BEHAVIOR OF RUTHENIUM TRAPPED ON AN YTTRIA FILTER UNDER REDUCTION AND OXIDATION CONDITIONS

Jin Myeong Shin, Jang Jin Park, Kwan Sik Chun, Jong Ho Kim, and Myung Seung Yang
Korea Atomic Energy Research Institute, Korea

ABSTRACT

The behavior of ruthenium (RU) trapped on an yttria filter has been studied under reduction and oxidation atmospheres using a Thermo-Gravimetric Analyzer (TGA), an X-ray Diffractometry analyzer (XRD) and an X-ray Photoelectron Spectroscopy analyzer (XPS). Ruthenium trapped on an yttria filter under an oxidation atmosphere was in the form of $Y_2Ru_2O_7$ and it was transformed into Ru metal under a reduction atmosphere. Under a re-oxidation atmosphere, the ruthenium trapped on an yttria filter was again $Y_2Ru_2O_7$. When the ruthenium trapped on an yttria filter was exposed to a reduction atmosphere, a weight loss of 2.5% was noticed at about 350~700°C. When it was exposed to a re-oxidation atmosphere, the ruthenium trapped on an yttria filter showed a weight gain of 2.5% at about 300~800°C.

INTRODUCTION

Ruthenium is known to be in the form of a metallic precipitate in spent nuclear fuel. It is easily oxidized to RuO_2 when heated in an oxidation atmosphere. RuO_4 is volatilized (Weast, 1977) at high temperature in an oxidation atmosphere. When contacted with gaseous RuO_4, the pipe walls of an off-gas treatment system are covered with a non-volatile black deposit of ruthenium and this phenomenon has caused difficult problems for process operations. Therefore, volatile ruthenium oxide must be trapped in the initial step of generation.

Many methods have been tried to treat gaseous ruthenium arising from related nuclear facilities. These are the physical condensation method (Eicher et al., 1992), the adsorption method using metals such as Ni, Cu, SUS (Sakurai et al., 1985) and the chemical method using alkaline earth metal compounds such as Ca, Ba, Sr (Mass & Longo, 1980). It is reported that the chemical method is most often recommended because of its high thermal stability and the formation of stable chemical compounds such as perovskites.

Cho et al.(1995) have studied the trapping of gaseous ruthenium using Fe_2O_3, Y_2O_3, Li_2O_3, TiO_2. Their results showed that Y_2O_3 formed $Y_2Ru_2O_7$ with a pyrochlore structure from its reaction with ruthenium oxide, which is thermally stable up to 1400°C and has a large theoretical capacity for trapping per unit mass. Also, Park et al. (1997) have studied the identification of reaction compounds as a function of reaction temperature and the thermal stability of reaction products after trapping ruthenium using Y_2O_3

Gaseous ruthenium compounds are considered to be released during the Oxidation and Reduction of Oxide fuel (OREOX) process in manufacturing Direct Use of Spent PWR Fuel in CANDU reactors (DUPIC) fuel. Most gaseous ruthenium compounds are released during the oxidation process of spent PWR fuel material. The oxidation and reduction processes are repeated about three times to obtain good sinterable powder. The purpose of this study is to evaluate the behavior of the ruthenium trapped on an yttria filter under reduction and oxidation atmospheres using a Thermo-Gravimetric Analyzer (TGA), an X-ray Diffractometry nalyzer (XRD) and an X-ray Photoelectron Spectroscopy analyzer (XPS).

EXPERIMENTAL

Y_2O_3 powder with a purity of 99.9% was used for the preparation of the filter. The ceramic foam filter used in this experiment was prepared by impregnating a polyurethane sponge into a slip solution of yttria, binder and water, and then drying and sintering it. Ru metal with a purity of 99.9% (Aldrich Co.) was used to generate gaseous ruthenium. Trapping gaseous ruthenium was first carried out in a muffle furnace (Lenton, UAF-17/12) under air at 1200°C for 36 hours (Step 1). Phases of ruthenium trapped on an yttria filter were determined by an XRD (Siemens, D5000). The chemical composition of ruthenium trapped on an yttria filter was analyzed by an Electron Probe Micro Analyzer (EPMA, JEOL, JXA-8600).

In order to understand the behavior of ruthenium trapped on an yttria filter during the OREOX process, experiments were performed using a TGA (Setaram, TG-DTA 92) with a changing atmosphere. The first TGA experiment was conducted under a reduction atmosphere (Step 2). About 50 mg of sample were heated up to 700°C in a hydrogen atmosphere. After cooling, a phase analysis for the reduced sample was carried out with the XRD using a Cu $K\alpha$ ray. The bond energy of ruthenium was determined by an XPS (VG, ESCALB) using an Al $K\alpha_1$ ray. Then the sample was also re-heated up to 1200°C in the air atmosphere (Step 3). The sample was then heated in a hydrogen atmosphere (Step 4) and again in air (Step 5) and then again in hydrogen (Step 6), as shown in Table 1. This type of operation simulated that of the OREOX operation for producing sinterable powder for the manufacturing DUPIC fuel.

RESULTS AND DISCUSSION

The ceramic foam filters of yttria are shown in Fig. 1, before and after trapping ruthenium.. The color of the ceramic foam filter was first white, then completely black, before and after trapping, respectively. The black color indicates that a volatile ruthenium compound is trapped on the surface of the ceramic foam filter of yttria. The EPMA result shows that the weight percent of Y_2O_3 and RuO_2 in the yttria filter after trapping are about 88 wt% and 12 wt%, respectively. This corresponds to the ruthenium loading capacity of about 0.14 g-RuO_2/g-Y_2O_3.

The XRD pattern of an initially oxidized sample (Step 1) shows that both Y_2O_3 and $Y_2Ru_2O_7$ exist (Fig. 2). The XRD pattern of the reduced sample (Step 2) is shown in Fig. 2, and it shows only the Y_2O_3 phase without the $Y_2Ru_2O_7$ phase. $Y_2Ru_2O_7$ is believed to be partially reduced to Ru metal and Y_2O_3 during the reduction process. However, the Ru metal phase cannot be found on the XRD pattern of the reduced sample. This may be due to the fact that the amount of ruthenium oxide trapped on Y_2O_3 was too small (about 12 wt%) to be detected by an XRD. The XRD pattern of a re-oxidized sample (Step 3) shows that both Y_2O_3 and $Y_2Ru_2O_7$ exist again (Fig. 2).

The result of TG analysis on an initially oxidized sample (Step 1) under a hydrogen atmosphere is shown in Fig. 3 (Step 2). It showed a weight loss of 2.5% at about 350~700°C, which is almost the same as the theoretical value of 2.9%. From this result, this 2.5% weight loss of oxygen can be taken as evidence of the decomposition of Ru metal and Y_2O_3 from $Y_2Ru_2O_7$. The result of TG analysis on a reduced sample (Step 2) under an air atmosphere is shown in Fig. 3 (Step3). In Fig. 3, a 2.5% weight gain is noticed at about 350~750°C. The weight loss which occurred in the reduction atmosphere was almost recovered to its initial weight in the re-oxidation atmosphere. This 2.5% gain of weight can be considered to be attributed to the reaction of ruthenium metal with oxygen in environmental air.

The X-ray photoelectron spectrum of a reduced sample (Step 2) is shown in Fig. 4. As shown in Fig. 4, the peak of Ru metal is observed at 280 eV of binding energy.

The results of TG, XRD and XPS during repeated oxidation and reduction atmospheres are summarized in Table 2. From these results, it can be found that ruthenium trapped on an yttria filter under the air atmosphere is in the form of $Y_2Ru_2O_7$, which is reduced to Ru metal in the hydrogen atmosphere.

Simultaneously, a small weight loss in a sample occurs under the hydrogen atmosphere. However, the weight loss under the hydrogen atmosphere can be recovered to its initial weight in the re-oxidation condition. Also, when the reduced sample was exposed to 1200°C in the re-oxidation atmosphere after regaining its weight, further weight loss was not observed. It might therefore be concluded that ruthenium trapped on an yttria filter can be thermally stable during repeated oxidation and reduction processes.

CONCLUSIONS

The behavior of ruthenium trapped on an yttria filter under reduction and oxidation atmospheres has been studied using TGA, XRD and XPS. The results are as follows;.

1. Ruthenium trapped on an yttria filter under the air atmosphere was in the form of $Y_2Ru_2O_7$ and was transformed into Ru metal under the hydrogen atmosphere. Under the re-oxidation atmosphere, $Y_2Ru_2O_7$ appeared again.

2. The weight loss which occurred in the reduction atmosphere was almost recovered to its initial weight in the re-oxidation atmosphere. It was concluded that ruthenium trapped on an yttria filter was thermally stable during repeated oxidation and reduction processes.

REFERENCES

1. Weast, R.C. *Handbook of Chemistry and Physics*. CRC Press, Cleveland, Ohio, 1977.
2. Eicher, By B., F. Zude, W. Fan, N. Trautmann and G. Herrmann. "*Volatilization and Deposition of Ruthenium Oxides in a Temperature Gradient Tube*". *Radiochimica Acta*, **56**, pp 133-140, 1992.
3. Sakurai, T., Y., Hinatsu, A. Takahashi and G. Fujisawa. "*Adsorption of Ruthenium Tetroxide on Metal Surfaces*". *J. Phys. Chem*, **89**, pp 1892-1896, 1985.
4. Mass, Jr., E.T., J. M. Longo. "*Confinement of Ruthenium Oxides Volatilized during Nuclear Fuels Reprocessing*". *Nuclear Technology*, **47**, pp 451-456. 1980.
5. Cho, Y. H., K. S. Chun, J. J. Park, J. M. Shin, H. S. Park and J. S. Ryu. "Development of Trapping material for radioactive ruthenium in OREOX Process". *Proceedings of the Korean Nuclear Society Autumn Meeting"* Vol (II), Seoul, Korea, October, pp 860-865, Korean Nuclear Society, Seoul, 1995.
6. Park, J. J., Y. H. Cho, K. S. Chun, J. M. Shin, and Y. K. Kim. "Trapping Characteristics of Gaseous Ruthenium by Using Yittria". *Proceedings of the Korean Nuclear Society Spring Meeting"* Vol.(II), Kwangju, Korea, May, p 324-328, Korean Nuclear Society, Seoul, 1997.

KEY WORDS

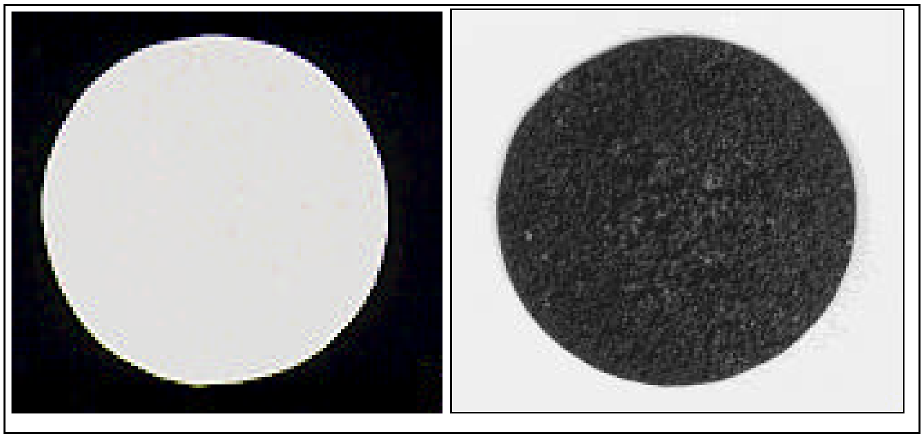
Yttria filter, DUPIC, Gaseous ruthenium, Yittrium ruthenate, Oxidation, Reduction

Table 1 Condition of thermogravimetric analysis

Items	Condition
Sample amount	50 mg
Atmosphere	Air/ Hydrogen
Temperature	Air : 1200°C, Hydrogen: 700°C
Flow rate	10 cc/min

Table 2 Behavior of ruthenium trapped on an yttria filter in the OREOX condition.

Condition	TG Analysis	XRD Analysis	XPS analysis
Oxidation (Step 1)	-	$Y_2Ru_2O_7$, Y_2O_3	-
Reduction (Step 2)	2.5% weight loss	Y_2O_3	Ru, Y, Y_2O_3
Oxidation (Step 3)	2.5% weight gain	$Y_2Ru_2O_7$, Y_2O_3	-
Reduction (Step 4)	2.5% weight loss	Y_2O_3	Ru, Y, Y_2O_3
Oxidation (Step 5)	2.5% weight gain	$Y_2Ru_2O_7$, Y_2O_3	-
Reduction (Step 6)	2.5% weight loss	Y_2O_3	Ru, Y, Y_2O_3



(A) **(B)**

Figure 1 Photographs of ceramic foam filters of yttria before trapping ruthenium (A) and after trapping ruthenium (B) under the air atmosphere.

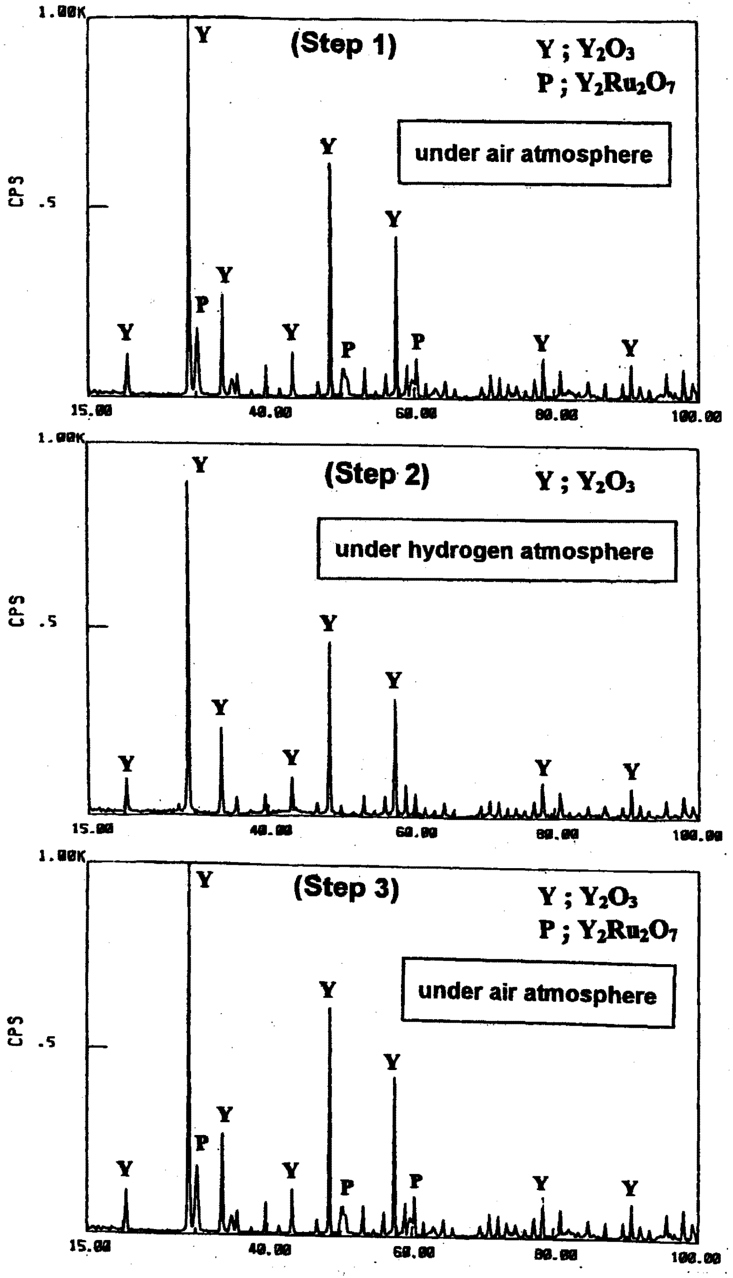


Fig. 2. XRD analyses of ruthenium trapped on an yttria filter under air atmosphere(Step 1), under hydrogen atmosphere (Step 2) and under air atmosphere((Step 3).

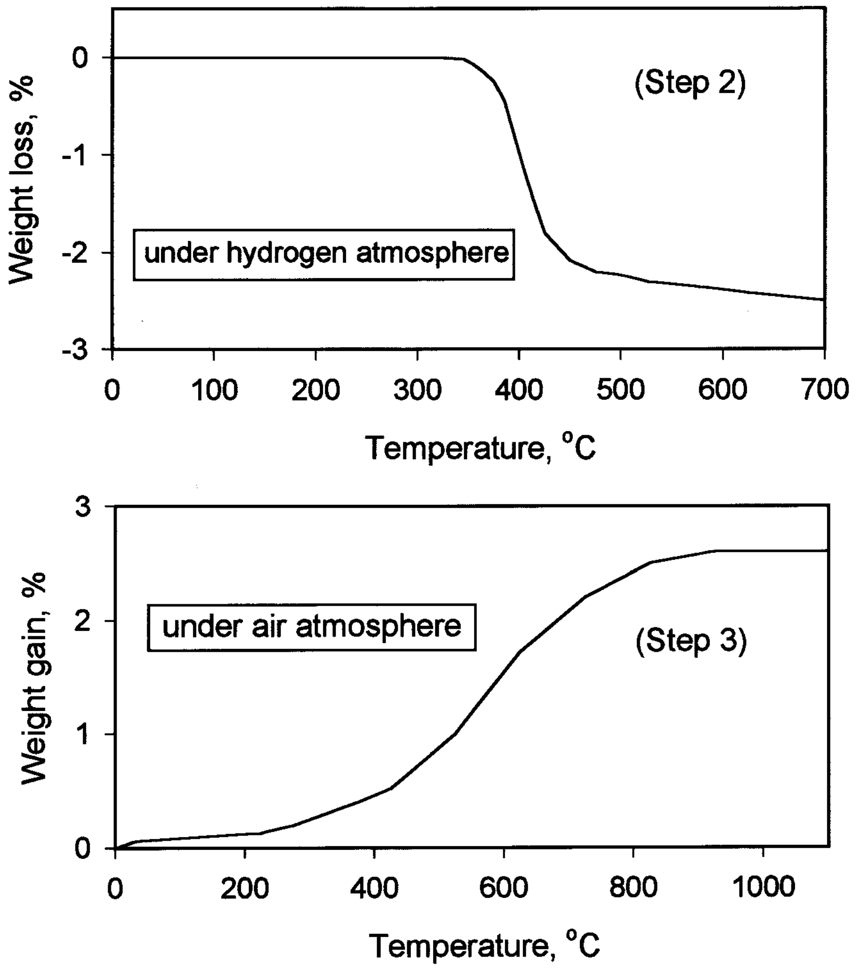


Fig. 3. TG analyses of ruthenium trapped on an yttria filter under hydrogen atmosphere(Step 2) and under air atmosphere (Step 3).

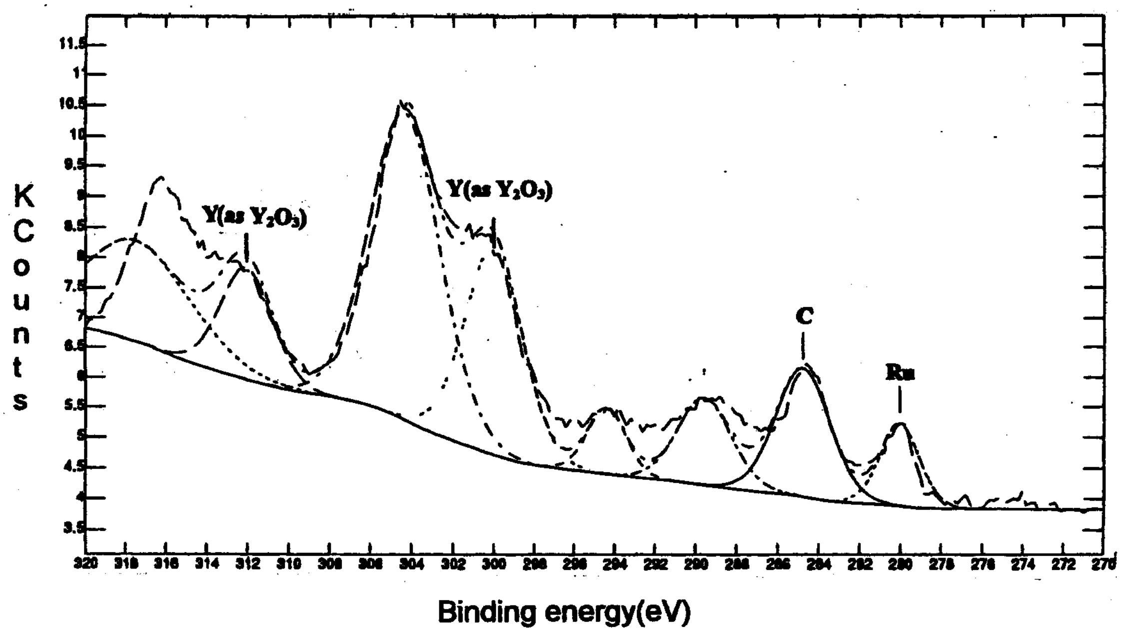


Fig. 4. X-ray photoelectron spectrum of reduced sample(Step 2).