Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 18-19, 2017

Physical and Chemical Properties of Simulated Spent Fuel: Urania Doped with Gd(III) and/or Th(IV)

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1. Introduction

Dissolution behaviors of radionuclides from spent nuclear fuel under disposal conditions can be influenced by reactivity of the UO_2 matrix. The major factors to affect to the reactivity of UO_2 matrix are stoichiometry of $UO_{2\pm x}$, rare earth (RE) doping in matrix and environmental conditions to contact with matrix. [1] Therefore, it is important to understand chemical and physical properties of UO_2 matrix determined by differential stoichiometry of matrix, control the release behaviors of radionuclides.

In addition, the stability of the cubic fluorite structures of U_4O_9-type, oxidized form of UO_2, is enhanced, and resists more oxidation until U_3O_8 depending on RE contents as compared with un-doped UO_2. [2-4] Also, the corrosion/dissolution behaviors of matrix are influenced by oxidative state of RE.

So, this work presents comparisons of changes in grain structures, lattice parameter, electrical conductivity and electrochemical dissolutions depending on RE dopants (Gd(III) or Th(IV)) on UO_2 matrix and its level, and stoichiometry of $UO_{2\pm x}$ matrix. Well-formed solid solutions with each dopants on $UO_{2\pm x}$ matrices were studied by non-destructive analysis of XRD and Raman. Finally, the influences of Gd(III) and Th(IV) dopants and stoichiometry of matrix on corrosion/dissolutions of $UO_{2\pm x}$ matrix were examined by electrochemical study.

2. Methods and Results

Green pellets prepared by using unirradiated UO2 powder mixed with Gd_2O_3 or ThO_2 powder were sintered in a linear type of furnace at 1700°C in a reducing mood for 24 h. And then, stoichiometry of Gd-, and/or Th-doped pellets only are adjusted through the mild oxidation step controlling the oxygen potential with CO/CO_2 mixed gas and temperatures depending on various Gd-contents according to the Ellingham diagram (thermodynamic conditions of solid solution forms).

2.1 Structural Analysis Using SEM and XRD

Stoichiometric and non-stoichiometric $U_{1-y}Gd_yO_{2\pm x}$ and $U_{1-y}Th_yO_{2\pm x}$ solid solution with y=0, 0.01, 0.05 and 0.10 were successfully prepared and characterized by non-destructive analysis of SEM and XRD.

Apparently, the grain structures of $U_{1-y}Gd_yO_{2\pm x}$ and $U_{1-y}Th_yO_{2\pm x}$ pellets have shown the different features depending on the dopant level as shown in Fig. 1. Although Th contents increase, the grain structure has not been changed to have a tolerance to retaining the grain size, however, Gd doping leads the contraction of grain size small with increased grain boundary dramatically. This structural property of grain depending on dopants can affect to other physical characterization as like electrical conductivity related with thermal conductivity of pellets.

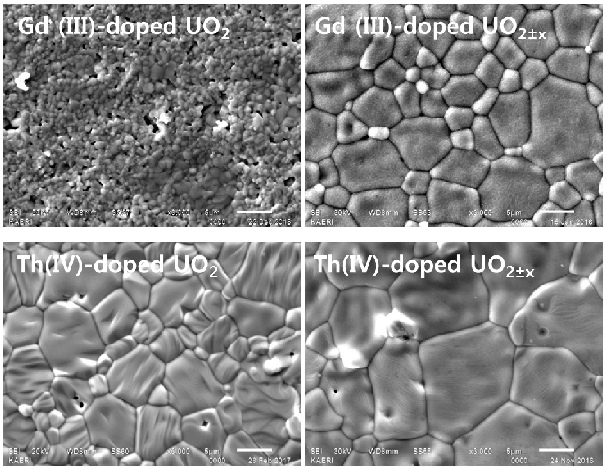

Fig. 1. Grain structures of 5 mol% of Gd(III)-, and/or Th(IV)-doped $UO_{2\pm x}$.

The electrical conductivity of $U_{1-y}Gd_yO_{2\pm x}$ and $U_{1-y}Th_yO_{2\pm x}$ pellets were investigated by using the 4-point probe technique (HM21-Jandel Co., UK) at room temperature. Fig. 2 shows that Th-doping level does not affect to electrical conductivity in stoichiometric UO_2 matrix but, dependent in non-stoichiometric matrix, and this result is similar with in Gd-doping case. A possible explanation has been proposed that there are two conductivity pathways, matrix and grain boundary, both attributed to the creation of UV ions leading to holes in the U5f level. These holes migrate by a polaron hopping process in which the normally localized electrons are transported between cations by a series of thermally-assisted jumps. [5-6]

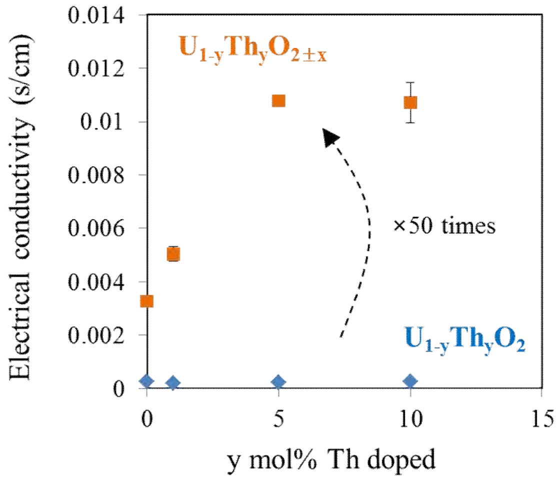

Fig. 2. Electrical conductivity of $U_{1-y}Th_yO_{2\pm x}$ depending on doping level and stoichiometry of matrix.

XRD patterns were recorded using a Bruker AXS D8 Advanced X-ray Diffractometer using Cu Kα radiation at room temperature. XRD data were collected in the 2θ range from 20° to 120° using 0.02° step size. And lattice parameters were calculated by Pawley's refinement process using the TOPAS (Version 4.2 Bruker AXS) analysis software. The lattice contraction factor of $U_{1-y}Gd_yO_{2\pm x}$, the slope of lattice parameter depends on dopant level, shows decreasing slope of -0.0173, however, $U_{1-y}Th_yO_{2\pm x}$ has increasing slope of 0.0098. In case of Gd-doped, the contraction could be caused by the possible charge compensation mechanisms as the Gd content increases; (i) the creation of the smaller U^V cation; and (ii) the formation of O_V. Meanwhile, Th-doping does not lead the charge difference, and only the size of Th(IV) dopant can affect to lattice expansion of $U_{1-y}Th_yO_2$. Also, the influences of dopants on UO_2 matrix on oxidative electrochemical behaviors were investigated by electrochemical study. Trivalent Gd-doped $U_{1-y}Gd_yO_{2\pm x}$ shows the lowest anodic activity, however, $U_{1-y}Th_yO_{2\pm x}$ presents relatively constant dissolutive current.

3. Conclusions

$U_{1-y}Gd_yO_{2\pm x}$ and $U_{1-y}Th_yO_{2\pm x}$ have shown distinctive structural features and electrochemical oxidation behaviors. And Gd(III) stabilized urania matrix by forming Gd(III)-oxygen vacancy clusters as increase the contents level, while Th(IV) substitution for U(IV) of UO_2 lattice leads no changes in structure and stability of electrochemical dissolution.

REFERENCES

[1] D. W. Shoesmith, The chemistry/electrochemistry of spent nuclear fuel as a wasteform, in "Uranium: Cradle to Grave", P. Burns, G. Simon (Eds.), Mineralogical Society of Canada, Short Course Series, Vol. 43, Ch. 11, 2013.

[2] H. He, M. Broczkowski, K. O'Neil, D. Ofori, O. Semenikhin and D. Shoesmith, Corrosion of nuclear fuel (UO_2) inside a failed nuclear waste container, Report NWMO TR-2012-09, Nuclear Waste Management Organization, Toronto, ON, 2012.

[3] H. He, Z. Qin and D. W. Shoesmith, Characterizing the relationship between hyperstoichiometry, defect structure and local corrosion kinetics of uranium dioxide, Electrochim. Acta, Vol.52, p. 53, 2010.

[4] H. He, R. K. Zhu, Z. Qin, P. Keech, Z. Ding and D. W. Shoesmith, Determination of local corrosion kinetics on hyper-stoichiometric UO_{2+x} by scanning electrochemical microscopy, Journal of Electrochemical Society, vol. 156, p. C87, 2009.

[5] T. Ishii, K. Naito and K. Oshima, Electrical conductivity and defect structures in non-stoichiometric UO_{2+x}, Journal of Nuclear Matererials, vol. 36, p.288, 1970.

[6] S.-H. Kanga, J.-H. Lee, H.-I. Yoo, H. S. Kim and Y. W. Lee, Non-stoichiometry, electrical conductivity and defect structure of hyper-stoichiometric UO_{2+x} at 1000°C, Journal of Nuclear Matererials, vol. 277, p.339, 2000.