

Influence of Metal-doping on the Surface Structure and Electrochemical Reactivity of Uranium Dioxide

Jeongmook Lee^{a)*}, Jandee Kim^a, Young-Sang Youn^{a)}, Seohyun Park^{a)b)}, Jeong-mi Park^{a)b)}, Jong-Yun Kim^{a)c)} and Sang Ho Lim^{a)c)}

^{a)} Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, Republic of Korea

^{b)} Chungnam National University, 99, Daehak-ro, Yuseong-gu, Daejeon, Republic of Korea

^{c)} University of Science & Technology, 217, Gajeong-ro, Yuseong-gu, Daejeon, Republic of Korea

*leejm@kaeri.re.kr

1. Introduction

Spent nuclear fuels (SNFs) 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 [1-3]. Additionally, the physical and chemical properties of UO_2 lattice were also changed. In particular, 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 [4-5]. Thus, it is critical to characterize the physical and chemical properties of SNFs affected by specific elements doping. Much information from those characterizations should be useful to plan the final disposal or interim storage of SNFs.

Herein, the influence of metal-doping on the surface structure of UO_2 has been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy. Various simulate fuels (Nd^{3+} -, Gd^{3+} -, Zr^{4+} -, Th^{4+} -doped UO_2) were used. Their electrochemical properties were also investigated.

2. Experimental sections

UO_2 and Nd_2O_3 (or Gd_2O_3 , ZrO_2 , ThO_2) powders for $\text{U}_{1-y}\text{Nd}_y\text{O}_2$ (or $\text{U}_{1-y}\text{Gd}_y\text{O}_2$, $\text{U}_{1-y}\text{Zr}_y\text{O}_2$, $\text{U}_{1-y}\text{Th}_y\text{O}_2$) with various y components were mixed and pelletized. The sample pellets were sintered in the tube furnace at 1700°C for 18 h with hydrogen atmosphere. XRD data was collected by Bruker D8 Advance using $\text{CuK}\alpha$ line source (beam current 40 mA at 40 kV). The lattice parameters of the samples were calculated from XRD spectra with refinement process. The surface morphologies of sample pellets were obtained by SEM. Raman spectra were measured using ANDOR Shamrock SR500i spectrometer with 632.8 nm He-Ne laser and analyzed by peak deconvolution method.

3. Results

The lattice parameters for $(\text{U,Nd})\text{O}_2$, $(\text{U,Gd})\text{O}_2$, $(\text{U,Zr})\text{O}_2$, and $(\text{U,Th})\text{O}_2$ linearly varied as the doping level increased. These linear variations represented that sample pellets were formed as a solid solution.

The grain size observed in SEM images for $(\text{U,Gd})\text{O}_2$, $(\text{U,Nd})\text{O}_2$, and $(\text{U,Zr})\text{O}_2$ decreased with increasing doping level. However, there was less change of the grain size with various Th doing levels in $(\text{U,Th})\text{O}_2$.

Raman spectra of $\text{U}_{0.9}\text{Th}_{0.1}\text{O}_2$ and UO_2 showed same feature as shown in Fig. 1. However, there were

defect structures related to oxygen vacancy in Raman spectra of $U_{0.9}Gd_{0.1}O_{2-x}$ and $U_{0.9}Nd_{0.1}O_{2-x}$ at $500 \sim 650 \text{ cm}^{-1}$. Trivalent elements replacing U^{4+} could make oxygen vacancy that distorts UO_2 fluorite lattice. For $U_{0.9}Zr_{0.1}O_2$, there was no defect structure related to oxygen vacancy. But distinct peak at $\sim 598 \text{ cm}^{-1}$ was observed. This peak would be assigned as a formation of ZrO_8 -type complex in UO_2 lattice.

Electrochemical experiments showed that this surface structure would be strongly related to chemical reactivity.

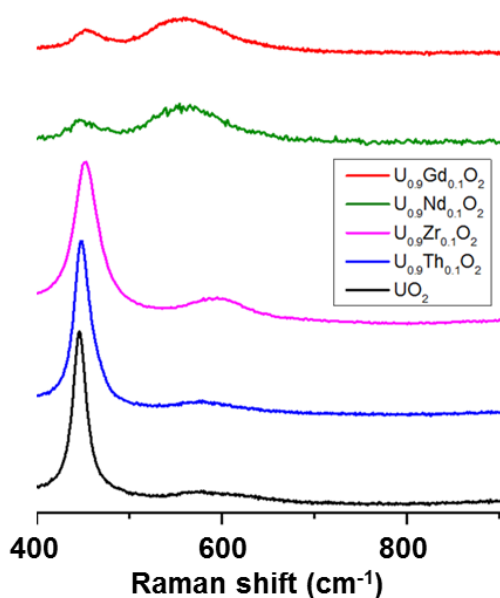


Fig. 1. Raman spectra of UO_2 , $U_{0.9}Th_{0.1}O_2$, $U_{0.9}Zr_{0.1}O_2$, $U_{0.9}Nd_{0.1}O_2$, and $U_{0.9}Gd_{0.1}O_2$ from bottom to top.

4. Conclusion

Summarizing results, trivalent doping elements, Gd^{3+} and Nd^{3+} , form the oxygen vacancy and the smaller grain size in UO_2 surface structure. Tetravalent dopant, Th^{4+} , has small influence on UO_2 surface structure. However, other tetravalent dopant, Zr^{4+} , shows large influence on UO_2 surface structure. Electrochemical properties depends on the doping

element.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (2017M2A8A5014754)

REFERENCES

- [1] H. Kleykamp, The chemical state of the fission products in oxide fuels, *Journal of Nuclear Materials*, 131, 221-246 (1985).
- [2] R. J. M. Konings, T. Wiss, and O. Beneš, Predicting material release during a nuclear reactor accident, *Nature Materials*, 14, 247–252, (2015).
- [3] R. C. Ewing, Long-term storage of spent nuclear fuel, *Nature Materials*, 14, 252–257 (2015).
- [4] M. Razdan and D. W. Shoesmith, Influence of Trivalent-Dopants on the Structural and Electrochemical Properties of Uranium Dioxide (UO_2), *Journal of the Electrochemical Society*, 161, H105–H113 (2013).
- [5] J. Kim, J. Lee, Y.-S. Youn, N. Liu, J.-G. Kim, Y.-K. Ha, S.-E. Bae, D. W. Shoesmith, and J.-Y. Kim, The Combined Influence of Gadolinium Doping and Non-stoichiometry on the Structural and Electrochemical Properties of Uranium Dioxide, *Electrochimica Acta*, 247, 942–948 (2017).