Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 29-30, 2014

Oxidation of Uranium Dioxide in R.F Plasma

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1. Introduction

In the conventional front and backend nuclear fuel cycle, the complex process of oxidation and reduction of uranium oxides are repeated. OREOX(oxidation and reduction of oxide fuel) process to reuse nuclear spent fuel also uses repetitive oxidation and reduction reaction of spent fuel pellets to pulverize it. In those process, the target material to be earned is oxide of uranium. However both reactions are performed at high temperature and needed long processing time. But plasma which has high reactivity is used that it could keep the high reactive species at low temperature. In addition, plasma process is performed in gaseous conditions, so it is expected that it can not only reduce the secondary waste but also ensure reliability and safety in low temperature process. However, lots of researchers who apply the plasma techniques to nuclear fuel cycle are not achieved yet. Also this application is initial stage of development of internationally. Previous researches tend to report the successful experimental cases rather than conduct basic research about the fundamental mechanism of oxidation process in plasma. Fundamental reactions about oxidation-reduction are core technology of nuclear fuel cycle and it is needed to develop effective dry process which can reduce the occurrence of secondary wastes problem and avoid the danger of nuclear proliferation.

In the view of this needs, the fundamental research is conducted about oxidation process of fuel material which is major part of nuclear fuel cycle. Applying the plasma technique to dry process is significant research in part of nuclear non-proliferation.

2. Experiment

2.1 Prepare the specimen

In this experiment, Uranium pellets were prepared as thin disk. Specimens were grinded by the sand paper what grits are 320 and 600, and then it was washed by using an ultrasonic washing machine. In order to remove the moisture of specimen, specimens were dried for 24hours in hume-hood. Oxidation rate was calculated for comparing the difference between before and after weight gain of the specimen using microbalance (Sartorius, BP210D) which can measure the weight 10^{-5}g at minimum.

2.2. Experiment apparatus

Reaction chamber is made by stainless steel, and quantity of plasma gas was controlled by mass flow controller. The plasma gas was injected to reactor chamber and pressure (0.5Torr) was maintained, R.F plasma was generated to parallel electrode plate by plasma generation apparatus which generated frequency 13.56MHz, 600W at maximum power. Also, heater in reaction chamber was designed by halogen lamps which have a maximum temperature of 800℃. Oxygen gas and argon gas used in this experiment are high purity of 99.999%. Temperature of specimen was measured by the thermocouple located center of the chamber. Gas flow can be adjusted 2-100sccm of oxygen and 1-50sccm of argon by mass flow controller.

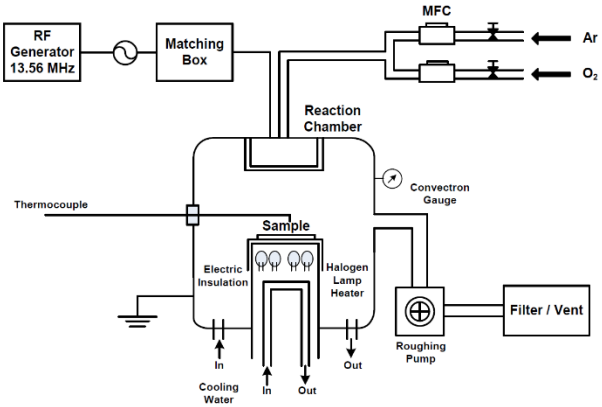

Fig. 1. Schematic diagram of plasma oxidation apparatus

After measuring the initial weight of specimen, it was put on the electrode which was placed center of the chamber. Because oxidation of uranium dioxide accompany the volume expansion, pulverization of specimen which cause the decrease of weight by loss of powder, specimen plate was used. Plate was made up of ceramic which had oxidation resistance and heat resistance in high temperature.

2.3 Experiment procedure

After measuring the initial weight of uranium specimen, the ceramic specimen plate which mounted specimen inside, was positioned on the electrode in the reactor chamber. Thermocouple was contacted outside of specimen plate. Using the rotary pump, pressure of chamber let down to ~10^{-3} Torr .If pressure was maintained, increased the temperature of specimen up to 400℃ - 450℃ using halogen lamp heater. After temperature was reached certain temperature, oxygen gas (47.5sccm) and argon gas (2.5sccm) were injected up to 0.5 Torr using a mass flow controller. The temperature of reaction is 400℃ and 450℃, plasma power was fixed to 50W, distance of electrode was located 5cm from specimen plate. Weight gain and rate are measured in

every 30 minutes intervals of whole reaction,

3. Results & Discussion

3.1 Oxidation acceleration at 450 ℃

According to the previous researchers, oxidation curve of uranium dioxide is well-known to have the oxidation process of the two-step S-shape curve. In this experiment, however, the reaction rate of oxidation is too fast to confirm the 2-step oxidation process. But there was difference of oxidation rate between plasma and gas. Oxidation rate of plasma is faster than that of gaseous conditions. The reason why there was tiny different is that molecules of gaseous process had enough energy compared with plasma process because of high temperature.

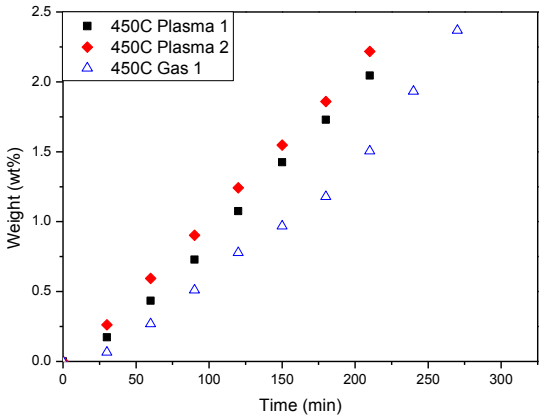

Fig. 2. Oxidation result of UO2 at 450℃

3.2 Oxidation acceleration at 400 ℃

It also didn't show up the 2-step S-shape oxidation process at 400℃. But it was observed the acceleration of oxidation rate by plasma. Acceleration rate of oxidation in plasma condition was increased about 20% compare to gaseous reaction. It was determined the reaction temperature is low to have the sufficient energy at gaseous reaction, whereas radicals and ions generated by plasma gave affected to oxidation process at plasma condition.

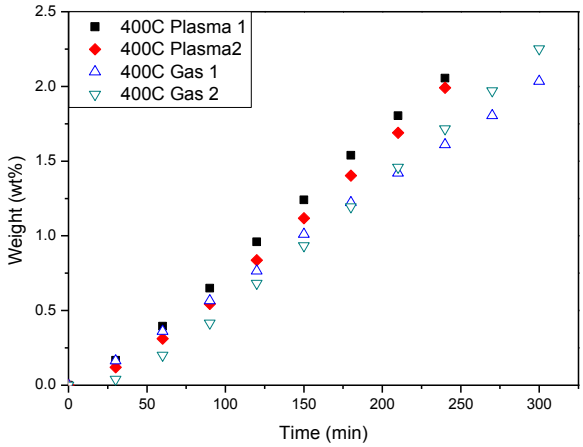

Fig. 3. Oxidation result of UO2 at 400℃

5. Conclusion

In this research, it is confirmed that the temperature is lower, the influence of oxygen plasma is greater in the experiment about acceleration of uranium dioxide using oxygen plasma at temperature of 400℃ and 450℃. It has enough energy not only plasma condition but gaseous condition, both reaction show fast reaction rate. On the other hand, it didn't have enough energy at gaseous condition compare to plasma, therefore it has lower reactivity. As temperature is increasing, both reactivity of plasma and gaseous reaction is increase. As temperature is increased, it effect upon the safety of oxidation using uranium. Therefore, the goal of this research is shorten the reaction time at low temperature using plasma. In order to achieve the goal, additional research about reactivity between plasma and gaseous condition at lower temperature is performed

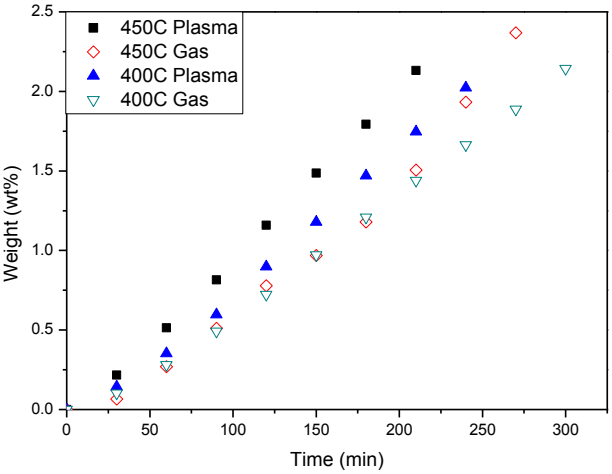

Fig. 4. Comparison of result about conditions

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