A Study on the Accelerated Oxidation Reaction of Uranium Dioxide in Oxygen Plasma

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1. Introduction

In the nuclear fuel cycle, the manufacturing process of uranium dioxide includes a multi-step reduction and oxidation process and that process is repeated several times. Moreover, those reactions occur mainly under wet process or at a very high temperature. OREOX(oxidation and reduction of oxide fuel) process to recycle spent UO_2 pellets also uses repetitive oxidation-reduction reaction of spent fuel pellets to pulverize the spent fuel. It needs the condition of high temperature and long processing time because of whose low reaction rates [1]. On the contrary dry process using reactive plasma is not only reducing secondary wastes from the wet process but also ensure reliability and safety with low processing temperature. In spite of low temperature, plasma reaction still maintains high reaction rate since it is catalytic reaction using high energetic radicals. However diverse researches using plasma techniques related to nuclear fuel cycle are not achieved yet. And it is in the early stage of development internationally. Up to the present almost of those researches tend to report successful experimental cases rather than investigate basic mechanisms. Fundamentally the reactions of oxidation-reduction and fluorination are core technology of nuclear fuel cycle and it is needed to develop effective dry process which can avoid the occurrence of secondary wastes problem and the danger of nuclear proliferation from the wet process. Therefore creative researches that apply dry plasma processing techniques can be a significant research. In this study dry processing using oxygen plasma that can be applied to the manufacturing and processing of nuclear fuel materials were researched. In order to establish the optimized parameters of oxidation plasma, ionization characteristics were experimentally evaluated with optical emission spectroscopy. And accelerated oxidation reaction experiment of UO_2 by oxygen plasma was carried out to develop a new dry processing technique of nuclear fuel materials for the future replacement of current wet processing. And dynamics of acceleration mechanism has been identified.

2. Experimental

2.1 Sample Preparation

In this work, thin disks (0.35 mm in thickness) of natural uranium dioxide cut out of a pellet are used as specimens. Prior to the sample loading, specimens are polished by 600-grit sandpaper, cleaned by an ultrasonic cleaner, and baked at 200^{o}C for 20 min in a ultra-high vacuum to evaporate the adsorbed moisture on the surface. The oxidation reaction rate is determined by intermittent weight gain measurement, before and after the reaction, with an electro-micro balance (BP210D, Sartorius) with a sensitivity limit of 10^{-5} g.

2.2 Experimental Apparatus

The reaction chamber of the apparatus is made of stainless steel and the flow rates of the plasma gases into the chamber are fine-controlled by mass flow controllers. After the reaction gas is injected into the reaction chamber under a certain pressure, r.f. power up to 600 W with 13.56 MHz is applied up between the parallel electrodes whose distance is 5 cm. The reaction chamber is designed to allow specimens to be heated up to 800 ^{o}C by halogen lamp heaters. Surface temperature of the specimen was measured by the thermocouple installed in the center of electrode. Oxygen and Argon gases whose purity is 99.999% are used in the experiment. The precise flow measurement up to 1-100 sccm was possible using mass flow controller.

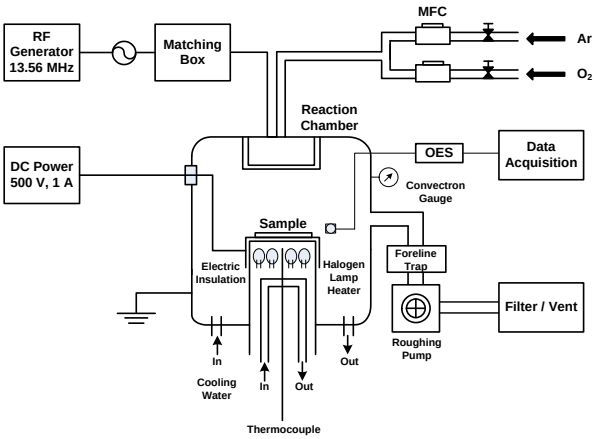

Fig. 1. Schematic diagram of cold plasma oxidation apparatus

Uranium dioxide specimens are put to a sample dish and loaded into a plasma chamber to prevent weight loss by scattering of uranium oxides powder which is arisen from volume expansion during oxidizing process of uranium dioxide. The sample dish is made of pure gold in order to prevent the increase of weight due to oxidation of itself.

2.3 Experimental Procedure

Weighed specimen is loaded into a reaction chamber and the pressure of reaction chamber is reduced to ~10^{-3}

Torr using an oil rotary pump and the temperature of the specimen is increased by halogen lamp heater.

When the temperature reaches the process condition, oxygen and argon mixture gases are injected to a certain pressure by mass flow controller. Plasma power can be varied by experimental purpose. The distance of the electrodes fixed at 5cm, and the total reaction time is 30 minutes. The reaction temperature is 400 to 500^oC. After the reaction, the weight of the specimen was measured and calculated to the wt% increase.

3. Results & Discussion

3.1 Oxygen Actinometry Optical Emission Spectroscopy

In this study OES (Optical emission spectroscopy) Actinometry technique is used to find out the optimum process condition. The amount of light generated from oxygen plasma was measured by OES. It is depending on the concentration of the oxygen gas pressure. And it can be calculated to the quantity of oxygen atoms by using following formula.

$$\frac{I_O}{I_{Ar}} = \frac{k_O n_O \eta_O}{k_{Ar} n_{Ar} \eta_{Ar}} = K \frac{n_O \eta_O}{n_{Ar} \eta_{Ar}} \qquad (1)$$

Where I_x is the optical-emission intensity from species x, n_x is the density of species x in the ground state, η_x is the excitation efficiency of the discharge to promote species x from the ground state to the electronically excited state responsible for the optical emission and k_x is a proportionality constant. In this approach, It is assumed that $n_o = k\, n_{Ar}$ as discharge parameters are varied. I_o an I_{Ar} are measured, n_{Ar} is known, and K is a constant independent of the discharge parameters [3, 4].

3.2 Accelerated oxidation reaction

In the previous research, uranium dioxide oxidation reaction was studied using oxygen gas oxygen plasma. Fig. 2. shows the oxidation reaction results at 400 ^oC under O_2 plasma and normal O_2 gases. It was found that the oxidation rate is increased about 300% in plasma condition. The oxidation reaction with oxygen gas is remained at a slow surface reaction of initial stage of S-shape reaction curve. However, that of oxygen plasma rapidly passed over the initial stage and entered into a linear reaction stage of S-shape reaction curve [2,5]. According to the experimental results of previous studies, the reason why oxidation reaction rate is accelerated under plasma condition is that very reactive oxygen radicals from the oxygen plasma participate in the reaction. The reactive radicals occur in the plasma by collisions between oxygen gases and electrons [1].

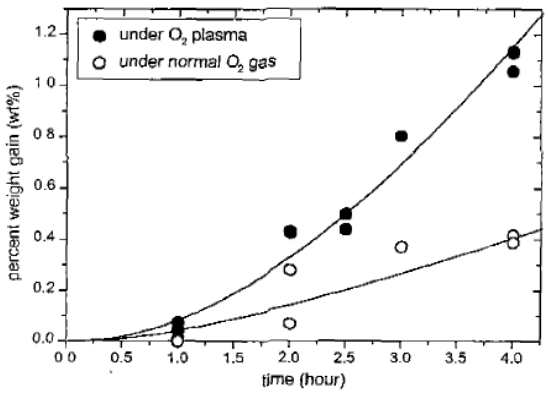

Fig. 2. Oxidation results of UO_2 at 400^{o}C [1]

4. Conclusions

In this research, accelerated oxidation reaction of uranium dioxide under oxygen plasma is studied and in the subsequent study more intensive experiments will be carried out. And reaction mechanism of accelerated oxidation will also be found out.

The increase in oxidation rate was ascribed to the direct participation of oxygen radicals produced in the plasma by OES analysis. OES actinometry technique, a quantitative assessment of oxygen atom will find out the optimum condition and on the basis of this result the processing temperature can be lowered.

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