

Compositional changes in the interface between thorium doped uranium dioxide and zirconium by high-temperature annealing

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Compositional changes of the interface between thorium doped uranium dioxide and zirconium in an $U_{0.97}Th_{0.03}O_2$ -Zr system before and after the annealing were investigated using X-ray photoelectron spectroscopy, X-ray diffraction, and Raman spectroscopy. The original samples of thorium doped uranium dioxide and zirconium were oxidized into hyperstoichiometric $U_{0.97}Th_{0.03}O_{2+x}$ and ZrO_2 with a small amount of Zr, respectively. After the annealing of the $U_{0.97}Th_{0.03}O_{2+x}$ -Zr system at 1700 °C for 18 h, the reduction of the uranium and zirconium elements in each sample was observed.

I. INTRODUCTION

The interaction between uranium dioxide and zirconium has been intensively researched to comprehend the interfacial phenomenon between UO_2 fuel and Zircaloy cladding in a fuel rod [1-3]. During the operation of a pressurized water reactor (PWR), various fission products are actually created in a fuel rod. To examine the effect of the fission product on the property of oxide fuel, thorium was selected as the representative element exhibiting only a +4 oxidation state in lanthanide and actinide elements. Thereafter, we studied the compositional changes of the interface between thorium doped uranium dioxide and zirconium by the annealing at 1700 °C for 18 h using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Raman spectroscopy. Therefore, we could infer the role of lanthanide and actinide elements having +4 oxidation states in a fuel rod.

II. EXPERIMENTAL METHODS

$U_{0.97}Th_{0.03}O_2$ pellets with a diameter of 6.35 mm were fabricated using UO_2 and ThO_2 powder, and Zr samples were obtained by cutting a Zr rod (Sigma-Aldrich 267724-20G). The $U_{0.97}Th_{0.03}O_2$ -Zr system in which a Zr sample was placed on a $U_{0.97}Th_{0.03}O_2$ pellet was annealed at 1700 °C for 18 h in an alumina tube furnace (Ajeon Heating Industrial) under a H_2 atmosphere. After the annealing, the bottom of the Zr sample and the top of the $U_{0.97}Th_{0.03}O_2$ pellet in the $U_{0.97}Th_{0.03}O_2$ -Zr system were analyzed for an inspection of the interface.

XPS data were collected in a high vacuum chamber installed using a ESCALAB 220i-XL system (VG Scientific Ltd.) using an Al K_{α} X-ray source (1486.6 eV) at a base pressure below 1.0×10^{-8} Torr. The binding energies of all spectra were calibrated relative to that of adventitious carbon (284.6 eV). XRD spectra were obtained in the range of 20° to 120° with a step size of 0.02° for 0.2 s using a D8 ADVANCE system (Bruker) with a Cu K_{α} X-ray source. Raman results were measured using a shamrock SR500i Raman spectrometer (ANDOR) with a helium-neon laser of 632.8 nm operating at 8 mW. The spectra were accumulated in the range of 400 to 1200 cm^{-1} .

III. RESULTS AND DISCUSSION

Before the annealing of thorium doped uranium dioxide, the diffraction patterns of UO_2 were shown in the XRD spectrum, and the signals at 445, 575, and 1150 cm^{-1} related to UO_2 were observed in the Raman results. In addition, the XPS data showed that its surface was oxidized into hyperstoichiometric $\text{U}_{0.97}\text{Th}_{0.03}\text{O}_{2+x}$ composed of U(IV), U(V), U(VI), and Th(IV), which occurred at 379.6, 380.1, 381.0, and 333.9 eV, respectively. In the case of zirconium before the annealing, diffraction patterns of Zr metal and ZrO_2 were exhibited in XRD data, and a ZrO_2 peak at 182.3 eV was displayed in the XPS spectrum. After the annealing of thorium doped uranium dioxide and zirconium in an $\text{U}_{0.97}\text{Th}_{0.03}\text{O}_2\text{-Zr}$ system at 1700 °C for 18 h, XRD and Raman data of the $\text{U}_{0.97}\text{Th}_{0.03}\text{O}_2$ pellet were similar with those before the annealing, whereas XPS data of the $\text{U}_{0.97}\text{Th}_{0.03}\text{O}_2$ pellet illustrated peaks related to U(IV) and Th(IV). In the zirconium after annealing, only ZrO_2 signals were obtained in the XRD, and the peaks of ZrO_2 were observed at 476, 502, 536, 559, 616, and 637 cm^{-1} in the Raman spectrum.

IV. CONCLUSIONS

The chemical characteristics of the interface between $\text{U}_{0.97}\text{Th}_{0.03}\text{O}_2$ and Zr after the annealing were analyzed using XPS, XRD, and Raman spectroscopy. We found that the original thorium doped uranium dioxide and zirconium were oxidized into hyperstoichiometric $\text{U}_{0.97}\text{Th}_{0.03}\text{O}_{2+x}$ and ZrO_2 with the low amount of Zr, respectively. After the annealing of the $\text{U}_{0.97}\text{Th}_{0.03}\text{O}_2\text{-Zr}$ system, a reduction of the uranium element in the thorium doped uranium dioxide pellet and of the zirconium element in the zirconium sample appeared.

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REFERENCES

1. P. HOFMANN and C. POLITIS, "The kinetics of the uranium dioxide-Zircaloy reactions at high temperatures," *J. Nucl. Mater.*, **87**, 375 (1979).
2. P. HOFMANN, "Current knowledge on core degradation phenomena, a review," *J. Nucl. Mater.*, **270**, 194 (1999).
3. Y.-S. YOUN, J.-G. KIM, S. D. PARK, and Y.-K. HA, "Temperature-dependent variations of the interface between UO_2 and Zr," *Bull. Korean Chem. Soc.*, **36**, 2068 (2015).