but rather by a crackling core model, which will be discussed in a subsequent section.

3.4. Effect of oxygen concentration

Data on the effect of the oxygen partial pressure is important in determining the mechanism of the conversion process. Experiments were conducted at 200 °C under mixtures of oxygen with argon to obtain five different oxygen partial concentrations. As shown in Fig. 8, an increase in oxygen concentration in the reactive gas results in a significant increase in the overall conversion rate. As expected, more oxygen will be adsorbed on the surface of the particle in the environments containing higher oxygen concentration, increasing the kinetics of the reaction and thus increasing the overall conversion rate.

3.5. Ignition of UN powders

Uranium dinitride ($UN_{1.73}$) powder prepared at 450 °C was liable to ignite on exposure to air at room temperature, presumably because of its large specific surface area. The ignition was recognized by the observation of red flame in the pack of the powders. Uranium mononitride (UN) powder prepared at 1350 °C was stable at room temperature, it ignited around 70 °C in air.

Ignition experiments on UN powder were carried at two different oxygen partial pressures at 200 °C, as shown in Fig. 9. One significant difference was observed between the two experiments. With 10% O_2, ignition did not occur until the oxidation had proceeded for about 15 min (~10% conversion). However, with 15% O_2, ignition occurred shortly after the reactive gas started blowing into the bed. Ignition of the uranium nitride powders should be a function of particle size, oxygen partial pressure, and gas velocity. The conversion of UN is much faster with ignition than the conversion without ignition shown in Fig. 8.

3.6. Effect of gas flowrate

The effect of gas flowrate on the conversion of UN has been measured using three different gas flowrates

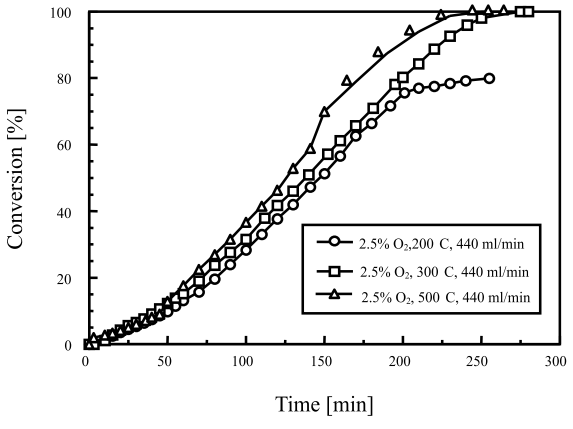

Fig. 7. Effect of temperature on conversion of UN into U_3O_8.

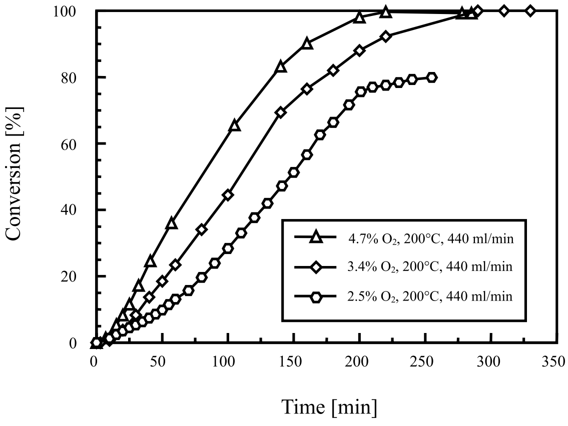

Fig. 8. Effect of oxygen concentration on conversion of UN into U_3O_8.

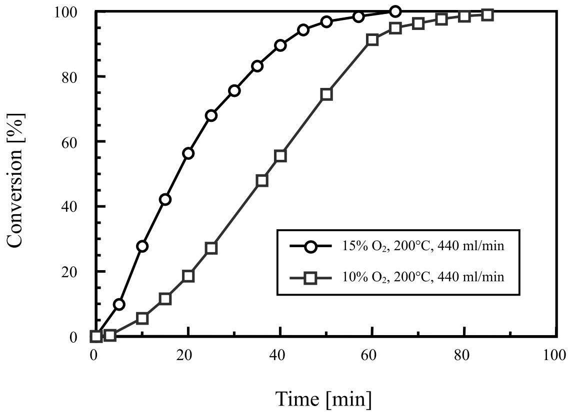

Fig. 9. Conversion of UN into U_3O_8 with ignition.

440, 530, and 650 $\mathrm{ml\,min^{-1}}$. The temperature was maintained constant at 200 °C. The experimental results are presented in Fig. 10. As shown in the figure, the conversion rate is increased with increasing gas flowrate. This finding simply indicates that the reaction rate is being limited by the available oxygen.

3.7. Reaction mechanism

Numerous kinetic models have been proposed and developed to explain gas–solid reactions based on characteristics of solid reactants and products, for example, the shrinking core model [6] for non-porous solids, the volume reaction model [7] for porous solids and the grain model for solids composed of grains [8]. More recently, the crackling core model was proposed by Park and Levenspiel to account for the sigmoidal behavior of conversion vs. time plots for some gas–solid reactions [9]. The model is basically an extension of the shrinking core model and views the particle to be initially non-porous. Under the action of reactant gases, the particle transforms progressively from the outside in, by crackling and fissuring, to form an easily penetrated porous grainy material, which then reacts away to the final product according to the shrinking core model. Therefore, in this model the reaction is assumed to occur in two steps:

(i) A (non-porous solid reactant) → A′ (grainy or porous intermediate).
(ii) A′ (grainy or porous intermediate) → A″ (grainy or porous product).

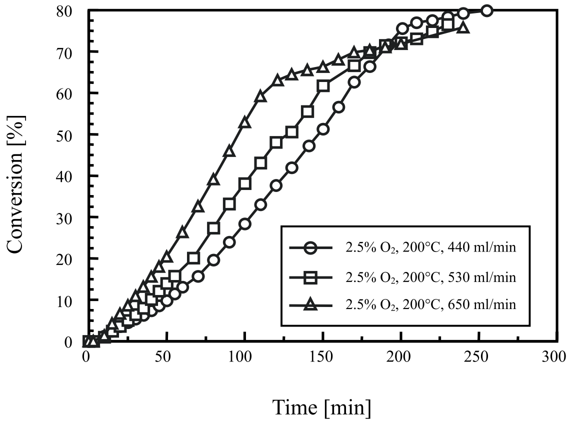

Fig. 10. Effect of gas flowrate on conversion of UN into U_3O_8.

The first stage is a physical transformation of A from a non-porous structure to a more reactive porous structure which then undergoes a reaction according to the second step. The model has been successfully used to represent a situation where the reaction of solid occurs in two consecutive steps. For example, the reduction of hematite to iron takes several steps in order of hematite (Fe_2O_3), magnetite (Fe_3O_4), wustite (FeO) and iron (Fe).

As shown in SEM micrographs for UN (Fig. 2) and U_3O_8 (Fig. 6) powders, UN powders are non-porous while UO_2 powders have pores and cracks. XRD analyses for the products shown in Fig. 5 indicate the presence of U_3O_7 which may be one of the intermediate species during the conversion. With the XRD and morphological analysis, the distinctly sigmoidal shape of the conversion–time curves as shown in Fig. 8 may suggest that the conversion of UN to U_3O_8 can be represented by the crackling core model with reaction control.

In addition, it should also be noted that the gas phase mass transfer through pores may also play an important role for the conversion process because the conversion rate is influenced by the gas flow rate.

4. Summary

The kinetics of oxidation of uranium nitride powders with O_2/Ar mixtures was determined in a fluidized bed using gas chromatography. The initial solid reactant and the final solid product were UN and U_3O_8, respectively. The conversion rate was found to increase with increasing oxygen concentration, temperature and gas flowrate. It can be concluded that both chemical reaction and gas phase pore diffusion control the conversion process. The crackling core model may be applied to the conversion kinetics in light of sigmoidal behavior of conversion–time plots and morphologies of solid reactants and products.

Acknowledgements

This work was performed under a contract with the US Department of Energy through the Lawrence Livermore National Laboratory.

References

[1] R.M. Alire, A.W. Czanderna, R.L. Wittaker, J. Nucl. Mater. 66 (1977) 112.

[2] G.W. McGillivray, D.A. Geeson, R.C. Greenwood, J. Nucl. Mater. 208 (1994) 81.

[3] H. Tagawa, Bull. Chem. Soc. Jpn. 46 (1973) 1158.

[4] R.M. Dell, V.J. Wheeler, E.J. McIver, Trans. Faraday Soc. 62 (1966) 3591.

[5] R.M. Dell, V.J. Wheeler, J. Nucl. Mater. 21 (1967) 328.

[6] S. Yagi, D. Kunii, Symposium on Combustion, Reinhold, New York, 1955, p. 231.

[7] M. Ishida, C.Y. Wen, A.I.Ch.E.J. 14 (1968) 311.

[8] H.Y. Sohn, J. Szekely, Chem. Eng. Sci. 27 (1972) 763.

[9] J.Y. Park, O. Levenspiel, Chem. Eng. Sci. 30 (1975) 1207.