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Physicochemical Behaviour of Zr(IV)-, and/or Th(IV)-doped UO_2 Pellets

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1. Introduction

Spent nuclear fuel (SNF) under the conditions of long-term storage in a geological repository has been received attentions for decades [1-2]. These efforts to understand the behavior of SNF lead to safe usage and storage of fuel.

The behaviour of SNF depends on the physicochemical property of the fuel consisted with fission products within uranium matrix [3]. These products induce many physical and chemical changes in the fuel during storage, and it might bring the unexpected situations. Therefore, fission products and their distribution in the uranium matrix, are the key factors to determine the SNF property and behaviors. Among the various kinds of fission products, we focus the rare earth elements in the SNF, because UO_2 is known to form substitutional solid solution with oxides of tetravalent (Th, Np, Pu), trivalent (rare earths), divalent (Mg, Ca, Sr) and monovalent (Li and Na) metal atoms [4]. Among all these oxides, tetravalent elements are natural substituents since uranium occur as U^{4+} in UO_2 and these elements are expected to form complete range (0–100 mol%) of solid solution with UO_2.

In this work, UO_2 and Zr(IV)- and/or Th(IV) doped UO_2 pellets were prepared and investigated to study about influences of tetravalent rare earth on the physicochemical properties such as grain structure, electrical conductivity and electrochemical oxidative dissolution.

2. Experimental

The un-irradiated UO_2 and Zr- and/or Th doped UO_2 pellets are fabricated by sintering pressed compacts pellets of fine-grained UO_2 powders and ZrO_2 and/or ThO_2 containing UO_2 powders at ~1700ºC in a H_2 reducing atmosphere. The doping amounts were 1 and 10 mol% contrasting with U^{4+} in UO_2, respectively. Prepared pellets have ~8 mm dia. and less than 1 mm thickness.

Electrical conductivities of pellets were determined by calculating specific resistivities analyzed with 4-point probe (HM21-Jandel Co., UK) Scanning electron microscopy (SEM-EDX, JEOL, Japan) results revealed morphological and dispersive features of dopants in UO_2.

To study the electrochemical oxidative behaviors and dissolution properties, Zr(IV)- and/or Th(IV) doped UO_2 electrodes were prepared by mounting pellets onto steel-working electrode. And three-electrode system is used for cyclic voltammetry (CHI-600D, USA) and RDE system of 2000 rpm (PINE, USA) in carbonate/bicarbonate dissolved in 0.1 M $NaClO_4$ solution ($[HCO_3^-/CO_3^{2-}]$=0.01 mol L^{-1}).

All electrodes were polished through mechanical polishing and followed electrochemical reductive polishing. Mechanical polishing was proceeded by using sand papers of 3000 grid and then, the electrochemical polishing carried out by applying the potential at -1.5 V in the electrolyte. This cleaning process removes any oxygen species can be existed on the fuel surface.

3. Results

3.1. Pellet-characteristics

High-density pellets were produced by sintering the pellets at 1700˚C for 24 hrs after pressed UO_2 powder which containing Zr(IV)- and/or Th(IV) as each gradients.

The electrical conductivities, obtained from measuring the specific resistivity of each pellets, decreased from 1.76×10^{-6} S/cm of undoped UO_2 pellet to 6.46×10^{-7} and 1.67×10^{-7} S/cm as increase to10 mol% doping level, respectively. The Zr(IV)- and/or Th(IV) doping affect to interrupt the electron to go through the pathway, as a resist. Moreover, the low electrical conductivity of Zr(IV)- and/or Th(IV)-doped pellets have to be considered that they have poor conductivities to detect electrochemical currents as the electrode.

Otherwise, analysis of conductivity might be a good tool to evaluate reproducibility of pellet preparation.

3.2. Grain structure

Figure 1 shows the surface morphological changes depends on dopants and its presents. The undoped pellets (Figure 1(a) and (c)) show the wrinkled polygonal grain structures which diameter is ranged about 5 to ~15 μm. However, Zr (Figure 1(c)) and/or Th (Figure 1(d)) doping increase, the polygonal structures are missed. Especially, the Zr(IV)-doping induces the decrease grain size and wrinkles, and moreover the some cracks are appeared. On the other hand, the morphology of Th(IV)-doped surface has become bumpy maintaining the size of grains and wrinkled texture.

Table 1. Electrical conductivities (σ, S/cm) of $U_{1-x}Zr_xO_2$ and/or $U_{1-x}Th_xO_2$ depend on the doping amount (x) in UO_2 matrices, respectively.

x mol dopants	Electrical conductivity, S/cm	
	$U_{1-x}Zr_xO_2$	$U_{1-x}Th_xO_2$
0.00	$1.76\times e^{-6}$	$1.77\times e^{-6}$
0.01	$1.82\times e^{-6}$	$1.29\times e^{-6}$
0.10	$6.46\times e^{-7}$	$1.67\times e^{-7}$

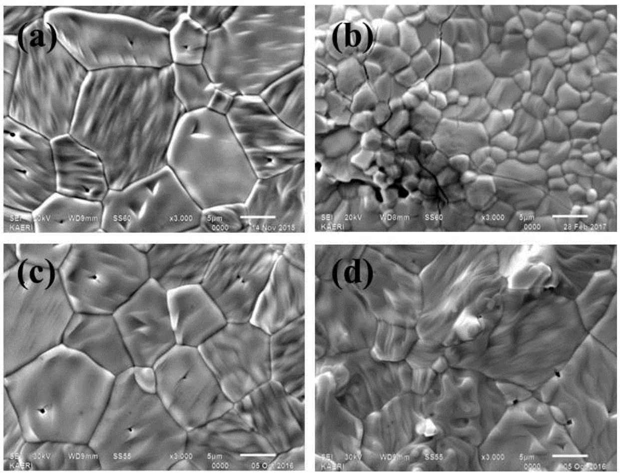

Fig. 1. SEM images of grain structures on the surfaces of (a-b) Zr(IV)-; and/or (c-d) Th(IV)-doped UO_2. Doping amounts of each pellets are (a,c) 0; and (b,d) 10 mol%, respectively. Scale bar indicates 5 μm of length.

3.3. Electrochemical behaviors

Figure 2 shows Cyclic voltammograms (CV) of undoped UO_2 and $U_{1-x}Zr_xO_2$ and/or $U_{1-x}Th_xO_2$ recorded in carbonate solutions. The anodic oxidation current of undoped UO_2 (black line) indicates forming the oxidation of a thin surface layer mixed with U(IV) and U(V) in the potential range from -0.2 V to 0.2 V. And the potential range of the surface oxidation has no changes in both of tetravalent RE doped pellets. However, the oxidation currents of Zr(IV)- and/or Th(IV)-doped pellets are enhanced than the undoped pellet though the electrical conductivities of tetravalent RE-doped pellets are lower. This can be explained with that the oxidation process of 10 mol% Zr(IV)- and/or Th(IV)-doped pellets have same mechanism with undoped UO_2, however, tetravalent dopants enhance the oxidation reaction and further oxidative dissolution of UO_2 pellets.

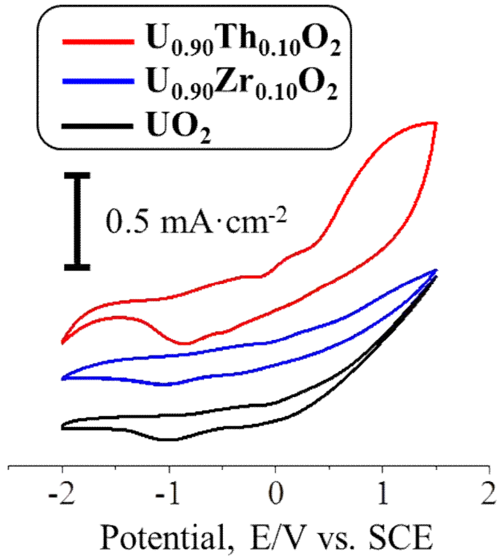

Fig.2. Cyclic voltammograms of undoped UO_2 and 10 mol% Zr(IV)-, and/or Th(IV)-doped UO_2 electrodes with 2000 rpm rotating in 0.1 $NaClO_{4(aq)}$ containing 0.01 M CO_3^{2-}/HCO_3^- at pH= 9. Scan rate is 0.05 V/sec.

3. Conclusions

Physical and chemical properties of tetravalent RE-doped UO_2 are investigated by analysis of electrical conductivity, grain structure and electrochemical oxidative behaviors. The polygonal grains of undoped UO2 change to small domains in Zr(IV)-doped pellets but Th(IV)-doped one maintain the size of grains.

Zr(IV)- and/or Th(IV) doping affect to enhance the electrochemical oxidation than undoped UO_2 though electrical conductivity decrease.

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REFERENCES

[1] R. C. Ewing, Long-term storage of spent nuclear fuel, Nature Materials, Vol.14, p.252, 2015.
[2] R.J. McEachern, P. Taylor, J. Nucl. Mater. 254 (1998) 87–121.
[3] J. C. Wren, D. W. Shoesmith, S. Sunder, Corrosion behavior of uranium dioxide in alpha radiolytically-decomposed water, Journal of Electrochemical Society, p.152, 2005.
[4] S. K. Sali, S. Sampath, V. Venugopal, Existence of fluorite-type solid solutions in alkali metal-uranium-oxygen systems, Journal of Nuclear Materials, Vol.232, p.23, 1996.