Physicochemical Properties of Trivalent Rare Earth Elements-Doped UO$_2$

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1. Introduction

Spent nuclear fuel is consisted with not only stoichiometric UO$_2$, but also parts of hypo-, and hyper-stoichiometric UO$_{2\pm x}$ matrix. Because the non-stoichiometry of the UO$_{2\pm x}$ matrix can influence on the corrosion/dissolution behavior of the spent fuel by itself, result in, radionuclides in matrix can be released. Therefore, it is important to understand the chemical and physical properties of UO$_{2\pm x}$ matrix, which determine the reactivity of UO$_{2\pm x}$ matrix [1-2]. And also, the influence of fission products including RE (Rare earth) element on the oxidation of UO$_2$ has been extensively investigated [3-4]. RE-doping enhances the stability of the cubic fluorite structures of U$_4$O$_9$-type to oxidize to U$_3$O$_8$ depending on RE contents as compared with un-doped UO$_2$. Oxidation of un-doped UO$_2$ occurs by simple two-step reaction to U$_3$O$_8$ via U$_4$O$_9$, however, RE-doped UO$_2$ represents the resistance to change from cubic U$_4$O$_9$ to U$_3$O$_8$. RE-dopants stabilized urania matrix by forming RE-oxygen vacancy clusters as increase the content of dopants, and resulted in decrease the interstitial sites could be occupied with O^{2-} during oxidation.

This work presents structural and electrochemical properties depending on stoichiometry of UO$_2$ matrix and Gd-doping level. Stoichiometry of all pellets was determined by non-destructive analysis of XRD, and distinguished into hypo-, hyper-, and stoichiometric U$_{1-y}$Gd$_y$O$_2$ series, respectively. Also, grain structure and electrical conductive property are estimated in terms of lattice structural changes depending on stoichiometry and Gd-doping. The influences of non-stoichiometric urania matrix and Gd-dopants on dissolution behaviors of UO$_{2\pm x}$ matrix were examined by electrochemical study.

2. Experimental

2.1 Pellet preparation

Green pellets prepared by using unirradiated UO$_2$ and/or mixed with Gd$_2$O$_3$ powder were pressed, and sintered in a linear type of furnace at 1700°C in a reducing mood for 18 h. And then, stoichiometry of all pellets are adjusted by followed mild oxidation controlling the oxygen potential with CO/CO$_2$ mixed gas ratio, and temperature according to the Ellingham diagram which shows thermodynamic conditions of solid solution forms of Gd-doped UO$_{2\pm x}$. Prepared pellets have ~8 mm dia. and less than 1 mm thickness. Electrodes were polished with 3000 grit SiC paper prior to an experiment and then cathodically cleaned at a potential of –1.2 V for 5 minutes before an experiment.

3. Results

3.1 Lattice parameter

The variation of lattice parameter as a function of the Gd-doping level for U$_{1-y}$Gd$_y$O$_{2\pm x}$ specimens shows the 3 types of linear slopes. The slope of stoichiometric U$_{1-y}$Gd$_y$O$_2$ is –0.0173, a reasonable contraction factor in agreement with published literature. This 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 $O_{Vacancy}$. For the hyperstoichiometric $U_{1-y}Gd_yO_{2+x}$ the contraction factor is –0.0233, considerably higher. By contrast, the lattice parameter for hypostoichiometric $U_{1-y}Gd_yO_{2-x}$ changes more gradually with Gd content (slope = –0.00995).

3.2 Grain structure and growth rates

Scanning electron microscopic results, using 20 keV electron acceleration voltage with 10 mm of working distance, revealed morphological evolutions and grain features of freshly prepared pellet depending on Gd-doped level and stoichiometry. The grain structures of $U_{1-y}Gd_yO_{2\pm x}$ changed drastically depend on Gd-doped level as shown in Fig. 1. In case of un-doped hypo-stoichiometric UO_{2-x}, it has polygonal structures consisted of wrinkled and flattened domains, are observed ~5 to ~10 μm sized, and the domain size decreases rapidly with increase of Gd doping level.

On the other hand, stoichiometric and hyper-stoichiometric pellets prepared by through the CO/CO_2 oxidation of hypo-stoichiometric pellets, have more big domains of over 20 μm sized and smooth textured surface. The interstitial oxygen activates internal strain of distorted cubic lattice, followed by enhanced uranium diffusion results in crystalline growths. Therefore, it can be explained that the distribution of excess O^{2-} makes to develop domain growth affects to domain structures of various size, texture and figurations. And as Gd-doping level increase, grain features got small in non-stoichiometric and stoichiometric pellets. However, hyper-stoichiometric pellets showed tolerance toward size-change to small. Probably, Gd plays a role to prevent inflowing of extrinsic oxygen into hyper-UO_{2+x} matrix. In fact, oxidation process of un-doped UO_{2-x} to UO_{2+x} needed more high oxygen potential than 10 mol% Gd-doped UO_{2-x}.

3.3 Electrochemical behaviors of oxidative dissolution

The influences of non-stoichiometric urania matrix and Gd dopant on dissolution behaviors of $UO_{2\pm x}$ matrix were investigated by electrochemical study. Cyclic voltammetry (CV) was recorded in carbonate solution with rotating electrode in scanning potential range from -3 V to 4 V, which can show catalytic behavior of water decomposition according to Gd-doping. Distinguished two oxidation peaks, indicating two steps of oxidation mechanisms, defined as surface oxidation and dissolutive oxidation, respectively. Because dissolution process includes these whole oxidation mechanisms, oxidative behaviors of each steps has been investigated to understand the dissolution of $U_{1-y}Gd_yO_{2\pm x}$.

4. Conclusion

Stoichiometric and non-stoichiometric Gd-doped $U_{1-y}Gd_yO_{2\pm x}$ pellets are prepared by mechanical blending method adjusting the oxygen potential. Stoichiometry of all pellets was confirmed by non-destructive X-ray analysis.

The interstitial oxygen in hyper-stoichiometric $U_{1-y}Gd_yO_{2+x}$ improves the uranium diffusion in solid solution to allow grain size to be large. And oxidative dissolution of $U_{1-y}Gd_yO_{2\pm x}$ can be described with surface oxidation and followed dissolutive oxidation mechanisms. Gd dopants influence on decrease the surface oxidation rate which can control the whole oxidative dissolution reaction. Gd doping in hypo-stoichiometric pellets induces more oxygen deficiency (x= y/2) by forming Gd-oxygen deficiency clusters which makes cubic structure unstable, however, the dissolutive behaviors show that the surface oxidation decrease as increase the Gd doping level.

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