

Structural and Electrochemical Properties of Non-Stoichiometric UO_{2-x} Doped With Trivalent Rare Earth

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1. Introduction

Currently, geological disposal is globally considered as a way to dispose of spent nuclear fuels (SNFs) [1]. In order to apply the geological disposal method, the reactivity of SNF and external environments such as unpredictable natural disasters and geochemical changes should be considered. Factors influence on the external of SNF including the reactivity of SNF by fission products (FPs), the reactivity of the UO_2 matrix itself, and disposal environment factors such as groundwater inflow [2]. Among the FPs, many studies on trivalent-rare earth have been performed [3-4]. In particular, Nd is one of the major FPs of spent fuels, and is a representative rare earth trivalent element used for estimating burn-up level using Nd isotopes [5]. In addition, since the stoichiometry of the UO_2 matrix affects to the reactivity of SNF, the physical and chemical properties of SNF according to stoichiometry need to be investigated.

In this study, we prepared simulated spent nuclear fuel doped with various molar concentrations of Nd(III) in hypostoichiometric UO_{2-x} and investigated the effects of carbonates in electrolyte aqueous solution on the electrochemical oxidation behaviors of SNF.

2. Experimental

The UO_2 powder and Nd_2O_3 powder were mixed with different molar concentrations of Nd(III) percentages (0, 2, 10, 18 mol%). After thoroughly grinding, resulting mixed powders were pelletized at 300 MPa pressure. And then, it was sintered under H_2 atmosphere at 1700 °C for 18 h to form a UO_{2-x} or $\text{U}_{1-y}\text{Nd}_y\text{O}_{2-x}$.

For observing the surface morphologies and estimating grain size of non-stoichiometric $\text{U}_{1-y}\text{Nd}_y\text{O}_{2-x}$ prepared in this study, Scanning electron microscopy (JSM-6610LV, JEOL, Japan) was used under specific(optimal) operation condition (25-30 keV accelerating voltage and 8 mm of working distance).

Electrical conductivities of each pellet were determined by measuring the specific resistivity at three positions on the surface of the pellet using a 4-point probe technique (HM21-Jandel Co., UK). As a working electrode in three electrode system, each pellet was placed on a stainless steel support, followed by molding with epoxy resin. After then, the working electrode was polished with a sand paper (3000 grids), and the oxide layer on the surface was removed by cathodic cleaning process (by applying 1.5 V for 5 minutes) prior to use. Pt mesh and SCE (Saturated Calomel Electrode) were used as a counter electrode and reference electrode, respectively. 0.1 M NaClO_4 and/or 0.01 M carbonate ion in 0.1 M NaClO_4 aqueous solutions were used as electrolytes. All electrochemical analyses were performed using potentiostat (CHI-600D, USA).

3. Result

Fig. 1 shows the SEM image of $\text{U}_{1-y}\text{Nd}_y\text{O}_{2-x}$ pellet depending on Nd(III) doping level. Initially, the surface of UO_{2-x} , which does not contain Nd, represented wrinkled morphology with more than 30 μm of a grain size having polygonal structure as shown in Fig. 1 (a). $\text{U}_{1-y}\text{Nd}_y\text{O}_{2-x}$ ($y = 0.02$, Fig. 1 (b)) indicated with a smaller grain size (less than 5 μm), and still retains its polygonal structure.

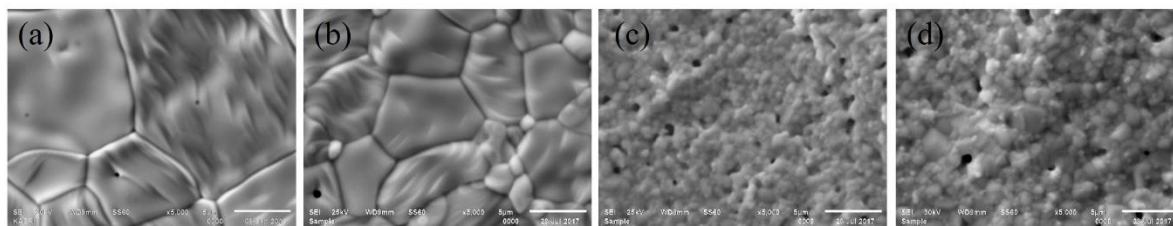


Fig. 1. SEM images of $U_{1-y}Nd_yO_{2-x}$ surface according to the Nd-doping level on the UO_{2-x} matrix. (a) $y=0$, (b) $y=0.02$, (c) $y=0.10$ and (d) $y=0.18$.

However, the grain size was significantly reduced and the polygonal structure disappeared at 10 mol% of Nd doping level. Moreover, pores started to appear on the surface (Fig. 1 (c)). At 18 mol% of Nd doping level, the numbers and sizes of pores were increased, which might cause the durability of pellet to deteriorate.

The electrical conductivities were also investigated depending on Nd(III) doping levels. The conductivity of $U_{1-y}Nd_yO_{2-x}$ pellet increased with increasing of doping level, but decreased sharply at the 18 mol% level.

In cyclic voltammetry (CV) analysis of Nd(III) doped UO_{2-x} electrode in 0.1 M $NaClO_4$ and/or 0.01 M carbonate ion in 0.1 M $NaClO_4$ as shown in Fig. 2, the surface oxidation occurred in the range of about -0.2 to 0.2 V, and dissolution started at ~ 0.2 V. The surface oxidation increased as the amount of Nd(III) increased. Comparing the CV results obtained in the two electrolyte system, it was confirmed that carbonate ions accelerated surface oxidation and dissolution of $U_{1-y}Nd_yO_{2-x}$ pellet. In addition, at a doping level of more than 10 mol%, the oxidation reaction peak by Nd itself might be observed in the -1.0 to 0 V region, so it seems that the solid solution did not form well.

4. Conclusion

The structure and electrochemical properties of $U_{1-y}Nd_yO_{2-x}$ were investigated. As the Nd doping level increased, the size of grain domain decreased and the size and the number of pores increased. Electrical conductivity also increased up to 10 mol% doping level, but decreased at 18 mol% level.

Through CV analysis, it was confirmed that the electrochemical behavior of $U_{1-y}Nd_yO_{2-x}$ pellet proceeded in the order of dissolution after the surface oxidation. Surface oxidation increased depending on the amount of Nd(III). The presence of carbonate ions is likely to have an effect on accelerating surface oxidation and dissolution as well.

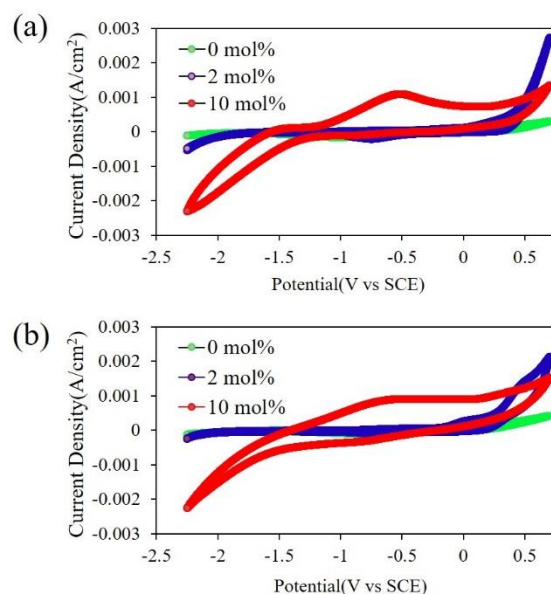


Fig. 2. CVs of $U_{1-y}Nd_yO_{2-x}$ depending on the Nd(III) doped amounts in the (a) 0.1 M $NaClO_4$, and (b) 0.01 M HCO_3^-/CO_3^{2-} contained 0.1 M $NaClO_4$ electrolyte, respectively.

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