Surface Characterization of Nd-doped UO_2 and its electrochemical study

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1. Introduction

Spent nuclear fuels are very complex and have totally different microstructure from initial fresh UO_2 fuel due to the formation of fission products, transuranium elements, and activation products with many different phases during irradiation. The physical and chemical properties of spent nuclear fuels are also totally different from initial fresh UO_2 fuel. For example, some actinide and lanthanide elements can form a solid solution with UO_2 lattice and make non-stoichiometry depending on their oxidation state and specific conditions. These alterations of UO_2 lattice could strongly be related to chemical reactivity such as corrosion and oxidation of UO_2 [1-2]. Thus, it is critical to characterize the physical and chemical properties of spent nuclear fuels affected by specific elements doping. Those characterizations should be useful to plan the final disposal or interim storage of spent nuclear fuels.

Herein, the influence of Nd-doping on the surface structure of UO_2 has been investigated by X-ray diffractionand Raman spectroscopy. Its electrochemical properties were also studied.

2. Methods and Results

$U_{1-y}Gd_yO_{2-x}$ pellets with various compositions (x = 0 ~ 0.1) were manufactured by mechanical blending solid reaction. Nd_2O_3 (or ThO_2) and UO_2 powder were thoroughly weighed mixed by grinding using an agate mortar. The powder mixtures were pressed into a pellet form. The pressed pellets were sintered at 1700℃ for 18 h in pure hydrogen atmosphere followed by annealing in same atmosphere at 1200℃ for 12 h. Hypo-stoichiometric $U_{1-y}Nd_yO_{2-x}$ form was manufactured by this reducing condition.

X-ray diffraction (XRD) technique was applied to confirm the lattice parameter and the solid solution state of $U_{1-y}Gd_yO_{2-x}$ pellets. XRD data were obtained by Bruker D8 Advance at room temperature. The CuKα line source filtered with a Ni foil (beam current 40mA at 40kV) was used. The lattice parameters of the samples were calculated from refinement process.

The surface structure of each pellet was measured by scanning electron microscopy (SEM) and Raman spectroscopy. SEM images were obtained using 20 keV electron acceleration voltage with 10 mm working distance. Raman spectra of each pellet were obtained using ANDOR Shamrock SR500i spectrometer with a 632.8nm wavelength He-Ne laser.

For electrochemical oxidation experiments, a standard three-electrode system with potentiostat (Pine) was employed to control applied potentials and to record current responses. The working electrode was $U_{1-y}Gd_yO_{2-x}$ pellet assembled on rotating disk electrode. Three-electrode system was worked in carbonate solutions.

3. Results

Nd in UO_2 solid solution cause a change in lattice parameter depending on its ion radius. For the rigid sphere model of a fluorite-type crystal structure [3, 4], the slope of lattice parameter against the dopant content (da/dy) can be calculated from mean cation radius and crystal radius of O^{2-} ions. If there is linear relationship with specific slope along the doping level, it is confirmed that the dopant is uniformly dissolved in UO_2 matrix as solid solution. For Nd doped UO_2, the lattice parameter decreased linearly as the Nd doping level is increased. This result is from that ion radius of Nd^{3+} is smaller than that of U^{4+}. Our experimental results show similar features with previous studies.

SEM images for $U_{1-y}Gd_yO_{2-x}$ pellets show that the grain size decreased with increasing Nd doping level. These features are strongly related to the oxygen vacancy and the interstitial oxygen.

Raman spectra of for $U_{1-y}Gd_yO_{2-x}$ pellets show the defect structure due to the oxygen deficiency at the region 500 to 650 cm^{-1} The defect structure was deconvoluted to three peaks at ~ ~530, ~575 and ~630 cm^{-1}. The peaks at ~530, ~575 and ~630 cm^{-1} were ascribed as defect due to oxygen vacancy associated with Gd^{3+}, first order L-O phonon mode due to crystal lattice disorder and formation of M_4O_9 during oxidation, respectively [5-7].

The Nd doping affects electrochemical oxidation of uranium dioxide. Cyclic voltametric experiments and electrochemical dissolution in carbonate solution were done to determine the susceptibility to anodic oxidation. The Nd-doping effect shows the suppression of both stages of anodic oxidation; matrix oxidation ($UO_2 \rightarrow UO_{2+x}$) and its further oxidation to soluble UO_2^{2+}.

4. Conclusions

The Nd doped uranium dioxide pellets with various doping level were investigated by XRD, Raman

spectroscopy, SEM, electrochemical experiments to investigate surface structure and electro chemical oxidation behaviors. The lattice parameter evaluated from XRD spectra indicated the formation of solid solutions. Raman spectra showed the existence of the oxygen vacancy. SEM images showed the grain structure on the surface of Nd doped uranium dioxide depending on doping level. In electrochemical dissolution experiment, both doping level and oxygen-to-metal ratio affected the oxidation behavior.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (No. 2021M2E3A3040092)

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