

Variation of Compositions at the Interface Between $U_{0.97}Th_{0.03}O_2$ and Zr From High-Temperature Annealing

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1. Introduction

The study on the interaction between uranium dioxide and zirconium has been intensively performed to understand the interfacial phenomenon between oxide fuel and Zircaloy cladding in fuel rods [1-5]. Under actual irradiation, a variety of fission products were produced, and they influenced the chemical properties of uranium dioxide. Therefore, the interaction between fission product doped uranium dioxide and zirconium has to be investigated to confirm the effect of fission product on their interaction. Among various fission products, we selected thorium as a representative with +4 oxidation state in actinide elements.

Herein, we will describe the variation of compositions at the interface between thorium doped uranium dioxide and zirconium from annealing at 1700°C for 18 h using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Raman spectroscopy.

2. Experimental Details

Pellets of thorium doped uranium dioxide, $U_{0.97}Th_{0.03}O_2$, were fabricated using UO_2 and ThO_2 powders. In addition, Zr samples were produced by cutting a Zr metal rod. The $U_{0.97}Th_{0.03}O_2$ -Zr system was heated at 1700°C for 18 h in an alumina tube furnace under H_2 condition. After the annealing, the interface between $U_{0.97}Th_{0.03}O_2$ and Zr samples was measured using XPS, XRD, and Raman spectroscopy.

XPS data were recorded in a high vacuum chamber installed using a VG Scientific ESCALAB 220i-XL system with 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 measured spectra were calibrated relative to that of adventitious C 1s (284.6 eV).

XRD spectra were collected in the range of 20-120° with a step size of 0.02° for 0.2 s using a Bruker D8 ADVANCE system with a Cu K_{α} X-ray source.

Raman results were obtained using a ANDOR shamrock SR500i Raman spectrometer with a helium-neon laser of 632.8 nm wavelength operating at 8 mW. The spectra were acquired in the wavenumber range of 400 to 1200 cm^{-1} .

3. Results

In XRD and Raman spectra obtained at room temperature, the peaks corresponded to those of cubic UO_2 crystal structure. In addition, XPS data acquired at room temperature exhibited that the surface of thorium doped uranium dioxide was oxidized to hyperstoichiometric $U_{0.97}Th_{0.03}O_{2+x}$ containing U(IV), U(V), U(VI), and Th(IV). In Zr sample at room temperature, the diffraction patterns of Zr metal and ZrO_2 were displayed in XRD data, and a ZrO_2 peak was obtained in the XPS spectrum.

After the annealing of $U_{0.97}Th_{0.03}O_2$ -Zr system at 1700°C for 18 h, XRD and Raman data obtained from the $U_{0.97}Th_{0.03}O_2$ pellet were similar to those before the annealing, while XPS spectrum of the

$U_{0.97}Th_{0.03}O_2$ pellet showed signals related to U(IV) and Th(IV). In the case of Zr sample after annealing, the peaks of ZrO_2 were obtained in XRD and Raman spectra.

“Temperature-dependent variations of the interface between UO_2 and Zr”, Bulletin of the Korean Chemical Society, 36, 2068-2072 (2015).

4. Conclusion

Change of compositions at the interface between $U_{0.97}Th_{0.03}O_2$ and Zr before and after the annealing was researched using XPS, XRD, and Raman spectroscopy. The $U_{0.97}Th_{0.03}O_2$ and Zr samples at room temperature were oxidized to hyperstoichiometric $U_{0.97}Th_{0.03}O_{2+x}$ and ZrO_2 with a small amount of Zr metal, respectively. After the annealing of the $U_{0.97}Th_{0.03}O_{2+x}$ -Zr system, the reduction of uranium and zirconium in each sample occurred in our experiments.

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