Surface Characterization and Electrochemical Oxidation of Metal Doped Uranium Dioxide

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1. Introduction

Fission products (FPs) including actinides, lanthanides, trans-uranium elements are produced and located in remaining UO_2 matrix after the irradiation of UO_2 nuclear fuel in the nuclear reactor [1-3]. Among them, actinides (An) and lanthanides (Ln) are doped in the UO_2 matrix as $(U, An, Ln)O_2$ solid solution form. It is considered that $(U,FP)O_{2\pm x}$ or stoichiometric form is produced depending on the location of the fuel and the circumstances of the nuclear reactor. To know and understand the structure and the characteristics of spent fuel, An or Ln doped $UO_{2\pm x}$ have been studied as simulated spent fuel [4-9]. Trivalent element in UO_2 matrix makes the oxygen vacancy from loss of oxygen for charge compensation. Tetravalent element alters lattice parameter of UO_2 due to diameter difference between the tetravalent element and replaced U. These structural changes have significant effect on not only relevant fuel performance but also the kinetics of fuel oxidation. Park and Olander explained the stabilization of Ln (III)-doped UO_2 against oxidation based on oxygen potential calculations [10].

In this work, we have been investigated the effect of Gd^{3+} and Th^{4+} doping on the UO_2 structure with Raman spectroscopy and X-ray diffraction to characterize the surface structure of nuclear fuel material. For Gd doped UO_2, its electrochemical oxidation behaviors are also investigated.

2. Experimental Section

$U_{1-y}Gd_yO_2$ and $U_{1-y}Th_yO_2$ solid solution pellets with various compositions were fabricated by mechanical blending solid reaction. Thoroughly weighed Gd_2O_3 (or ThO_2) and UO_2 powder were mixed by grinding using an agate mortar. The powder mixtures were compacted into a pellet form at 1400 psi for 15 seconds. 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. For Gd doped UO_2, hypo-stoichiometric $U_{1-y}Gd_yO_{2-x}$ form was manufactured by this reducing condition. To make stoichiometric and hyper-stoichiometric form of Gd doped UO_2, sintered $U_{1-y}Gd_yO_{2-x}$ pellets were further heated at specific temperature over 24h under specific atmosphere CO/CO_2

To confirm the solid solution state of each metal doped UO_2, X-ray diffraction (XRD) technique was applied. XRD data were obtained by Bruker D8 Advance at room temperature. The $CuK\alpha$ 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 SR303i 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 Gd doped UO_2 pellet assembled on rotating disk electrode. Three-electrode system was worked in carbonate solutions.

3. Results

The fission products in UO_2 solid solution cause a change in lattice parameter depending on their ion radii. For the rigid sphere model of a fluorite-type crystal structure [11, 12], 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 Gd doped UO_2, the lattice parameter decreased linearly as the Gd doping level is increased [8]. But it is opposite for Th doped UO_2 [9]. These results are from that ion radius of Gd^{3+} is smaller than that of U^{4+} and ion radius of Th^{4+} is larger than that of U^{4+}. Our experimental results show similar features with previous studies. For $U_{1-y}Gd_yO_{2-x}$, the oxygen vacancy is estimated from da/dy.

For Gd doped UO_2 solid solutions, their Raman spectra show the defect structure due to the oxygen deficiency at the region 500 to 650 cm^{-1} in Fig 1. But there is no defect structure in Raman spectra of Th doped UO_2 solid solutions because the replacement from U^{4+} to Th^{4+} is not suitable to produce the oxygen deficiency due to charge compensation.
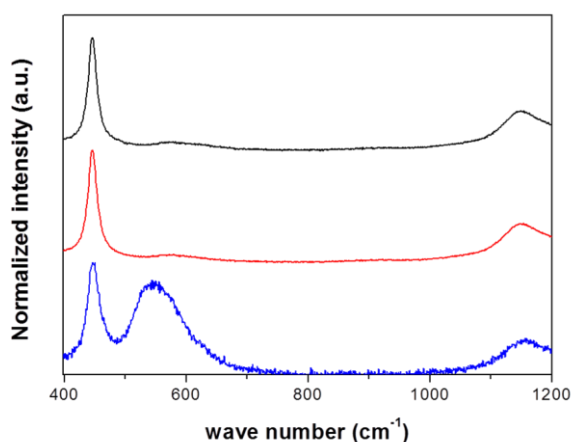
Fig. 1. Raman spectra of UO_2 (up, black line), $U_{0.95}Th_{0.05}O_2$ (middle, red line), and $U_{0.95}Gd_{0.05}O_2$ (bottom, blue line) pellets at room temperature, respectively

For Gd doped UO_2, three type solid solutions are categorized as hypo-stoichiometric ($U_{1-y}Gd_yO_{2-x}$), stoichiometric ($U_{1-y}Gd_yO_2$) and hyper-stoichiometric form ($U_{1-y}Gd_yO_{2+x}$). SEM images for those types show that the grain size decreased with increasing Gd doping level and decreasing oxygen-to-metal ratio. These features are strongly related to the oxygen vacancy and the interstitial oxygen. And the lattice contraction of pellets depending on stoichiometry was observed. From hypo-stoichiometric form to hyper-stoichiometric form, the lattice parameter decreased at same Gd content. Because increasing oxygen-to-metal ratio results in formation of U^{5+} and U^{6+} that have smaller ion radius that U^{4+}, hyper-stoichiometric form has lower lattice parameter.

The Gd 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 Gd-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+}. Not only Gd doping effect but also oxygen-to-metal ratio affects the kinetic of oxidation.

4. Conclusions

The Gd and Th doped uranium dioxide solid solution 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 Gd doped uranium dioxide depending on doping level and oxygen-to-metal ratio. In electrochemical dissolution experiment, both doping level and oxygen-to-metal ratio affected the oxidation behavior.

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