

The Influence of Neodymium Doping and Non-stoichiometry on the Structural and Electrochemical Properties of Uranium Dioxide

Seohyeon Park^{1),2)}, Jandee Kim¹⁾, Jeongmook Lee¹⁾, Jeong-mi Park^{1),2)}, Young-Sang Youn¹⁾,
Choong Kyun Rhee²⁾, and Sang Ho Lim^{1),3),*}

¹⁾ Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu,
Daejeon, Republic of Korea

²⁾ Chungnam National University, 99, Daehak-ro, Yuseong-gu, Daejeon, Republic of Korea

³⁾ University of Science and Technology, 217, Gajeong-ro, Yuseong-gu, Daejeon, Republic of Korea

* slim@kaeri.re.kr

1. Introduction

The deep geological disposal method has been internationally considered as final disposal of spent nuclear fuels (SNFs) [1]. However, this method has risks such as the exposure of SNFs to ground water due to container failure or unpredictable natural disasters. The geologic disposal condition could be significantly changed for long-term disposal period, hundreds of thousands of years and could affect the physical and chemical properties of SNFs. Thus, it is necessary to characterize SNFs under various conditions to evaluate the safety of disposal strategy.

SNFs include various fission products and have partially non-stoichiometry. Those are strongly related to the structure and reactivity of SNFs [2-4].

In this study, the influence of Nd doping and non-stoichiometry on the structural and electrochemical properties of UO_2 has been investigated to understand the behavior of SNFs in deep geologic repositories.

2. Experimental

The UO_2 and/or Nd_2O_3 (weighed as 0, 2, 6, and 10mol% Nd) powders were mixed and pelletized.

The pellets were sintered in a linear tube furnace with H_2 atmosphere at 1700°C for 18 h to form UO_{2-x} or $\text{U}_{1-y}\text{Nd}_y\text{O}_{2-x}$. And then sintered pellets were oxidized with CO/CO_2 mixed gas at 1500°C for 12 h to form UO_{2+x} or $\text{U}_{1-y}\text{Nd}_y\text{O}_{2+x}$. The surface morphologies of prepared pellets were observed by scanning electron microscopy (SEM). To obtain the lattice parameter of prepared pellets, X-ray diffraction (XRD) was conducted under Bruker AXS D8 Advance using $\text{Cu K}\alpha$ line source filtered with a Ni foil at room temperature. Raman spectroscopy was conducted with ANDOR Shamrock SR500i spectrometer with a wavelength of 632.8 nm from He-Ne laser. All electrodes were polished with 3000 grid sand paper and then the oxide layer on the surface was removed through a cleaning process at a potential of -1.5 V for 5 minutes prior to an electrochemical experiment. Electrochemical experiments were carried out with cyclic voltammetry (CHI-600D, USA) with 0.01 M carbonate ion in 0.1 M NaClO_4 aqueous solution.

3. Results

The grain structures of $\text{U}_{1-y}\text{Nd}_y\text{O}_{2+x}$ greatly vary depending on the Nd-doping level as shown in Fig 1.

In case of the hypo-stoichiometric $U_{1-y}Nd_yO_{2-x}$, the domain size sharply decreases as the Nd doping level increases. On the other hand, hyper-stoichiometric pellets produced through CO/CO₂ oxidation have larger domain sizes.

The lattice parameters of $U_{1-y}Nd_yO_{2-x}$ pellets linearly decreased with doping levels. However, the lattice parameters for $U_{1-y}Nd_yO_{2+x}$ pellets do not show a linear change but have much lower value than those of $U_{1-y}Nd_yO_{2-x}$ pellets.

Raman spectra of $U_{1-y}Nd_yO_{2-x}$ pellets have defect structures related to oxygen deficiency (500 to 650 cm⁻¹). As the Nd doping level increased, the defect structure grew. Raman spectra of $U_{1-y}Nd_yO_{2+x}$ also have similar features.

In the cyclic voltammetry (CV) analysis of the $U_{1-y}Nd_yO_{2+x}$ electrodes, the surface oxidation are observed at about -0.2 to 0.2 V in a 0.01 M carbonate ion in 0.1 M NaClO₄ electrolyte. The surface oxidation of the hypo-stoichiometry pellets is characterized by the increasing Nd doping level. The surface oxidation of the hyper-stoichiometry pellets decreased as Nd doping level decreased.

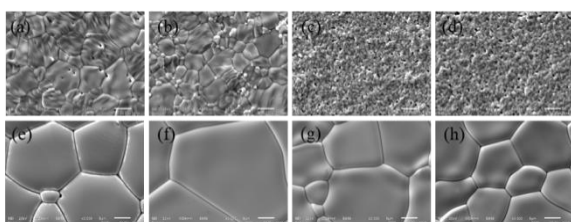


Fig. 1. SEM images for (a-d) $U_{1-y}Nd_yO_{2-x}$ surface (hypo-stoichiometric) and (e-h) $U_{1-y}Nd_yO_{2+x}$ (hyper-stoichiometric): (a, e) $y = 0$, (b, f) $y = 0.02$, (c, g) $y = 0.6$ and (d, h) $y = 0.10$.

4. Conclusions

The influence of Nd doping and non-stoichiometry on the physical and electrochemical properties of

UO₂ is investigated by SEM, XRD, Raman spectroscopy and electrochemical measurement. $U_{1-y}Nd_yO_{2-x}$ and $U_{1-y}Nd_yO_{2+x}$ have shown distinctive surface structure and electrochemical oxidation behaviors. Non-stoichiometry is more effective than Nd doping.

ACKNOWLEDGEMENT

This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (No. 2017M2A8A5014754)

REFERENCES

- [1] P. Hofmann, C. Politis, "THE KINETICS OF THE URANIUM DIOXIDE-ZIRCALOY REACTIONS AT HIGH TEMPERATURES", J. Nucl. Mater. 87, 375-397(1979).
- [2] M. Miyake, M. Katsura, S. Yamanaka, "A STUDY OF THE REACTION BETWEEN UO₂ AND Zr", J. Nucl. Mater. 154, 123-127(1988).
- [3] H. KLEYKAMP, "The Chemical State of the Fission Products in Oxide Fuels", J. Nucl. Mater, 131, 221-246 (1985).
- [4] R.C. Ewing, "Long-term storage of spent nuclear fuel", Nat. Mater, 14, 252-257 (2015).