

Trapping Characteristics of Volatile Ruthenium Oxides by Y_2O_3 Filter

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Abstract—Yttria filter has been suggested as a trapping agent for gaseous oxides of ruthenium volatilized during DUPIC fuel fabrication process. Experiments were performed to evaluate the trapping characteristics of gaseous ruthenium oxides by yttria ceramic foam filters in the two-zone furnace under air condition. Yttria filter is expected to offer stable material in which the volatility of the ruthenium can be effectively trapped because of its incorporation into a lattice of high stability over 900 °C under air condition. The XRF result of ruthenium trapped on an yttria filter under air condition showed that concentrations of ruthenium on the back and the front faces of the filter decreased linearly with increasing superficial air velocity, and the back face concentration of filter was lower than the front face concentration by about 30-45%. The TGA result of ruthenium trapped on an yttria filter indicates that there is weight loss of 5.8 wt% up to 1,400 °C, which is believed to be due to the fact that the thermally stable $Y_2Ru_2O_7$ phase was formed on an yttria filter.

Key words: Yttria Filter, Ruthenium Oxides, $Y_2Ru_2O_7$, DUPIC Nuclear Fuels, Volatilization

INTRODUCTION

Spent nuclear fuels from nuclear power generation require safe and efficient management for the long run. As the fissile contents of the spent PWR fuel released from the irradiation of PWR reactor with a discharge burnup of 35,000 MWD/MTU are about 1% of U-235 and 0.5% of Pu-239, it can be directly reused in CANDU reactors that are designed for natural uranium fuel. The DUPIC (Direct Use spent PWR fuel In CANDU reactors) process is a dry processing technology to manufacture CANDU fuel from spent PWR fuel material without any separation of fissile elements and fission products [Lee et al., 1995a; Yang et al., 1998]. DUPIC has received renewed interest recently as a PWR/CANDU synergistic fuel recycling option [Lee et al., 2000b].

The DUPIC fuel fabrication process consists of rod-cut, decladding, repeated OREOX (Oxidation and REDuction of OXide fuel), pelletizing and sintering processes [Park et al., 1993]. The OREOX process was performed to control powder characteristics and sinterability of produced DUPIC fuel. Repetition of oxidation/reduction has greatly improved the power sinterability. The schematic diagram of the DUPIC fuel fabrication process is shown in Fig. 1. During the rod-cut process, tritium can be generated. In addition to the rod-cut process, during the OREOX and sintering processes, volatile fission gases (tritium, carbon-14, krypton, iodine etc.) and semi-volatile fission gases (ruthenium, cesium etc.) might be released.

The off-gas treatment problems associated with the volatility of ruthenium are generated by the substantial quantities of heat and radiation produced by Rh^{106} decay, which in turn rapidly decays to Pd^{106} . A certain amount of ruthenium is known to be in spent nuclear fuel as a fission product. It generally exists in the form of me-

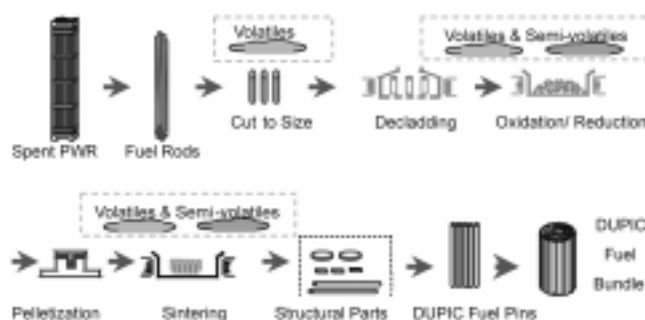


Fig. 1. DUPIC fuel fabrication process.

tallic precipitate and is easily oxidized to RuO_2 when heated in oxidation condition. When RuO_2 is exposed to high temperature and oxidation condition in the dissolution or separation processes of wet reprocessing treatment, it is oxidized and volatilized to gaseous RuO_4 whose boiling point is 25.4 °C [Kim et al., 2000; Seddon and Seddon, 1984; Weast, 1997; Cains et al., 1998].

When this semi-volatile ruthenium gas, RuO_4 , is contacted with off-gas treatment system, the pipe walls of the off-gas treatment system are covered with a non-volatile black deposit of ruthenium. Since this phenomenon might cause difficult problems for process operation such as line plugging etc., volatile ruthenium oxide must be trapped in the initial step of generation.

In order to treat gaseous ruthenium oxides arising from related nuclear facility, many studies on the fixation materials have been done. There are the physical condensation method [Eicher et al., 1992], adsorption method [Sakurai et al., 1985] using metals such as Ni, Cu, SUS, and chemical method [Mass and Longo, 1980] using alkaline earth metal compounds such as Ca, Ba, Sr. It is reported that the chemical method has been most recommended because of high thermal stability and formation of stable chemical compounds such as $MRuO_3$ ($M=Ba, Ca, Sr$) of perovskites formulation, MRu_2O_7 ($M=Nd, Sm, Eu, Bi, Lu$) of pyrochlores formulation, and MRu_4O_8

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[‡]This paper is dedicated to Professor Dong-Sup Doh on the occasion of his retirement from Korea University.

(M=K, Rb) of hollandites formulation, et al. [Seddon and Seddon, 1984]. Pyrochlores are ternary compounds that crystallize into a cubic structure with an $A_2B_2O_7$ stoichiometry, where A is a trivalent cation and B is a tetravalent cation.

Cho et al. [1995] have studied the trapping of gaseous ruthenium by using Fe_2O_3 , Y_2O_3 , Li_2O_3 and TiO_2 . Their results showed that Y_2O_3 could be transformed into $Y_2Ru_2O_7$ of the pyrochlores structure by reaction with ruthenium oxide, which is thermally stable up to 1,400 °C and has large theoretical capacity of trapping per unit mass. Shin et al. [1998] analyzed the behaviors of ruthenium trapped on an yttria filter under reduction and oxidation conditions.

In order to efficiently trap ruthenium oxides volatilized from the DUPIC fuel fabrication process, yttria powder must be manufactured as a disk form applicable for off-gas treatment system. Also, it is necessary to obtain information on the operating conditions of a ruthenium trapping unit using the yttria filters.

In this work, therefore, experiments were performed to evaluate the trapping characteristics with changing trapping temperature, air velocity and filter depth by yttria filters in a two-zone furnace. Reaction products formed by the reaction of gaseous ruthenium compounds with yttria filters were investigated by using XRD (X-ray diffractometry analyzer), XRF (X-ray Fluorescence), and SEM (Scanning Electron Microscope). To analyze the volatility of ruthenium metal and thermal stability of ruthenium trapped on an yttria filter, TGA (Thermo-Gravimetric Analyzer) analysis was also performed.

EXPERIMENTAL

To manufacture a ceramic foam filter, yttria and polyvinyl alcohol as a binding material were mixed together to make a uniform slip solution. Polyurethane sponge was impregnated with slip solution and surplus slip was removed from the sponge. And then it was dried at 90 °C and sintered at 1,600 °C. The heating rate was constantly maintained at 5 °C/min and sintering time was 12 hours. Each yttria filter has an inner diameter of 45 mm, thickness of 7 mm and average weight of about 5 g. The number of pores on the yttria filter ranged from about 13 to 40 pores per linear centimeter. Two-zone furnace of 5.0 cm I.D. alumina tube is shown in Fig. 2. In the first hot zone, Ru metal was used to generate a controlled source of gaseous ruthenium, which was scheduled to pass through the yttria filters mounted in the second hot zone. Filters were tightly packed in an alumina tube of furnace by using an alumina mat.

To analyze the volatility of ruthenium metal, this sample was heated to 1,400 °C at 10 °C/min under air by TGA. The volatility of ruthenium metal maintained for an hour at each temperature in air was also analyzed.

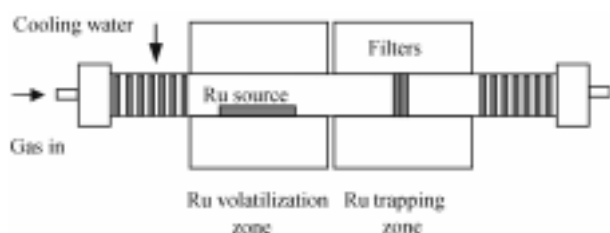


Fig. 2. Schematic diagram of the experimental apparatus for trapping gaseous ruthenium.

In the meantime, pressure drop across the filter was measured by a manometer to evaluate the characteristics of reactor sealing for the yttria filter with changing superficial air velocity and number of filter. Trapping experiments of the ruthenium oxides were conducted with changing superficial air velocity and trapping temperature of the filters at constant superficial air velocity. Superficial air velocity was measured and controlled with a rotameter. The experiments were conducted under air condition because gaseous ruthenium is considered to be released during the oxidation step of OREOX process in manufacturing DUPIC fuel.

In order to determine minimum trapping temperature necessary for the reaction of yttria filter and ruthenium oxides to occur, trapping experiments were conducted by heating the trapping zone from 800 to 1,200 °C for 5 hours, and then cooling it down to room temperature. Source temperature of elemental ruthenium was constantly maintained at 1,200 °C. The superficial air velocity was controlled as 0.05 m/sec at the trapping zone. The XRD (Siemens, D5000) technique was applied to analyze reaction products on the yttria filters. The X-ray used was Cu K α ray, and the scanning rate was 2°/min. The angle, 2 θ , was within the angle of 15° to 60°.

In order to understand the effect of contact time on the ruthenium trapping quantity of the yttria filter, the superficial air velocity was varied between 0.02 and 0.10 m/sec. The trapping temperature was constantly maintained at 1,100 °C and trapping time was 5 hours under air condition. XRF (X-ray Fluorescence, Siemens, G-5000) was also applied for the both faces of the yttria filter to determine the trapping concentration profile. The X-ray used was Cu, and the measurements were conducted at 40 kV and 40 mA. Ruthenium trapping quantity was calculated by measuring the weight change of yttria filter before and after trapping gaseous ruthenium on the basis of 1 g of volatilized Ru metal in volatilization zone.

In the meantime, in order to know the change of ruthenium trapping quantity with the filter depth of the yttria filter, trapping experiments were also conducted with changing temperatures of trapping zone from 900 to 1,200 °C for 5 hours, number of filter from 1 to 5 and superficial air velocity from 0.02 to 0.10 m/sec.

The morphology of reaction products between yttria filter and gaseous ruthenium was observed by SEM (Jeol, JSM-5200).

To analyze the thermal stability of $Y_2Ru_2O_7$, yttria filter after trapping gaseous ruthenium at 1,100 °C under air condition was tested on a TGA. This sample was heated to 1,400 °C under air condition in the TGA, and the weight of sample monitored as temperature was slowly raised. The flow rate of carrier gas was 10 cc/min. The weight loss was calibrated for the buoyancy effect. The ruthenium trapping quantity was calculated by weight gain of ruthenium compound trapped on an yttria filter per unit gram of yttria filter.

RESULTS AND DISCUSSION

The TGA result of ruthenium metal heated to 1,400 °C under air condition is shown in Fig. 3. The weight loss of ruthenium metal is about 3% decrease up to 1,000 °C, 36% decrease up to 1,400 °C. Fig. 4 shows that the volatility of ruthenium metal maintained for an hour at each temperature in air is 0.25%/hr at 800 °C, 1.8%/hr at 1,000 °C, 19%/hr at 1,200 °C, and, 3 %/min at 1,400 °C. It indicates that the ruthenium metal can be completely volatilized in 5 hours at 12,000 °C and an hour at 1,400 °C.

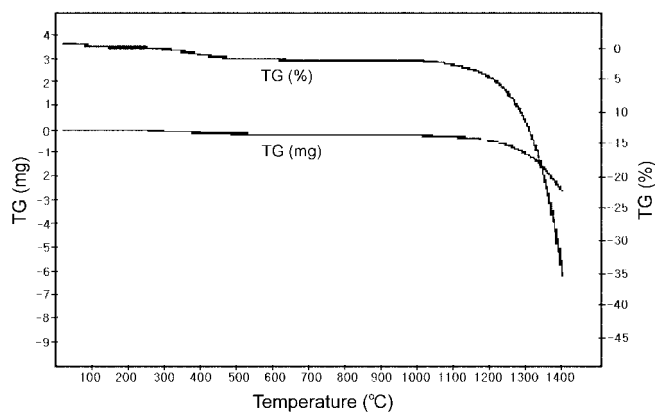


Fig. 3. TGA curve of the Ru metal heated up to 1,400 °C under air.

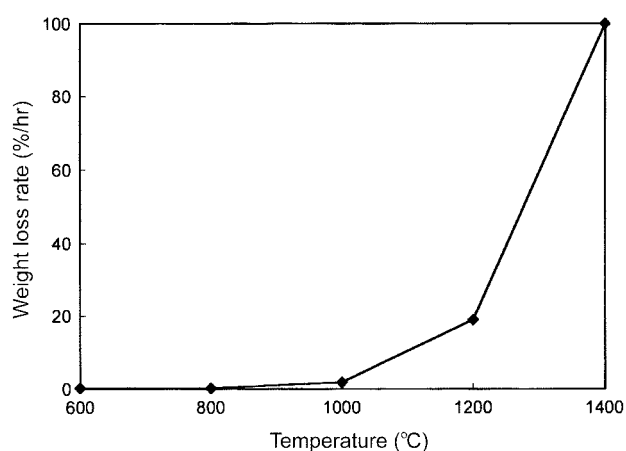


Fig. 4. Volatility of the Ru metal maintained for an hour at each temperature under air.

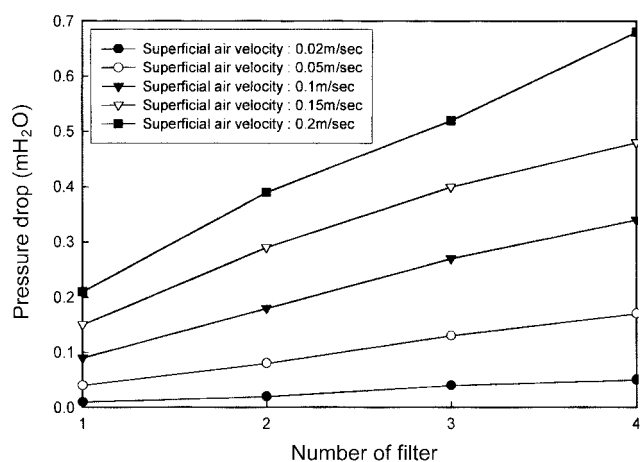


Fig. 5. Pressure drops with changing the number of filter at different superficial air velocity of yttria filter.

Pressure drop measured across the yttria filter is shown in Fig. 5: the pressure drop linearly increases with increasing superficial air velocity and number of yttria filters. This indicates that when the gaseous ruthenium is passed through yttria filter, yttria filter can be reacted to homogeneously contact with gaseous ruthenium without channeling phenomena. This measurement indicates that there

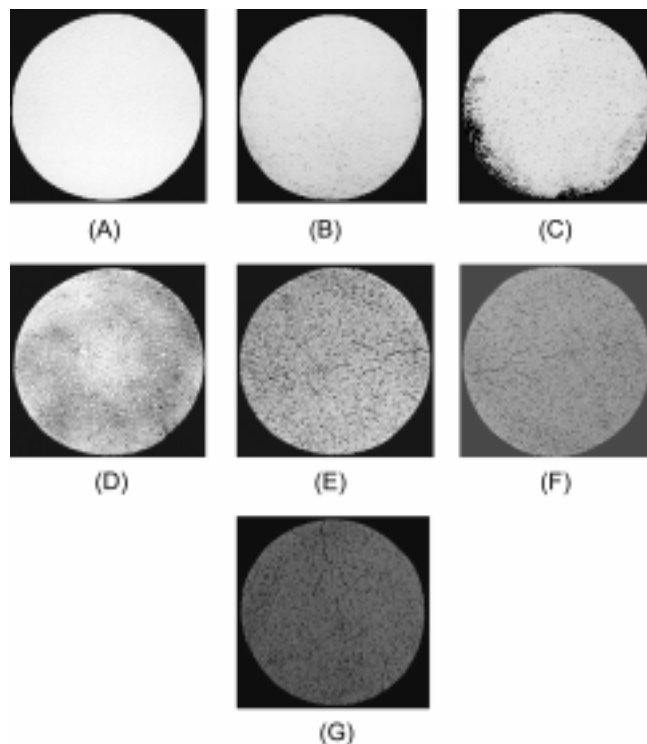


Fig. 6. Photographs of the ceramic foam filters of yttria before trapping ruthenium (A) and after trapping ruthenium (B, C, D, E, F, G) under air condition (Trapping temperature, B; 800 °C, C; 850 °C, D; 900 °C, E; 1,000 °C, F; 1,100 °C, G; 1,200 °C).

is no by-pass of gas through gaps between alumina tube and yttria filters, and the ceramic foam filters of yttria are arranged to have a good contact with an air.

As shown in Fig. 6, when gaseous ruthenium oxide is transported along the tube by the flowing air stream, a gradual darkening on the surface of yttria filter is indicated with increasing temperature of trapping zone. It is indicated that $\text{Y}_2\text{Ru}_2\text{O}_7$ is being formed on the surface of yttria filter. Fig. 6 shows that the color of the yttria filter after trapping experiment at 800 °C is white, but becomes darker above 900 °C. From the results of Fig. 6, it is known that the trapping characteristics of gaseous ruthenium by the yttria filter could

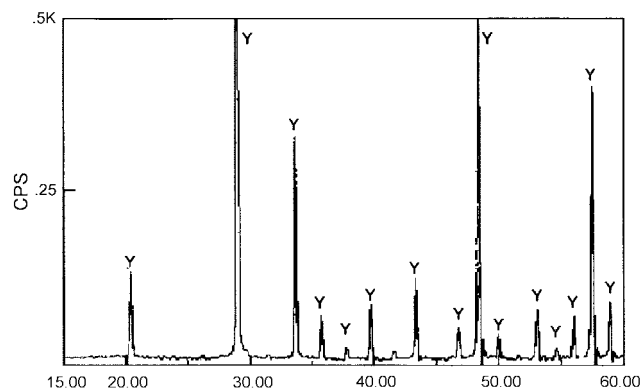


Fig. 7. XRD analysis of the yttria filter after trapping ruthenium at 850 °C (Y: Y_2O_3).

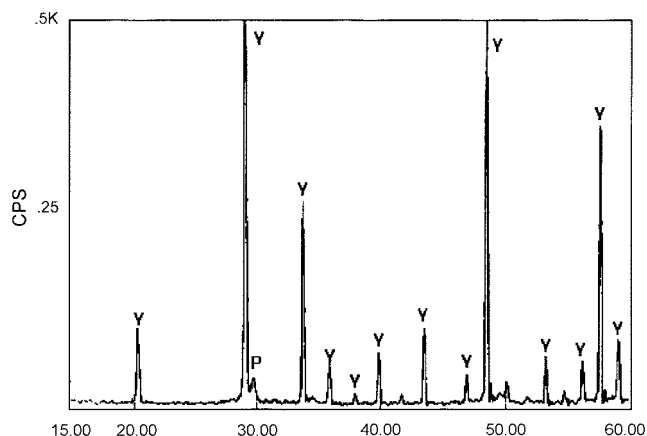


Fig. 8. XRD analysis of the yttria filter after trapping ruthenium at 900 °C (Y : Y_2O_3 , P : $Y_2Ru_2O_7$).

be changed with the trapping temperature.

As shown in Fig. 7, in the trapping experiment at 850 °C, Y_2O_3 phase is formed and metal ruthenate structure is not formed. However, the XRD pattern of an yttria filter after trapping gaseous ruthenium at 900 °C shows that $Y_2Ru_2O_7$ phase is formed as shown in Fig. 8. This shows that yttria filter is reacted with gaseous ruthenium oxide (RuO_4) to become having $Y_2Ru_2O_7$ phase of pyrochlores structure. From the above results, yttria filter is expected to offer stable material in which the volatility of the ruthenium can be effectively trapped because of its incorporation into a lattice of high stability over 900 °C under air condition.

The result of XRF analysis of ruthenium concentration at the front and back faces of the filter is shown in Fig. 9. It is understood that the ruthenium concentration linearly decreases with increasing superficial air velocity and the amount of ruthenium oxide trapped on the filter increased with decreasing superficial air velocity. As the superficial air velocity increases from 0.02 to 0.1 m/sec, the trapped amount decreases from 0.022 g- RuO_2 /g- Y_2O_3 to 0.006 g- RuO_2 /g- Y_2O_3 on the front face of the filter, which is almost equal to 73% decrease. In the same superficial air velocity, trapping quantity of ruthenium decreases from 0.013 g- RuO_2 /g- Y_2O_3 to 0.004 g- RuO_2 /g- Y_2O_3 on the back face of the filter, which is almost equal to 69% decrease.

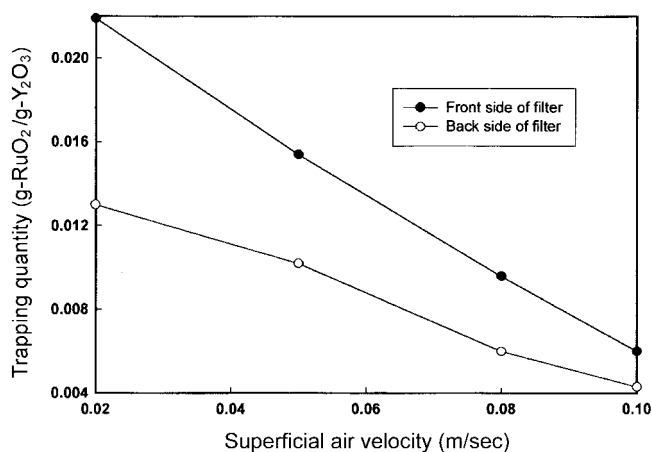


Fig. 9. Effect of superficial air velocity on trapping quantity of ruthenium at front and back faces of filters.

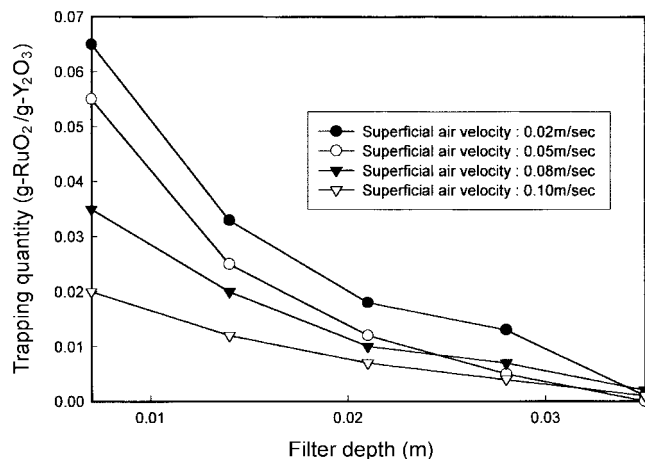


Fig. 10. Change of the trapping quantity of ruthenium on filter depth from 0.02 to 0.10 m/sec (Trapping temperature: 1,100 °C).

g- Y_2O_3 at the front face of the filter, which is almost equal to 67% decrease. The ruthenium concentration gradient across the filter after trapping gaseous ruthenium is about 40% decrease at superficial air velocity of 0.02 m/sec, 34% of 0.05 m/sec, and 28% at 0.10 m/sec. It might be that the contact time between the yttria and gaseous ruthenium decreases with increasing superficial air velocity.

Fig. 10 shows the effect of filter depth on the trapping quantity of ruthenium. As can be seen, the trapping quantity of filters stacked was decreased with increasing filter depth and superficial gas velocity. This is because that the contact time between the yttria filters and gaseous ruthenium was decreased with increasing superficial air velocity.

The results of removal efficiency of ruthenium according to the change of superficial air velocity are presented in Fig. 11. The removal efficiency of ruthenium is decreased as the superficial air velocity is increased. The removal efficiency of ruthenium is 99% at 0.02 m/sec, 75% at 0.05 m/sec, 51% at 0.08 m/sec, and 24% at 0.10 m/sec, respectively. This result shows that the trapping efficiency of ruthenium is affected by contact time between yttria filter and gaseous ruthenium.

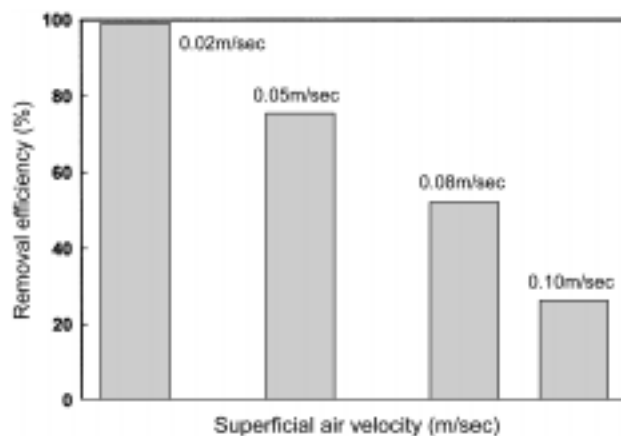


Fig. 11. The removal efficiency of ruthenium according to the change of superficial air velocity.

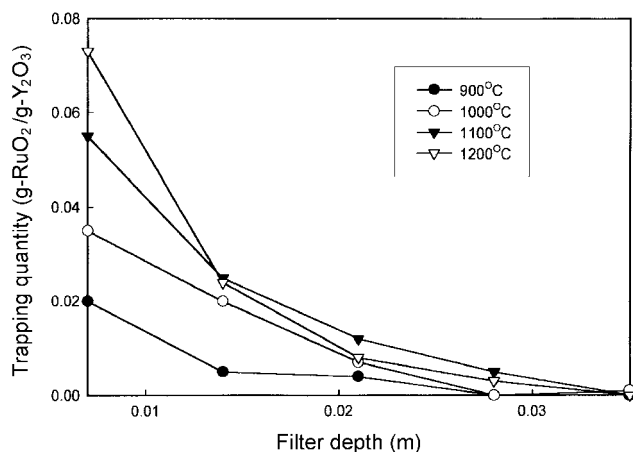


Fig. 12. Change of the trapping quantity of ruthenium on filter depth from 900 °C to 1,200 °C (superficial air velocity: 0.05 m/sec).

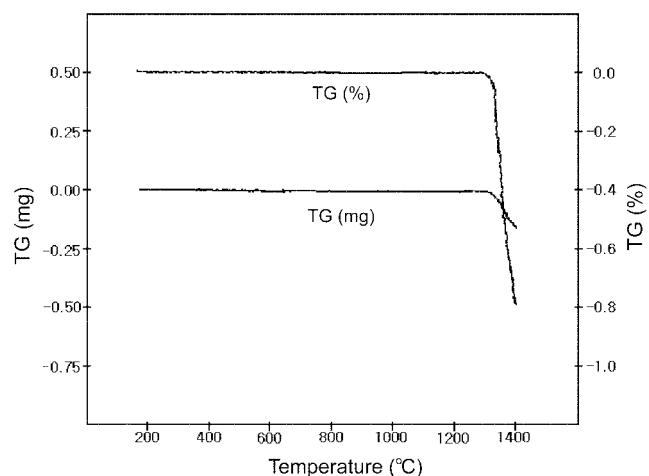


Fig. 14. TGA curve of ceramic foam filter heated to 1,400 °C under air after trapping ruthenium oxides at 1,100 °C.

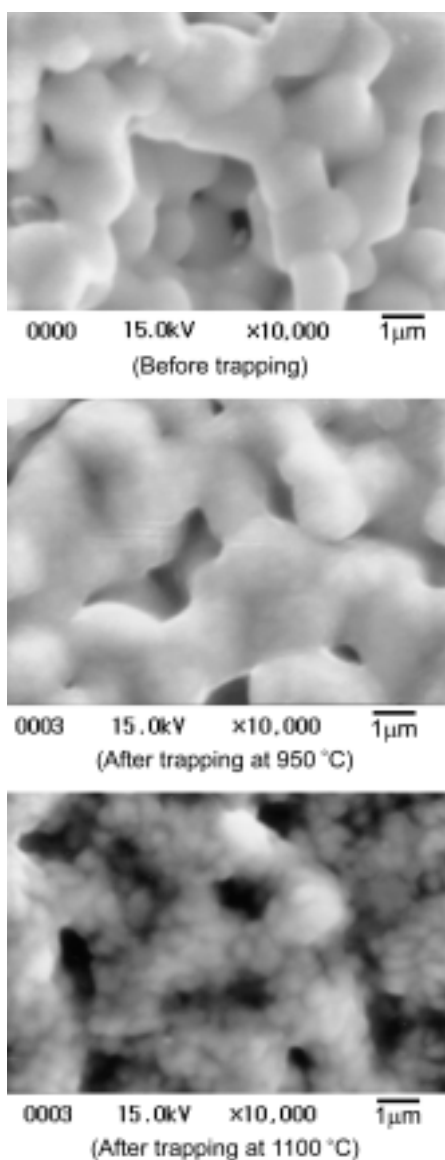


Fig. 13. Scanning electron micrographs of yttria filters before and after trapping ruthenium oxides.

Concentration profiles of trapped ruthenium with changing trapping temperature at 0.05 m/sec of superficial air velocity are shown in Fig. 12. As shown in Fig. 12, the trapping quantity of ruthenium increases with increasing trapping temperature. It might be that the reaction rate is increased with increasing reaction temperature.

Micrographs of yttria filters at 10,000× magnifications before and after trapping gaseous ruthenium under air condition are shown in Fig. 13. As shown in Fig. 13, the structure of the yttria filter indicates that pores are widely interconnected with each other throughout the whole structure of the filter. Meanwhile, microscopic observation of yttria filters taken at 10,000× magnifications after trapping gaseous ruthenium, as shown in Fig. 13, indicates that regular cubic pyrochlores phase was developed with increasing trapping temperature, which is determined to have $\text{Y}_2\text{Ru}_2\text{O}_7$ phase of pyrochlores structure by XRD analysis.

The TGA result of ruthenium trapped on an yttria filter after trapping gaseous ruthenium at 1,100 °C under air condition is shown in Fig. 14. Ruthenium trapping quantity of the yttria filter used in TGA analysis is 0.06 g-RuO₂/g-yttria filter. As shown in Fig. 14, the TGA result of ruthenium trapped on an yttria filter indicates that there is weight loss of 5.8 wt% up to 1,400 °C, which is believed to be due to a thermally stable $\text{Y}_2\text{Ru}_2\text{O}_7$ phase being formed on an yttria filter.

CONCLUSIONS

The behavior of ruthenium trapped on an yttria filter has been studied by using XRD and XRF techniques. Ruthenium compound formed on yttria filter under air condition over 900 °C was determined as $\text{Y}_2\text{Ru}_2\text{O}_7$ of pyrochlores structure. Yttria filter is expected to offer stable material in which the volatility of the ruthenium can be effectively trapped because of its incorporation into a lattice of high stability over 900 °C under air condition. Ruthenium trapping quantity of yttria filter decreased linearly with increasing superficial air velocity. Also, quantity of ruthenium trapped on an yttria filter increased with increasing temperature and decreasing superficial air velocity. The TGA result of ruthenium trapped on an yttria filter indicates that there is weight loss of 5.8 wt% up to 1,400 °C, which

is believed to be due the thermally stable $Y_2Ru_2O_7$ phase formed on an yttria filter.

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