Study on the change in properties of uranium dioxide by co-doping of trivalent and tetravalent elements

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1. Introduction

After irradiation of UO₂ nuclear fuel in the reactor, fission products (FPs), lanthanides (Ln), actinides (An) and activation products are produced and located in the fuel [1-3]. Those elements are doped in the nuclear fuel as (U,FP,Ln,An)O_{2-x} form. To understand the structural character of the spent nuclear fuel, element doped UO₂ have been studied as simulated spent fuel. The element doping effect has influence on the phase stability in U-FP/Ln/An-O system, thermal conductivity and the relevant fuel performance. Raman spectroscopy has been used to investigate surface structure of the nuclear fuel materials, because of its sensitivity, convenience and non-destructive sample preparation [4]. The Raman studies on trivalent-doped UO₂ directly show the defect due to oxygen vacancy that could be created by loss of oxygen for charge compensation [5-7]. This defect has significant effect on the kinetics of fuel oxidation. Previous studies have been focused on single element doped UO₂. In this study, we have been investigated the effect on both Gd-and Zr-doping on the UO₂ structure with various experimental techniques to characterize the influence of co-doping of trivalent and tetravalent elements.

2. Experimental Section

U_{1-x-y}Gd_xZr_yO_2 (x=0, y=0; x=0.005, y=0.05; x=0.005, y=0.1; x=0.01, y=0.05) pellets were prepared by using a powder mixing method. The pellets were sintered at 1700 °C for 18 h and then cooled to room temperature in a reducing atmosphere with hydrogen gas.

Scanning electron microscopy (SEM, Jeol, USA) results revealed morphological and dispersive features of Gd and Zr in UO₂. X-ray diffraction (XRD) patterns of samples were performed with a Bruker AXS D8 Advance X-ray Diffractometer using Cu Kα radiation. The Raman spectroscopy was measured with an ANDOR Shamrock SR500i spectrometer, using a He-Ne laser with a wavelength 632.8 nm. Electrical conductivities of pellets were determined by calculating specific resistivities analyzed with 4-point probe (HM21-Jandel Co., UK).

3. Results & Discussion

In case of UO₂ sample has polygonal structures consisted of wrinkled and flattened domains. It is also observed that the domain size decreases rapidly with increase of Gd and Zr doping level.

XRD patterns of all samples show similar features each other (Fig. 1). The lattice parameters are refined from each XRD spectrum and they show linearly decreasing of lattice change with increasing doping level. Because Gd^{3+} (1.053 Å) and Zr^{4+} (0.84 Å) have difference ionic radii than U^{4+} (1.001 Å), the lattice parameter decreases with increasing doping level. The portion of Zr^{4+} is higher than that of Gd^{3+} for all doped samples.

To study the electrochemical behaviors of samples, U_{1-x}Gd_xZr_yO_2 electrodes were prepared mounting pellets onto steel-working electrode. And 3 electrode system (CHI-600D, USA) is used for cyclic voltammetry and RDE system of 1000 rpm (PINE, USA) in carbonate/bicarbonate dissolved in 0.1 M NaCl solution ([HCO₃⁻/CO₃²⁻]=0.01 mol L⁻¹). All electrodes were polished with sand papers of 1000 grid before electrochemical analyses.

Fig. 1. Raman spectra of UO₂ (up, black line) and U_{1-x}Gd_xZr_yO_2 (bottom, colored lines) pellets

Raman spectra of all samples show significant two peaks at ~445 and ~1150 cm⁻¹ that were assigned to U-
O symmetric stretching mode in the fluorite structure [14-16] and an overtone of the first order longitudinal optical (L-O) phonon mode regarded as fingerprint for quasi-perfect fluorite structure, respectively. For doped samples, the intensities of two peaks at ~445 and ~1150 cm\(^{-1}\) markedly decrease, but the broad band in the region 500 to 650 cm\(^{-1}\) increase. The decreasing intensity of peaks at ~445 and ~1150 cm\(^{-1}\) means the lattice distortion of perfect fluorite structure. The broad band was deconvoluted to three peaks at ~530, ~575, ~600 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 \(\text{M}_4\text{O}_{9}\), respectively. The peaks at ~530, ~575 and ~630 cm\(^{-1}\) were assigned as ZrO\(_8\)-type complex forms in the fluorite UO\(_2\) matrix via successive accommodation of doped Zr. The relative area ratios of each peak to the peak at ~445 cm\(^{-1}\), give qualitative information about formation of each lattice disorder.

Electrical conductivities, obtained from measuring the specific resistivity of each pellets, increased as increasing doping level. However there is no clear trend.

Cyclic voltametric experiments were done to determine the susceptibility to anodic oxidation. It has been known that Gd-doping suppresses both stages of anodic oxidation; matrix oxidation (UO\(_2\) → UO\(_{2+x}\)) and its further oxidation to soluble U\(^{6+}\) (as UO\(_{2+2}\)). Our samples, both Gd and Zr doped, show similar results.

4. Conclusions

\(\text{U}_{1-x-y}\text{Gd}_x\text{Zr}_y\text{O}_2\) pellets have been characterized by SEM, XRD, Raman spectroscopy, electrical conductivity and electrochemical experiment. The substitution of Gd and Zr atoms into the UO\(_2\) lattice is confirmed by lattice parameters from XRD spectra. Raman spectra show that presence of Gd\(^{3+}\)-oxygen vacancy clusters and ZrO\(_8\)-type complex in the structure of \(\text{U}_{1-x-y}\text{Gd}_x\text{Zr}_y\text{O}_2\). Electrochemical experimental results also show the influence of Gd-and Zr-doping on kinetics of oxidation.

REFERENCES