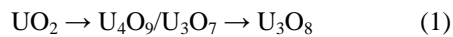


Influence of Gd-Dopant on Structural and Electrochemical Property of Uranium Dioxide

Jeongmook Lee, Jandee Kim, Young-Sang Yoon, Sang-Eun Bae, Jong-goo Kim, Yeong-Keong Ha & Jong-Yun Kim*
Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute,
989-111 Daedeok-daero, Yuseong-gu, Daejeon, 34057, Republic of Korea
*Corresponding author: kji@kaeri.re.kr

1. Introduction

The permanent disposal of spent nuclear fuel in deep geologic repositories has been under consideration internationally for decades. It is hard to expect the container failure due to multiple barriers, however, if failure will occur, ground water contacts the fuel and radionuclide and fission products will be released [1]. The release rate of radionuclides in used fuel (UO₂) matrix will be controlled by the corrosion/dissolution rate of UO₂. The UO₂ oxidation reaction occurs in two stages.



The key feature of this oxidation reaction is that the rate of oxidation is influenced by the presence of dopants and the nature of the intermediate phase changes with the doping level [2]. Park and Olander studied that rare earth (III)-doped UO₂ is more stable for oxidation [3-4]. For example, as the Gd content increased the Gd-doped UO₂ is stabilized by the formation dopant-oxygen vacancy clusters. This reduces the interstitial sites required for the incorporation of other oxygen under oxidation.

In spent nuclear fuel, there are large number fission products such as rare earth elements with typical yields. Among them, Gd has often been chosen as a dopant in simulated spent nuclear fuel [5-7] because it has been proposed as a burnable absorber for the uranium-gadolinia fuels [8] and it is one of representative element of rare earth (III).

In this present work, we have investigated the structure of Gd-doped uranium dioxide determined by XRD and Raman spectroscopy, and correlated their electrochemical reactivity under oxidation condition.

2. Experimental Details

U_{1-x}Gd_xO₂ solid solution pellets were prepared by a solid-state reaction. Calculated amounts of Gd₂O₃ and UO₂ powder were weighed, and blended using an agate mortar. Then, the mixture was pressed into a pellet form and sintered at 1700°C for 18 h in hydrogen atmosphere.

The microstructures were observed by scanning electron microscopy (SEM) and elemental mapping was done by energy-dispersive X-ray spectroscopy analysis (EDS). X-ray diffraction (XRD) data were obtained in the range 20° to 120° (scan step 0.02°) by Bruker D8

Advance at room temperature. The CuK α line source filtered with a Ni foil (beam current 40mA at 40kV) was used. Raman spectra were acquired using a SR303i Raman spectrometer with a 632.8nm excitation wavelength HeNe laser. Individual spectrum was acquired using an exposure 100 s over the wavenumber range from 400 to 1200 cm⁻¹. The laser was focused onto sample using an Olympus microscope with 50x lens. The surface resistivity of each pellet was also measured by four point probe meter (Jandel, HM-21) in order to acquire electrical conductivity. For electrochemical experiments, a standard three-electrode system was employed with carbonate solutions. The working electrode was U_{1-x}Gd_xO₂ pellet assembled rotating disk electrode and a potentiostat CHI606A was used to control applied potentials and to record current responses.

3. Results

The lattice parameter refined from each XRD spectrum, a (nm) of each pellets decreased linearly as the Gd doping level is increased [x values in U_{1-x}Gd_xO₂]. Applying Vegard's law [9] to the results, this linear relationship indicates that Gd is uniformly dissolved in UO₂ matrix as solid solution and their structure remained as a fluorite structure of UO₂ in the given range x = 0 to 0.10 of Gd content. In case of Gd₂O₃-dispersed UO₂, in which Gd₂O₃ particles are just dispersed in the UO₂ matrix, there is no change in lattice parameter with increasing Gd content as shown in Fig. 1 and XRD peaks of monoclinic Gd₂O₃ were observed together with those of fluorite-type UO₂.

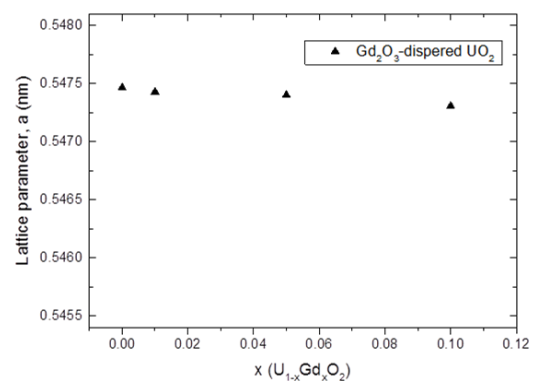


Fig.1. Lattice parameter of Gd₂O₃-dispersed UO₂ (U_{1-x}Gd_xO₂) versus Gd content (x) in (U_{1-x}Gd_xO₂) at a room temperature.

Raman spectrum of pure UO_2 shows significant two peaks, at $\sim 445 \text{ cm}^{-1}$ and at $\sim 1150 \text{ cm}^{-1}$ as shown in Fig. 2. The $\sim 445 \text{ cm}^{-1}$ peak is assigned to $\text{U}^{\text{IV}}\text{-O}$ symmetric stretching mode in the fluorite structure of UO_2 , and $\sim 1150 \text{ cm}^{-1}$ band is ascribed as an overtone of the first order lattice-oxygen phonon [10] or a finger print for quasi-perfect fluorite structure [11].

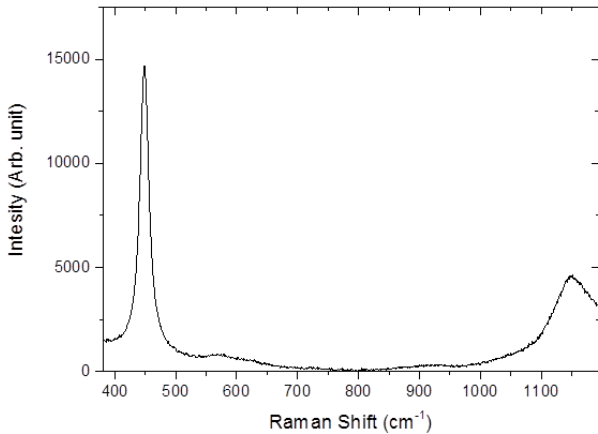


Fig. 2. Raman spectrum of UO_2 pellet at a room temperature.

The relative ratio between the peak at $\sim 445 \text{ cm}^{-1}$ and the broad band in the region 500 to 650 cm^{-1} is dramatically changed with increasing Gd doping level. Previous studies assigned this broad band as combined peaks at ~ 540 , 570 and 640 cm^{-1} . The peak at 540 cm^{-1} dominates over other peaks in broad band and could be from the formation of phase with a perovskite (ABO_3) structure [12]. The dominance of this peak in $\text{U}_{1-x}\text{Gd}_x\text{O}_2$ explains the influence of Gd^{III} -doping that makes the creation of oxygen vacancy in UO_2 lattice due to the need for charge compensation.

The Gd-doping affects the electrical conductivity and electrochemical property of uranium dioxide. The electrical conductivity increases with increasing Gd content but slightly decreases at $x = 0.10$ of Gd content in $\text{U}_{1-x}\text{Gd}_x\text{O}_2$. Cyclic Voltametric (CV) experiments were done to determine the susceptibility to anodic oxidation. The Gd-doping suppresses both stages of anodic oxidation; matrix oxidation ($\text{UO}_2 \rightarrow \text{UO}_{2+x}$) and its further oxidation to soluble U^{VI} (as UO_2^{2+}).

4. Conclusions

$\text{U}_{1-x}\text{Gd}_x\text{O}_2$ solid solution pellets have been characterized by SEM-EDS, XRD, Raman spectroscopy, electrical conductivity and electrochemical experiment. The substitution of Gd atoms into the UO_2 lattice is confirmed by lattice parameters from XRD spectra. Raman spectra shows that presence of Gd^{III} -oxygen vacancy clusters are increasingly dominated in the structure of $\text{U}_{1-x}\text{Gd}_x\text{O}_2$ as the Gd content increases. This reduces the number of oxygen vacancy which can be filled by the interstitial oxygen required for oxidation to occur. Electrochemical experimental results also show

the influence of Gd-doping on kinetics of oxidation. The fundamental results in this work are applicable to interpret the oxidation behavior of spent nuclear fuel containing various fission products.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (No.2012M2A8A5025925)

REFERENCES

- [1] D. W. Shoemith, Fuel corrosion processes under waste disposal conditions, *Journal of Nuclear Materials*, Vol.282, p. 1-31, 2000.
- [2] H. He, M. Broczkowski, K. O'Neil, D. Ofori, O. Semenikhin and D. W. Shoemith, *Corrosion of Nuclear Fuel (UO₂) Inside a Failed Nuclear Waste Container*, Nuclear Waste Management Organization, Toronto, Ontario, 2012.
- [3] K. Park and D. R. Olander, A defect model for the oxygen potential of urania, *High Temperature Science*, Vol.29, p. 203-222, 1990.
- [4] K. Park and D. R. Olander, Defect models for the oxygen potentials of gadolinium and europium-doped Urania, *Journal of Nuclear Materials*, Vol.187, p. 89-96, 1992.
- [5] L. E. Thomas, R. E. Einziger and H. C. Buchanan, Effect of fission products on, air-oxidation of LWR spent fuel, *Journal of Nuclear Materials*, Vol.201, p. 310-319, 1993.
- [6] T. K. Campbell, E. R. Gibert, G. D. White, G. F. Piepel, and B. J. Wrona, Oxidation behavior of nonirradiated UO_2 , *Nuclear Technology*, Vol.85, p. 160-171, 1989.
- [7] G.-S You, K.-S Kim, D.-K Min and S.-G Ro, Oxidation kinetic changes of UO_2 by additive addition and irradiation, *Journal of Nuclear Materials*, Vol.277, p. 325-332, 2000.
- [8] IAEA, International Atomic Energy Agency Report, IAEA-TECDOC-844.
- [9] A.R West, *Basic Solid State Chemistry*, Wiley, New York, p. 253, 1991.
- [10] T. Livneh and E. Sterer, Effect of pressure on the resonant multiphonon Raman scattering in UO_2 , *Physical Review B*, Vol.73, p. 0851181-9, 2006.
- [11] D. Manara and B. Renker, Raman spectra of stoichiometric and hyperstoichiometric uranium dioxide, *Journal of Nuclear Materials*, Vol.321, p.233-237, 2003.
- [12] H. He, P. G. Keech, M. E. Broczkowski, J. J. Noel and D. W. Shoemith, Characterization of the influence of fission product doping on the anodic reactivity of uranium dioxide, *Canadian Journal of Chemistry*, Vol.85, p. 1-12, 2007.