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Oxygen non-stoichiometries in $(Th_{0.7}Ce_{0.3})O_{2-x}$

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ABSTRACT

Oxygen non-stoichiometry in $(Th_{0.7}Ce_{0.3})O_{2-x}$ oxide solid solutions was investigated from the viewpoint of Ce reduction. The oxygen non-stoichiometry was experimentally determined by means of thermogravimetric analysis as a function of oxygen potential at 1173, 1273 and 1373 K. Features of the isotherms of oxygen non-stoichiometry in $(Th_{0.7}Ce_{0.3})O_{2-x}$ similar to those in oxygen non-stoichiometric actinide and lanthanide dioxides were observed. The oxygen non-stoichiometry in $(Th_{0.7}Ce_{0.3})O_{2-x}$ was compared with those of CeO_{2-x} and $(U_{0.7}Ce_{0.3})O_{2-x}$. It was concluded that the Ce reduction has some relation to defect forms and their transformations in the solid solutions.

1. Introduction

ThO_2-based oxides have attracted special attention for use in various nuclear fuel systems owing to their superior properties. For example, a solid solution of $(Th,Pu)O_{2-x}$ is being investigated as a fast breeder reactor fuel in India [1], and a solid solution of $(U,Th)O_{2\pm x}$ is generally used as a fuel for gas-cooled reactors [1]. The present authors have been investigating a ThO_2-based oxide as a novel fuel form dedicated to minor actinide incineration in a fast reactor system [2].

Oxygen non-stoichiometry in ThO_2-based fuels is of particular importance because it significantly affects various properties that are indispensable for fuel design, such as thermal conductivity, melting point, and lattice parameter. Oxygen non-stoichiometry emerges when cations having lower valence than Th^{4+} are doped to form oxygen vacancies to maintain electrical neutrality. For instance, when two trivalent rare earth cations such as Nd^{3+} are doped to replace two Th ions, one oxygen vacancy is formed. Oxygen non-stoichiometry in ThO_2-based nuclear fuels is complicated because large amounts of fission products and actinides can dissolve into the ThO_2 matrix [3]. It is, therefore, very important to investigate oxygen non-stoichiometric features of ThO_2-based nuclear fuels.

In this study, oxygen non-stoichiometry in $(Th_{0.7}Ce_{0.3})O_{2-x}$ was experimentally investigated. Oxygen non-stoichiometry were determined as a function of oxygen potential by thermogravimetric analysis (TGA) at 1173, 1273 and 1373 K. Cerium is a representative rare earth fission product. It is well known that Ce can also be utilized as a surrogate of Pu owing to physical/chemical properties that are similar to Pu [4]. Because CeO_{2-x} can be considered a solute in a ThO_2 solvent to form a solid solution $(Th,Ce)O_{2-x}$ from a thermochemical point of view [5], focus is placed on the effects of solvents on the non-stoichiometric features of CeO_{2-x}.

2. Experimental

A $(Th_{0.7}Ce_{0.3})O_{2-x}$ solid solution sample was prepared by a conventional powder metallurgical route. Appropriate amounts of ThO_2 and CeO_2 powders were weighed and thoroughly mixed in acetone medium in an agate mortar using a pestle. The ThO_2 powder was obtained from Nakarai Chemicals, Ltd. The CeO_2 powder was obtained from Wako Pure Chemical Industries, Ltd. (99.9% purity). The mixed powder was then compacted into a columnar pellet by a uni-axial pressing unit at 70 MPa. The compacted pellet was heated at 1673 K for 15 h under air atmosphere. The heat-treated pellet was ground, thoroughly mixed and milled again. This sample preparation procedure was repeated three times in order to form a single phase solid solution. Temperatures and heating times for the second and third heat-treatments were changed to 1773 K, 20 h and 1873 K, 40 h, respectively.

Details of the TGA procedure were reported elsewhere [6]. In brief; approximately 200 mg of sample was subjected to TGA to determine the deviation from stoichiometry, x, as a function of oxygen partial pressure, p_{O_2}, at pre-determined temperatures, specifically 1173, 1273 and 1373 K. A Rigaku TGA apparatus (model TG-8120) with gas supply system was used. The $(Th_{0.7}Ce_{0.3})O_{2-x}$ sample was loaded into an alumina pan and placed in the TGA apparatus. For reference, an alpha-alumina sample was loaded into another alumina pan and placed in the apparatus. Equilibrium p_{O_2} was adjusted in the range from 10^{-22} to 10^{-16} MPa at 1173 K, from 10^{-20} to 10^{-14} MPa at 1273 K and from 10^{-18} to 10^{-12} MPa at

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1373 K by changing the ratio of H_2O to H_2 in the flowing gas. Equilibrium p_{O2} in the outlet gas flow was measured with a stabilized zirconia oxygen sensor. The oxygen sensor was calibrated prior to the TGA measurements using the oxidation reaction of pure chromium metal and a standard gas containing a known amount of oxygen. Microgram order weight changes in the sample were continuously monitored while changing p_{O2} at the pre-determined temperatures step by step. Equilibrium for both p_{O2} and weight was attained within 1 h after each successive p_{O2} change. This has been clarified by the TGA of CeO_{2-x} using the present apparatus [7]. As the relation between oxygen non-stoichiometry and p_{O2} for CeO_{2-x} was well established [8], CeO_{2-x} is frequently used as a standard material for experiments of oxygen non-stoichiometry. Deviation from stoichiometry at various p_{O2} levels at the pre-determined temperatures was calculated from the weight changes relative to the stoichiometry, $x = 0$. Oxygen partial pressures that give the stoichiometry at each temperature were defined as those at $p_{O2} = 10^{-3}$ MPa [5], which was obtained by using dilute O_2 gas.

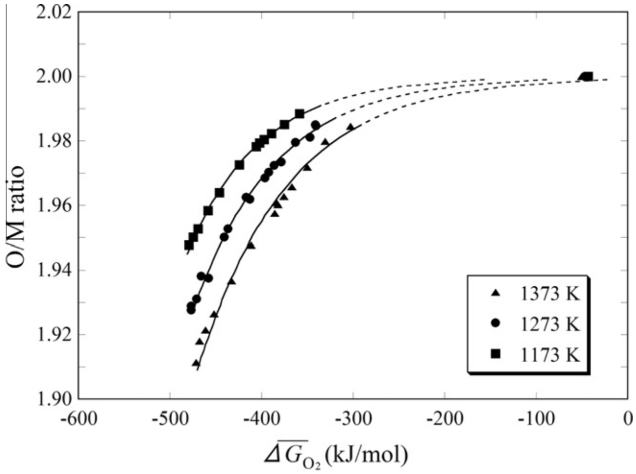


Fig. 2. Oxygen non-stoichiometries in $(Th_{0.7}Ce_{0.3})O_{2-x}$ as a function of oxygen potential.

3. Results and discussion

X-ray diffraction analysis of the final heat-treated sample showed the formation of a single phase solid solution with a fluorite-type structure, $(Th_{0.7}Ce_{0.3})O_{2-x}$, as shown in Fig. 1. Fig. 2 shows oxygen non-stoichiometry in $(Th_{0.7}Ce_{0.3})O_{2-x}$ at 1173, 1273 and 1373 K as a function of oxygen potential, $\Delta\overline{G}_{O_2}$. $\Delta\overline{G}_{O_2}$ is defined as $\Delta\overline{G}_{O_2} = RT \ln p^*_{O_2}$, where R is the gas constant, T is temperature and $p^*_{O_2}$ is oxygen partial pressure, which is derived from the ratio of p_{O2} to its standard state, 0.101 MPa. The oxygen to metal (O/M) ratio was taken as a vertical axis, where O/M = 2.00–x. The O/M ratios increase with increasing $\Delta\overline{G}_{O_2}$ and approach to O/M = 2.00, the stoichiometry, at all temperatures. The O/M ratios are smaller when the temperatures are higher at a constant $\Delta\overline{G}_{O_2}$ value. These features are common to non-stoichiometric actinide and lanthanide dioxides. The O/M ratio is approximately 0.013 smaller at 1373 K than at 1273 K, which is also 0.013 smaller than at 1173 K at a $\Delta\overline{G}_{O_2}$ of −400 kJ/mol.

Fig. 3 compares the mean Ce valences in $(Th_{0.7}Ce_{0.3})O_{2-x}$ with those in CeO_{2-x} [9] and $(U_{0.7}Ce_{0.3})O_{2-x}$ [5] as a function of $\Delta\overline{G}_{O_2}$ at 1173 K. Since non-stoichiometric ThO_{2-x} can only be observed above 2027 K [10], Th(IV) can be considered the only valence in the present temperature ranges. Thus, as the chemical form of $(Th_{0.7}Ce_{0.3})O_{2-x}$ can be written as $(Th^{4+}_{0.7}Ce^{4+}_{0.3-2x}Ce^{3+}_{2x})O^{2-}_{2-x}$, the mean Ce valence can be calculated as $4-x/0.15$. The mean Ce valence can be used as a replacement index for the x or O/M ratio. In the case of $(U_{0.7}Ce_{0.3})O_{2-x}$, a variety of valence states for each cation could be expected since the U cation also has multivalence, U^{4+}, U^{5+} and U^{6+}, as does the Ce cation. A single valence U^{4+} was, however, assumed to exist in this study, as only small amounts of U cations were estimated to have oxidized to become pentavalent U^{5+} according to Ref. [5]. The chemical formula can, therefore, be written approximately as $(U^{4+}_{0.7}Ce^{4+}_{0.3-2x}Ce^{3+}_{2x})O^{2-}_{2-x}$. The mean Ce valence can be calculated as above for $(U_{0.7}Ce_{0.3})O_{2-x}$ as well. A direct comparison of non-stoichiometries can, thus, be made between pure CeO_{2-x} and solid solutions including CeO_{2-x}, i.e. $(Th_{0.7}Ce_{0.3})O_{2-x}$ and $(U_{0.7}Ce_{0.3})O_{2-x}$, by using the mean Ce valence [11]. Since oxygen non-stoichiometries in each solid solution are assumed to be caused by the CeO_{2-x} solute, the mean Ce valence is a useful index for the present purpose; namely, discussion of the effects of solvent on the oxygen non-stoichiometric features of CeO_{2-x}. Oxygen non-stoichiometries of CeO_{2-x} [9] and $(U_{0.7}Ce_{0.3})O_{2-x}$ [5] are those estimated by a chemical thermodynamic method developed by Lindemer and Besmann [12]. The chemical thermodynamic method is acknowledged as capable of giving an accurate reproduction of oxygen non-stoichiometries, especially for nuclear fuel-related oxide systems including Ce [13]. It is seen that the mean Ce valences of $(Th_{0.7}Ce_{0.3})O_{2-x}$ are higher than those in CeO_{2-x} at $\Delta\overline{G}_{O_2}$ values ranging from about −500 to −400 kJ/mol. In other words, Ce in $(Th_{0.7}Ce_{0.3})O_{2-x}$ is more resistant to reduction than Ce in CeO_{2-x} in this $\Delta\overline{G}_{O_2}$ range. The corresponding range of

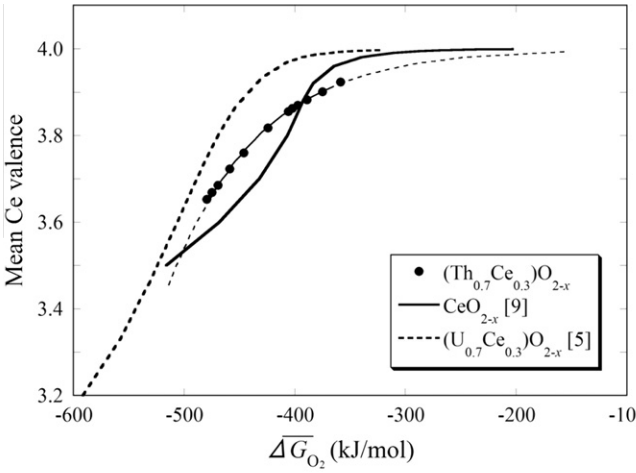


Fig. 3. Comparison of oxygen non-stoichiometries in $(Th_{0.7}Ce_{0.3})O_{2-x}$ with those in CeO_{2-x} and $(U_{0.7}Ce_{0.3})O_{2-x}$ as a function of mean Ce valence at 1173 K.

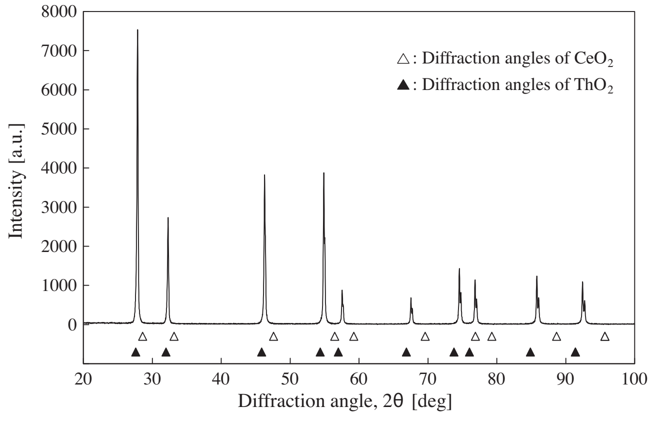


Fig. 1. X-ray diffraction pattern of $(Th_{0.7}Ce_{0.3})O_{2-x}$.

mean Ce valence is from 3.50 to 3.85. The same feature of Ce reduction in $(U_{0.7}Ce_{0.3})O_{2-x}$, i.e. more resistant to reduction, can be seen in the comparison of $(Th_{0.7}Ce_{0.3})O_{2-x}$ with $(U_{0.7}Ce_{0.3})O_{2-x}$ through the entire measured $\Delta\overline{G}_{O_2}$ range.

The above-mentioned features of Ce reduction are discussed in terms of the defect forms in each solid solution. Slopes of log $p^*_{O_2}$ versus log x are used as an index for the discussion. The slope suggests a predominant defect structure in each solid solution, and the slope remains unchanged unless the predominant defect structure is changed as a result of, for example, interaction between oxygen vacancies and dopant cations [14]. Fig. 4 shows a comparison of the slope of $(Th_{0.7}Ce_{0.3})O_{2-x}$ with those of CeO_{2-x} and $(U_{0.7}Ce_{0.3})O_{2-x}$ at 1173 K. The slope of $(Th_{0.7}Ce_{0.3})O_{2-x}$ is constant and smaller than those of both CeO_{2-x} and $(U_{0.7}Ce_{0.3})O_{2-x}$, while the latter two are comparable. The fact that the slope, which represents a predominant defect structure, of $(Th_{0.7}Ce_{0.3})O_{2-x}$ is different from that of CeO_{2-x}, is in accordance with results for $(Th_{0.75}Ce_{0.25})O_{2-x}$ obtained by Hammou et al. [15]. They elucidated that defect forms in $(Th_{0.75}Ce_{0.25})O_{2-x}$ were different from those in CeO_{2-x} in the p_{O2} range less than 10^{-15}, which corresponds to log x of less than approximately -1.8 in the case of $(Th_{0.7}Ce_{0.3})O_{2-x}$. In addition to the above-mentioned features, the slopes of CeO_{2-x} and $(U_{0.7}Ce_{0.3})O_{2-x}$ change at a log x of -1.75 and -1.25, respectively, which correspond to the mean Ce valences of 3.70 and 3.62, while the slope of $(Th_{0.7}Ce_{0.3})O_{2-x}$ remains unchanged. This indicates that the mean Ce valences at which the defect forms change varied according to the solvents, ThO_2 and UO_2. The mean Ce valence of 3.70 for CeO_{2-x} roughly corresponds to the case in which Ce in $(Th_{0.7}Ce_{0.3})O_{2-x}$ is more resistant to reduction, from 3.50 to 3.85, as shown in Fig. 2. From these facts, the features of Ce reduction could have some relation to defect forms and their transformation in each solid solution. A similar relation of Ce reduction to defect forms is also observed at 1273 and 1373 K.

Fig. 5 shows (a) partial molar entropies, $\Delta\overline{S}_{O_2}$, and (b) enthalpies, $\Delta\overline{H}_{O_2}$, of oxygen, respectively, as a function of mean Ce valence. $\Delta\overline{S}_{O_2}$ and $\Delta\overline{H}_{O_2}$ were calculated using the following thermodynamic relationships:

$$\Delta\overline{S}_{O_2} = -\frac{\partial\Delta\overline{G}_{O_2}}{\partial T} \tag{1}$$

$$\Delta\overline{H}_{O_2} = \Delta\overline{G}_{O_2} + T\Delta\overline{S}_{O_2} \tag{2}$$

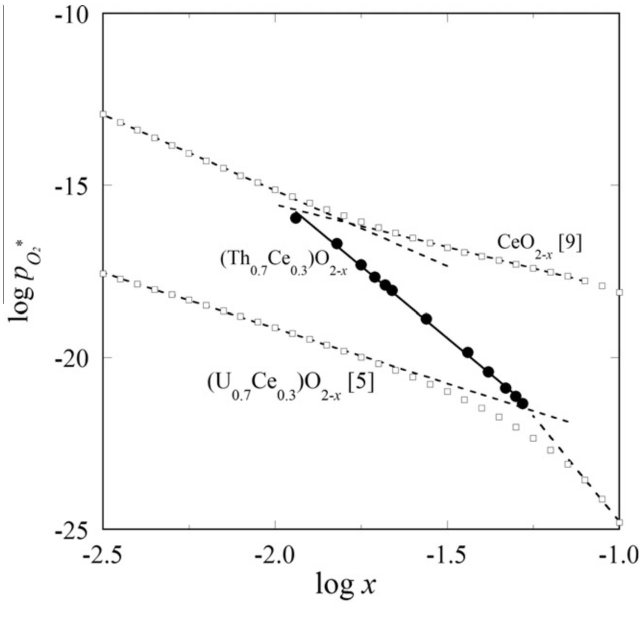
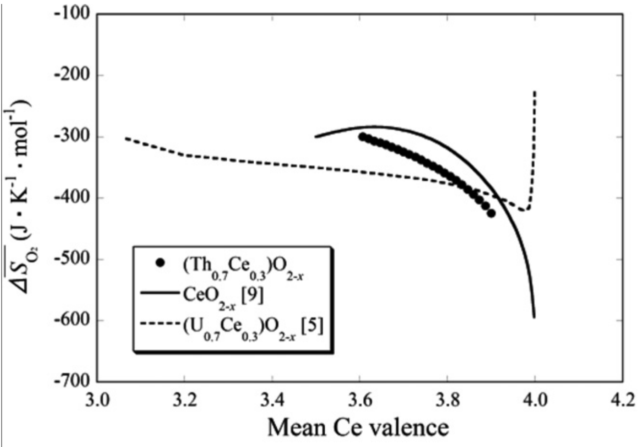
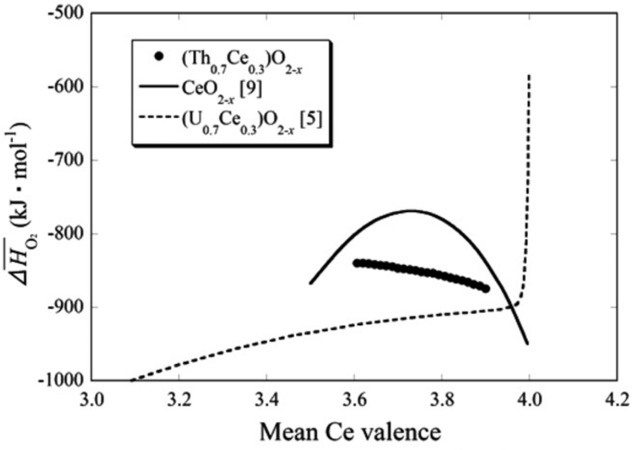


Fig. 4. Log of oxygen partial pressure versus deviation from stoichiometry at 1173 K.



(a) Partial molar entropy, $\overline{\Delta S_{O_2}}$



(b) Partial molar enthalpy, $\overline{\Delta H_{O_2}}$

Fig. 5. Partial molar entropy $\Delta\overline{S}_{O2}$ and enthalpy $\Delta\overline{H}_{O2}$ of oxygen as a function of mean Ce valence.

The $\Delta\overline{G}_{O_2}$ values used in these calculations were taken from those calculated from fitting isotherm lines, as shown in Fig. 4. It is thought that $\Delta\overline{S}_{O_2}$ and $\Delta\overline{H}_{O_2}$ reflect information on defect structures [16]. A similarity between the profile of $\Delta\overline{S}_{O_2}$ for $(Th_{0.7}Ce_{0.3})O_{2-x}$ and that for CeO_{2-x} is observed, while the profiles of $\Delta\overline{H}_{O_2}$ are different between those in mean Ce valence ranging from 3.6 to 3.9. This range roughly corresponds to the case in which Ce in $(Th_{0.7}Ce_{0.3})O_{2-x}$ is more resistant to reduction than in CeO_{2-x}, from 3.50 to 3.85, as shown in Fig. 2. On the other hand, the profiles of both $\Delta\overline{S}_{O_2}$ and $\Delta\overline{H}_{O_2}$ for $(U_{0.7}Ce_{0.3})O_{2-x}$ are completely different from those for $(Th_{0.7}Ce_{0.3})O_{2-x}$. In particular, steep increases of both $\Delta\overline{S}_{O_2}$ and $\Delta\overline{H}_{O_2}$ for $(U_{0.7}Ce_{0.3})O_{2-x}$ toward mean the Ce valence of 4.0 are noticeable. Such steep increases are considered to be due to a fundamental change of the defect form beyond the stoichiometry; the change of the defect form from an oxygen deficient- to an oxygen excess-based defect [16]. These completely different features of $\Delta\overline{S}_{O_2}$ and $\Delta\overline{H}_{O_2}$ for $(U_{0.7}Ce_{0.3})O_{2-x}$ could provide evidence that U cations show multivalence in $(U_{0.7}Ce_{0.3})O_{2-x}$ as opposed to the assumption in the present study, i.e. that U^{4+} is the only valence state. One possible valence state in $(U_{0.7}Ce_{0.3})O_{2-x}$ is $(U^{4+}_{0.4+2x}U^{5+}_{0.3-2x}Ce^{3+}_{0.3})\ O^{2-}_{2-x}$ as with many other cases of rare earth-doped UO_2 [5]. This point is, however, out of the scope of the present study and should be further discussed with sufficient experimental and theoretical information.

4. Conclusion

Oxygen non-stoichiometry in $(Th_{0.7}Ce_{0.3})O_{2-x}$ was examined mainly from the viewpoint of Ce reduction based on experimental results obtained by means of thermogravimetric analysis at 1173, 1273 and 1373 K. It was observed that Ce in $(Th_{0.7}Ce_{0.3})O_{2-x}$ was more resistant to reduction than Ce in CeO_{2-x} in a specific range of oxygen potential. The obtained results were analyzed through comparison with those of CeO_{2-x} and $(U_{0.7}Ce_{0.3})O_{2-x}$. It was concluded that the Ce reduction could have some relation to the defect forms and their transformations in each solid solution.

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