Effects of gadolinium content in the Gd-doped UO_2 pellet on the corrosion current density

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1. Introduction

Spent fuel is mainly UO_2 (> 95%), and radioactive fission products and actinides species are produced during reposition. These products lead to many physical and chemical changes within the fuel, and result in unexpective situations.

Container failure is not expected, since model calculations predict a loss of wall thickness by general corrosion of only a few microns [1-2]. However, it can be assumed that some containers will fail allowing groundwater to contact the fuel causing radionuclide release. Because the majority of the radio nuclides in used fuel are located within the oxide matrix, their release rate to the groundwater will be controlled by the fuel corrosion/dissolution rate. [3-4]

In determining fuel corrosion and radionuclide release rates, the reactivity of the UO_2 matrix and how it is modified by prior irradiation, is important. The one of the important changes expected to influence the reactivity of the fuel is the rare earth doping of UO_2 which will change the conductivity and structural properties of the UO_2 matrix.

In this work, UO_2 and Gd doped UO_2 pellets were prepared and investigated to study about influences of trivalent rare earth of Gd(III) doped UO_2 on corrosion and dissolution rates.

2. Experimental

The un-irradiated UO_2 and Gd doped UO_2 pellets are fabricated by sintering pressed compacts pellets of fine-grained UO_2 powders and/or Gd_2O_3 containing UO_2 powders at ~1700 ºC in a reducing atmosphere. The doped Gd amounts were 1, 5 and 10 mol% contrasting with uranium, 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, USA) results revealed morphological and dispersive features of Gd in UO_2.

To study the electrochemical behaviors and dissolution properties, Gd doped UO_2 electrodes were prepared mounting pellets onto steel-working electrode. And 3 electrode system is used for cyclic voltammetry (CHI-600D, USA) and RDE system of 1000 rpm (PINE, USA) in carbonate/bicarbonate dissolved in 0.1 M NaCl solution ($[HCO_3^-/CO_3^{2-}]$=0.01 mol L^{-1}).

All electrodes were polished with sand papers of 1000 grid before electrochemical analysises.

3. Results

3.1. Pellet-characteristics

High-density pellets were produced by sintering the pellets at 1700 ˚C for 12 hrs after pressed UO_2 powder which containing Gd_2O_3 as each gradients. Interesting point is that sintered Gd doped UO_2 pellets have curvatures looked like arch shapes as much as increase the Gd doped amount (Fig. 1)

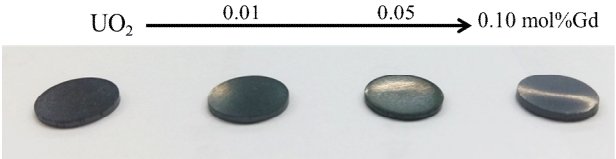

Fig. 1 Photograph of Gd doped UO_2 pellets contain 0, 0.01, 0.05 and 0.10 mol% of Gd, respectively.

And electrical conductivities, obtained from measuring the specific resistivity of each pellets, increased from 7.11 $\times 10^{-4}$ S/cm to 5.08$\times 10^{-2}$ S/cm as increasing Gd mol%. However, in case of 10 mol% Gd/UO_2 pellet shows decreasing region of curve shown in Fig. 2, indicating highly doped Gd does not affect to increase the electrical conductivity of electrode, any more. Otherwise, analysis of conductivity might be a good tool to evaluate reproducibility of pellet preparation.

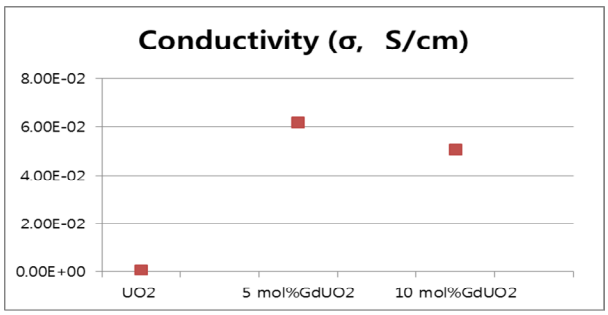

Fig. 2 Electrical conductivity of prepared UO_2 pellets doped with 0, 5 and 10 mol%Gd.

3.2 Electrochemical analysises

Fig. 3 shows a series of CVs recorded in carbonate solutions. The distinguishable anodic oxidation current (~–0.2 V), indicates forming the oxidation of a thin surface layer mixed with U(IV) and U(V), moves from –0.2 V to 0.1 V as increasing the Gd mol%. This can be explained with that the doped Gd inhibit oxidation of UO_2 matrix surface, hence, to delay the followed dissolution of UO_2 electrode ranged over 0.2 V.

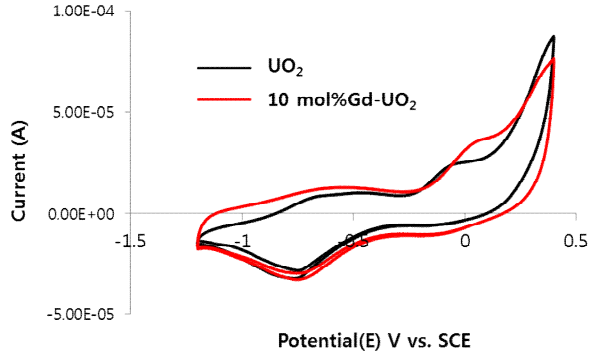

Fig. 3 CV series of Gd doped UO_2 in 0.1 M NaCl containing $[HCO_3^-/CO_3^{2-}]$=0.1 mol·L^{-1} solution (pH=10). Scan rate is 0.01 $Vsec^{-1}$.

On the reverse scan, a broad and weak cathodic reduction peak occurs with a maximum at ~−0.7 V. This reduction peak is generally associated with the reduction of a $U(IV)_{1-2x}U(V)_{2x}O_{2+x}$ /$UO_3.yH_2O$ surface layer.[5] The disappearance of this reduction peak on highly doped Gd/UO_2 is attributed to the decreased dissolution of U(VI) on the forward scan. The presence of this reduction peak in Fig. 3 stands for that an oxidized surface layer is maintained on the Gd-UO_2 surface despite the presence of carbonate.

This tolerance against UO_2 oxidation and dissolution can be grasped in Tafel plots. The corrosion potential (E_{corr}) shows that highly doped Gd/UO_2 electrode has high over potential to be corroded. And also how much Gd/UO_2 materials is corroded, indicating quantitative information of corrosion, determined by using corrosion current, i_{corr} at E_{corr} in Tafel plot. It shows that the corrosion rate is significantly reduced as increasing amount of Gd doping onto UO_2 matrix.

Moreover, the corrosion rate are can be obtained by translating the corrosion current through some calculations, and this might be a one of important factors to predict chemical changes and release of radionuclide at the accident.

4. Conclusion

Gd doped UO_2 pellets are prepared by compress the Gd_2O_3 and UO_2 mixed powder following sinter at high temperature in reducing mood. The reproducibility of pellets preparation has been verified by observing resistivity of pellets using 4-probe method.

The effect of Gd doping (0 to 10 mol% of Gd) on the electrochemical behavior of UO_2 has been investigated in slightly alkaline solutions with carbonate. The anodic oxidation/dissolution mechanism on Gd-UO_2 is similar to that observed on pure UO_2 electrode although the overall reactivity of Gd- UO_2 is much lower. Gd-doping inhibits the anodic oxidation of UO_2.

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