Journal of Nuclear Materials 480 (2016) 429–435

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Effect of Ce doping on UO_2 structure and its oxidation behavior

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ARTICLE INFO

Article history:
Received 28 March 2016
Received in revised form
19 August 2016
Accepted 21 August 2016
Available online 3 September 2016

Keywords:
Cerium
Uranium dioxide
Oxidation state
Lattice parameter
Oxidation behavior

ABSTRACTS

The structure of $U_{1-y}Ce_yO_2$ was studied in terms of added Ce cation. The oxygen vacancy, the oxidation state of cerium and uranium, and changes in the lattice parameter were investigated. Most Ce ions exist as tetravalent ions, which cause a lattice contraction due to the ionic radius. However, some Ce ions exist as trivalent Ce^{3+} ions, causing the oxidation of U^{4+} into higher oxidation states as well as a formation of oxygen vacancy for a charge balance. In addition, the effect of Ce on the oxidation of uranium dioxide was also studied by thermo-gravimetric analysis. The oxidation of Ce doped UO_2 proceeds through dominant path given as two step reaction $U_{1-y}Ce_yO_{2-\delta} \rightarrow (U_{1-y}Ce_y^{4+})_4O_9 \rightarrow (U_{1-y}Ce_y^{4+})_3O_8$. However, for higher Ce content ($y = 0.136$ to 0.332), an alternative pathway is proposed as $(U_{1-y}Ce_y^{4+})_4O_9 \rightarrow (U_{1-y}Ce_y^{3+})_4O_9$. The increasing Ce content stabilizes the cubic $(U_{1-y}Ce_y)_4O_9$ phase, prohibits the formation of a metastable tetragonal $(U_{1-y}Ce_y)_3O_7$ phase, and inhibits the formation of $(U_{1-y}Ce_y)_3O_8$ proportional to the Ce content.

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1. Introduction

Uranium dioxide has been investigated continuously because of its use as a nuclear fuel. During the irradiation, a large number of fission products are generated and affect the integrity of the nuclear fuel. Among them, rare earth elements (REE's) are known to be dissolved as a solid solution in a UO_2 matrix [1], and it has influences on thermal conductivity, phase stability, and the relevant fuel performance [2–5].

In this study, we investigated the effect of Ce doping on the UO_2 structure and its oxidation behaviors. Concerning the urania-ceria mixtures, there have been numerous studies on phase diagram [6,7], oxidation thermodynamics [8,9], magnetic properties [10,11], and the charge state of Ce in the UO_2 lattice [12,13], since cerium is the fission products which performs a role as an analogue of plutonium, owing to the similar oxidation states and ionic radius with those of Pu. The phase diagram for stoichiometric U-Ce-O phase ($O/M = 2$) and nonstoichiometric U-Ce-O phase has been well characterized [6,7], and a variety of properties such as lattice parameter and electronic structure are also well characterized.

In our previous studies [14–16], the effects of doped Gd and Th as a trivalent and a tetravalent cation, respectively, on UO_2 were reported. Different from Gd and/or Th, cerium is a multivalent cation having both charges of 3+ and 4+. For stoichiometric U-Ce-O phase ($O/M = 2$), the ideal Ce charge in mixed oxide $(U,Ce)O_2$ is 4+. However, the presence of both trivalent and tetravalent states is expected by the charge transfer reaction between U and Ce as proposed by Griffiths et al. [17] as follows.

$$Ce^{4+} + U^{4+} \rightarrow Ce^{3+} + U^{5+} \tag{1}$$

Therefore, it is necessary to consider the alteration of O/M ratio and loss of oxygen for charge compensation upon the addition of Ce, regarding the mixed charge states. The oxidation states of U and Ce in $U_{1-y}Ce_yO_{2-\delta}$ solid solution prepared under hydrogen atmosphere were investigated in terms of Ce content. The oxygen deficiencies (δ) and the changes in lattice parameter caused by Ce addition were also discussed. In addition, the effect of Ce on the oxidation behavior of $U_{1-y}Ce_yO_{2-\delta}$ was also studied.

2. Experimental

Mixed oxides of uranium and cerium were prepared from U_3O_8 and CeO_2 using a powder mixing technique, which is most widely used for preparation of ceramic samples. U_3O_8 and CeO_2 powders were of regent grade. The content of U in U_3O_8 was experimentally determined by Davis & Grey potentiometric titration. CeO_2 powers

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http://dx.doi.org/10.1016/j.jnucmat.2016.08.026
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with 99.999% purity were purchased from Aldrich. The starting materials were weighed precisely to 10 μg by micro balance, and the amount of Ce in U + Ce powder mixtures were calculated from 0 to 0.332 as shown in Table 1. To avoid inhomogeneity, the powders were mixed well by grinding for 20–30 min using an agate mortar in a glove box, which generates a small particle size and maximizes the surface contact area. The powder mixtures were divided into two parts, and each mixture was compacted at 1400 psi for 15 s. The size of pellet from compressed powder mixtures is about 6 mm diameter and 0.5 mm thickness. The prepared pellets were placed on a molybdenum boat, and were sintered in a tube furnace for 12 h at 1700 °C, and then annealed for 12 h at 1200 °C under a pure hydrogen atmosphere. The sintered pellets were weighed and oxygen deficiencies (δ) of the prepared pellets under H_2 atmosphere were theoretically calculated as follows:

$$\text{the oxygen deficiencies } (\delta) = 2 - \frac{O}{U+Ce} = 2 - \frac{(W_T - W_U - W_{Ce})/16}{W_U/238 + W_{Ce}/140.1} \qquad (2)$$

where $\frac{O}{U+Ce}$ is atomic ratio in the pellet, W_T is the weight of a sintered pellet, W_U and W_{Ce} are the weight of uranium and cerium in the pellet, respectively.

The lattice parameters were calculated by employing the least-square method from the powder X-ray diffraction spectra in the range of 2θ value from 15 to 90° as measured by a Siemens D5000 diffractometer after powdering samples from pellets. The Cu Kα line was used and filtered through Ni foil (beam current 40 mA at 40 kV). To determine the lattice parameter, tungsten powder was used as a reference material. The diffraction measurements were carried out with a scanning step of 0.02° for 10 s at each count.

During the oxidation of the powdered samples, the oxygen weight gains were measured from 50 to 700 °C at a heating rate of 1 °C/min using a SETARAM TGA-92 thermoanalyser under a continuous clean air flow of about 1 atm.

3. Results and discussion

3.1. *Effects of Ce doping on UO_2 structure*

To confirm oxygen deficiencies calculated from Equation (2) for the samples prepared under H_2 atmosphere, the pellets were heat treated at 800 °C for 24 h under an atmosphere of $CO/CO_2 = 11.5$. The samples were weighed before and after heat-treatment under CO/CO_2 atmosphere. The oxygen deficiencies of the prepared pellets under pure H_2 atmosphere were measured from the weight gains while heating under CO/CO_2 atmosphere assuming that a stoichiometric $U_{1\text{-}y}Ce_yO_{2.00}$ is formed under such conditions. The reference O/M ratio of 2 ± 0.001 was performed by heating sample at 800 °C for 24 h under an specific atmosphere of $CO/CO_2 = 10$ [5]. These experimental oxygen deficiencies and theoretical values from Equation (2) are listed in Table 1. Theoretical calculated oxygen deficiencies are totally larger than experimental values. These differences could come from deviation of CO/CO_2 from the reference [5] and may reflect that the sample under heat-treatment did not reach a stoichiometric form. However, the co-existence of Ce^{3+} with Ce^{4+} is responsible for the non-stoichiometry. These trivalent ions cause the oxygen vacancy as well as an oxidation of U^{4+} to a higher oxidation state such as U^{5+} or U^{6+} for charge balance [4]. Fig. 1 compares the oxygen deficiencies of Ce with those of Gd and Th which were obtained using the same method as described above. Th doped UO_2 gives almost constant values near zero though a little lower, which indicates the formation of stoichiometric mixed oxides as expected for tetravalent cation. Contrarily, the obtained δ values increased with dopant content for both Gd and Ce doping. It indicates that a hypo-stoichiometric mixed oxide was formed under a hydrogen atmosphere. However, Ce doping gives much smaller δ values than Gd doping. It can be explained that most of Ce ions exist as tetravalent (Ce^{4+}) cations, and some of Ce ions exist as trivalent (Ce^{3+}) ions.

The fission product forming a solid solution with UO_2 causes a change in lattice parameter depending on the ion radii, as reported by other people following Vegard's law [18–20]. For the rigid sphere model of a fluorite-type crystal structure [19,21], the slope of lattice parameter against the dopant content (d*a*/d*y*) can be calculated from following equation,

$$a = \frac{4}{\sqrt{3}}(MCR + r_{O^{2-}}), \qquad (3)$$

where *a* is the lattice parameter of the sample, *MCR* is the mean

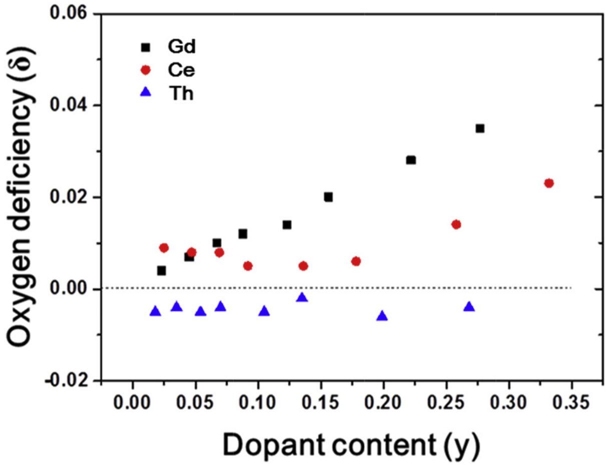

Fig. 1. The oxygen deficiency (δ) as a function of dopant contents for sintered pellet $U_{1\text{-}y}R_yO_{2\text{-}\delta}$ (R = Gd, Ce, and Th) under pure H_2 atmosphere. Measurement error is ±0.005.

Table 1
The contents of Ce (*y*) and theoretical and experimental oxygen deficiency (δ) in $U_{1\text{-}y}Ce_yO_{2\text{-}\delta}$.

Sample	U (1-*y*)	Ce (*y*)	Theoretical oxygen deficiency (δ)[a]	Experimental oxygen deficiency (δ)[b]
1	0.975	0.025	0.019	0.009
2	0.953	0.047	0.014	0.008
3	0.931	0.069	0.015	0.008
4	0.908	0.092	0.015	0.005
5	0.864	0.136	0.018	0.005
6	0.822	0.178	0.017	0.006
7	0.742	0.258	0.023	0.014
8	0.668	0.332	0.030	0.023

[a] Theoretically calculated values from Equation (2).
[b] Experimentally obtained values from weight gain measurement.

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