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Chemical diffusion of oxygen in thoria–urania solid solution

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Abstract

The chemical diffusion coefficients of oxygen were measured for the $(Th_{1-y}, U_y)O_{2+x}$ with uranium content y of 1, 3 and 5 mol% in the temperature range of 1213–1313 K under the oxidizing or reducing atmosphere. The magnitude of activation energies obtained for oxygen diffusion was in good agreement with the migration energy which is calculated based on interstitialcy mechanism by Colbourn. With increasing uranium content, the chemical diffusion coefficient increased and the activation energy for oxygen diffusion decreased slightly in the present experimental conditions. The excess oxygen were soluble into the $(Th_{1-y}, U_y)O_{2+x}$ sample, so that the interaction energy between the higher valence uranium ions and interstitial oxygen ions might increase with decreasing uranium content. The effect of oxygen partial pressure on both the chemical diffusion coefficient and the lattice parameter of $(Th_{1-y}, U_y)O_{2+x}$ could not be found. The lattice constant decreased linearly with uranium content, which indicated that the relation between these parameters obeyed Vegard's law.

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Keywords: Thoria; Urania; Chemical diffusion coefficient; Lattice parameter; Thermogravimetry

1. Introduction

Thorium is an available fuel material as well as uranium and plutonium. And thorium-based fuels have some advantages: thorium as the alternative of the uranium resources exists richly in nature; the amount of long-lived actinides, e.g., ^{137}Np ($T_{1/2} = 2.14 \times 10^6$ y), generated in the fuel cycle is small.

Oxygen to metal ratio (O/M) has a strong effect on the physical and chemical properties, e.g., thermal conductivity, oxygen potential, chemical forms of fission products and so on, of thorium–uranium mixed oxide fuel under irradiation conditions. Relation between the oxygen potential of $(Th_{1-y}, U_y)O_{2+x}$ and O/M has been discussed in some reports [1–4]. On the other hand, the chemical diffusion coefficients of oxygen in $(Th_{1-y}, U_y)O_{2+x}$ was measured in a limited number of studies [5,6]. Mutsui and Naito [5] measured the chemical diffusion coefficients of oxygen in $(Th_{1-y}, U_y)O_{2+x}$ with y of 0.2 and 0.4 in the temperature region from 1282 to 1373 K, and Furuya [6] measured its values with y of 0.3, 0.5 and 0.7 from 518 to 728 K.

This study is an attempt to understand the oxygen diffusion mechanism in the thorium–uranium mixed

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oxide fuel for Light Water Reactor utilization. Therefore, the oxygen chemical diffusion of the $(Th_{1-y}, U_y)O_{2+x}$ with uranium content y of 1, 3 and 5 mol% were measured in the temperature range from 1213 to 1313 K under the reducing or oxidizing atmosphere, using the micro-balance technique. The lattice parameter as a function of uranium content was measured with X-ray diffraction (XRD).

2. Experimental

(Th, U)O_2 solid solution having the thorium concentrations of 1%, 3% and 5% were prepared by the coprecipitation, calcination, pressing and sintering (Fig. 1). The density of specimen with the geometrical size of nearly 8.3 mm in diameter and 1.3 mm in height was above 94% of theoretical. Chemical diffusion coefficient was determined from the weight change of specimen heated at constant temperature in the temperature range from 1213 to 1313 K under the oxidizing or reducing atmosphere. Fig. 2 shows a schematic of experimental apparatus. Using Cahn 2000 micro-balance, the measurement of mass change is carried out in the controlled CO_2, 1% CO/CO_2, or N_2/5% H_2 atmosphere. The samples are oxidized in the CO_2 or 1% CO/CO_2 atmosphere and reduced in the N_2/5% H_2 atmosphere. Oxygen partial pressure are 1.12×10^{-4}, 2.27×10^{-11}, and 1.90×10^{-16} bar for CO_2, 1% CO/CO_2, and 5% H_2/N_2 atmosphere, respectively, and are monitored throughout the equilibration with solid-state oxygen sensor, Calcia-stabilized-zirconia.

In order to determine a lattice parameter of (Th, U)O_2 solid solution, X-ray pattern was taken on the specimen, using a Geigerflex-2013 Rigaku diffractometer. The diffractometer was used with Cu Kα radiation and at conditions of 30 keV and 15 mA. The diffraction angle 2θ was scanned between 80° and 140°.

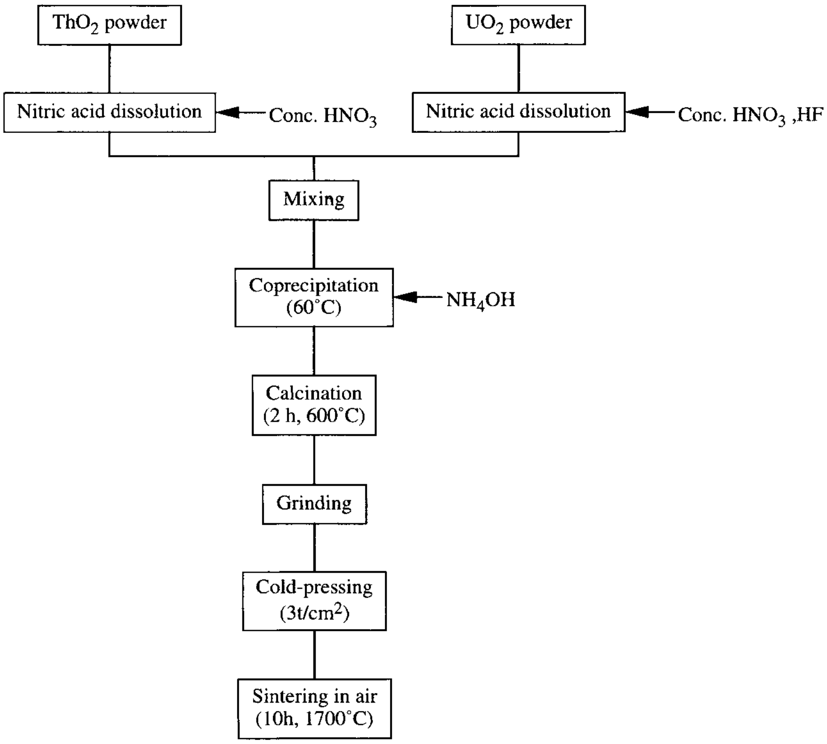

Fig. 1. Flowsheet of production of (Th, U)O_2 pellet.

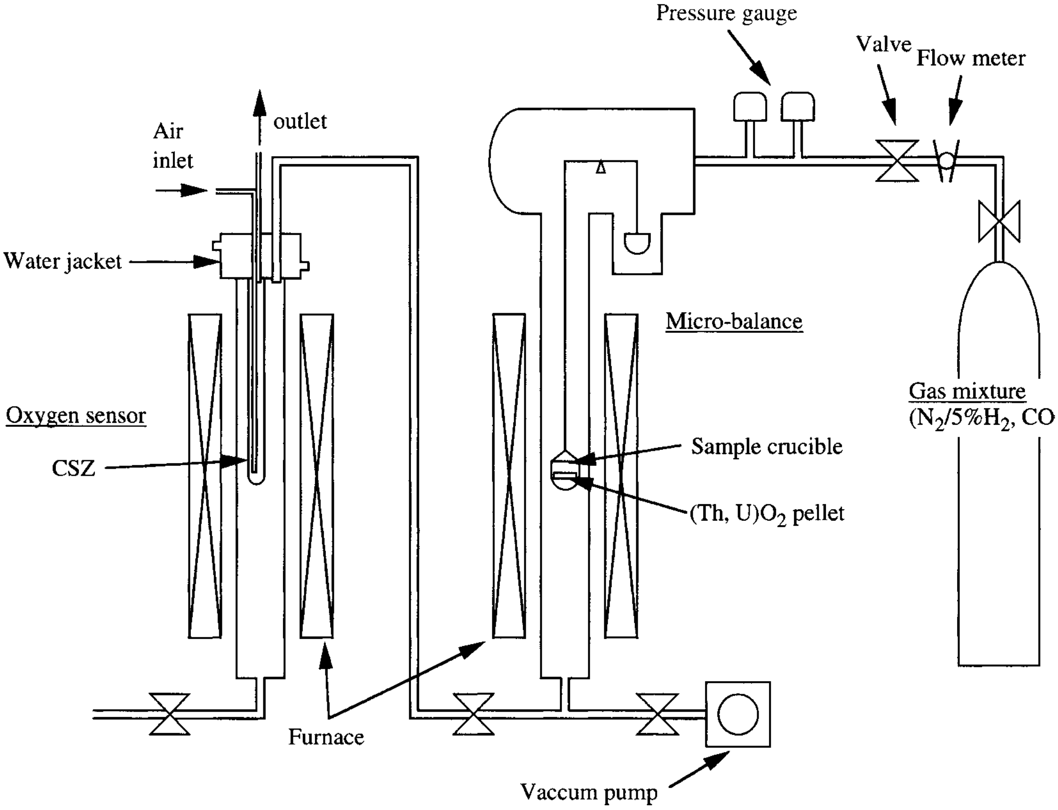

Fig. 2. Schematic diagram of the experimental apparatus. It consists of micro-balance, oxygen sensor, and associated gas supplying equipment.

3. Results

3.1. Thermogravimetry

Assuming that oxygen concentration on the surface of specimen is constant during heating, the weight change of cylindrical specimen with a size of a in radius and $2b$ in height changes with time t according to the following equation [5,7]:

$$\log\left(\frac{M_\infty - M_t}{M_\infty - M_0}\right) = -0.578 - \left(\frac{2.405^2}{a^2} + \frac{\pi^2}{4b^2}\right) D\cdot t, \qquad (1)$$

where D is the chemical diffusion coefficient, M_∞, M_t and M_0 are the weight after infinite time, the weight in time t and the initial weight. Fig. 3 shows a typical weight change as a function of time of $(Th_{0.95}, U_{0.05})O_{2+x}$ specimen heated at 1253 K under a reducing $N_2/5\%\ H_2$ atmosphere. In this figure, the axes of ordinate and abscissa are expressed in logarithmic scale of weight change and in linear scale of time, respectively. For other experimental conditions, the weight of specimen changed linearly in such a plot. According to Eq. (1), the chemical diffusion coefficient of oxygen was obtained from the slope of weight gain curve. Same kinds of runs were carried out on the other specimens of different compositions in the temperature range described above. The effect of experimental atmosphere, i.e., oxygen partial pressure, on the chemical diffusion coefficient for $(Th_{0.95}, U_{0.05})O_{2+x}$ specimen is shown in Fig. 4. The data is little scattered, but we could not find the effects of atmosphere for other specimens of different composi-

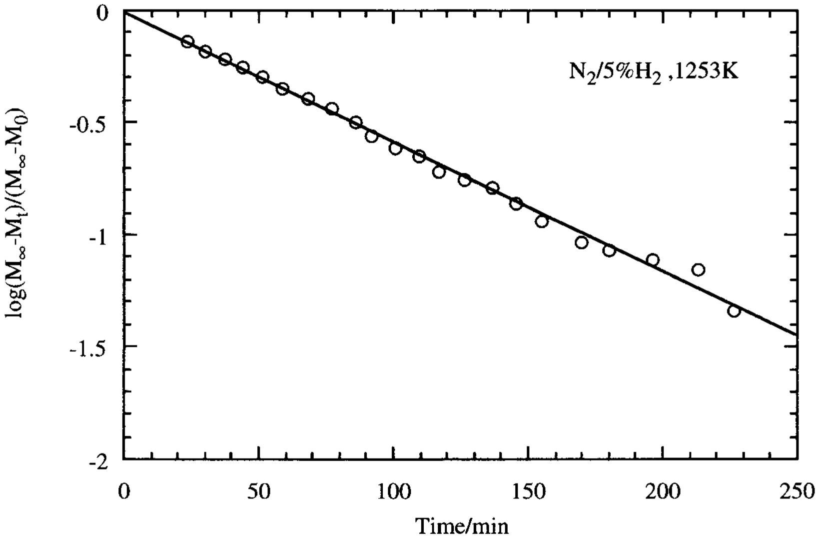

Fig. 3. Weight change of $(Th_{0.95}, U_{0.05})O_{2+x}$ in the N_2/5% H_2 atmosphere at 1253 K.

tions. Fig. 5 shows the Arrhenius plots of diffusion coefficients obtained by the least square fitting, and they can be given by the following equations:

$$D = 4.52 \times 10^{-8}\exp\left(-\frac{71.0}{RT}\right)$$
$$\text{for } (Th_{0.95}, U_{0.05})O_{2+x}, \quad (2)$$

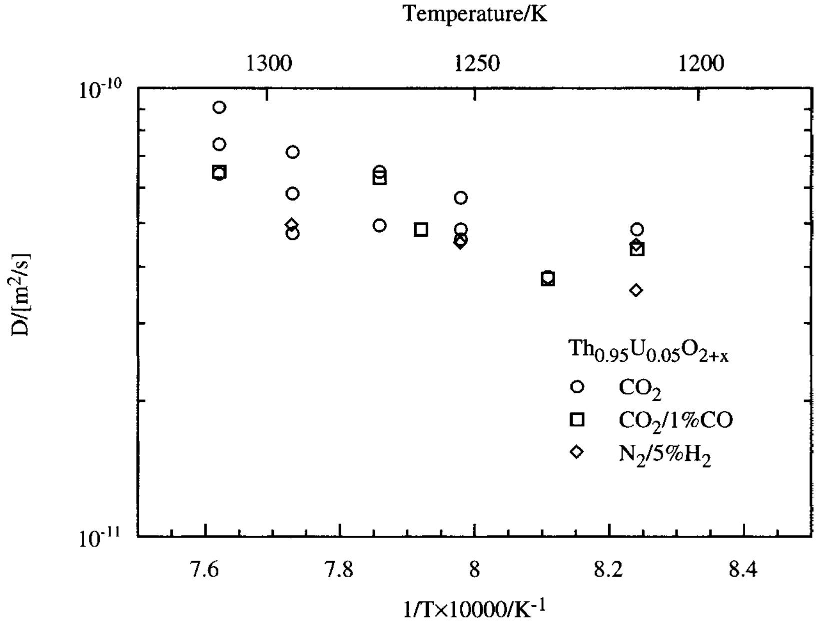

Fig. 4. Effect of the atmospheric gas on chemical diffusion coefficients of oxygen.

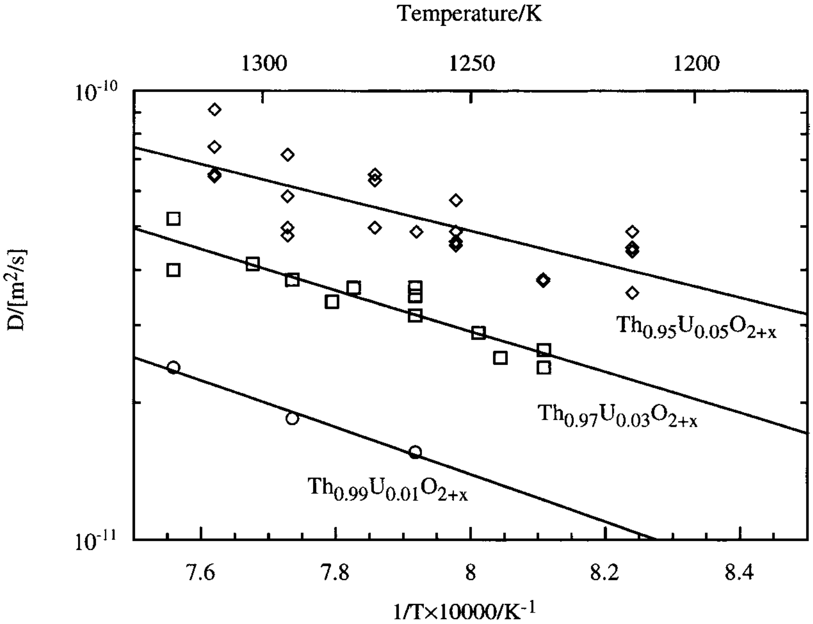

Fig. 5. Effect of uranium content on chemical diffusion coefficients of oxygen.

$$D = 1.42 \times 10^{-7}\exp\left(-\frac{88.3}{RT}\right)$$

for $(Th_{0.97}, U_{0.03})O_{2+x}$, (3)

$$D = 2.02 \times 10^{-7}\exp\left(-\frac{99.6}{RT}\right)$$

for $(Th_{0.99}, U_{0.01})O_{2+x}$, (4)

where D is in m²/s and the activation energy is in kJ/mol. R is the gas constant, and T is the temperature in K. The result shows that the chemical diffusion coefficient of $(Th_{1-y}, U_y)O_{2+x}$ solid solution increases with uranium content y and on the contrary, the activation energy decreases with y in the present experimental conditions.

3.2. XRD examination

The crystal structure of (Th, U)O_2 solid solution is of the fluorite (CaF_2) type. Cations are arranged in a face-centered cubic, in which the tetrahedral positions are filled with anions. The lattice parameter was calculated using interplanar spacing corresponding to each diffraction peak of (4 2 2), (5 1 1), (4 4 0), (5 3 1), (6 0 0), (6 2 0), and (5 3 3). All diffraction peaks existed in the 2θ range between 80° and 140°, and the peaks from other compounds, e.g., U_3O_8, were not found. The lattice parameters thus obtained are plotted in Fig. 6 [8,9]. The result is in good agreement with Vegard's law, and the lattice parameter is getting smaller with increasing uranium content. This is the reason why an ionic radius of uranium (0.083–0.093 nm) is smaller than that of thorium (0.099 nm) because of actinide contraction. In addition, the ionic radius of uranium is influenced by its valence state, and this value is small for high valence state. The lattice parameter of (Th, U)O_{2+x} decreases with the addition of excess oxygen [9]. In practice, we measured the lattice parameter of sample after reduction and oxidation. However, significant difference between these conditions could not be found for lattice parameters since an amount of excess oxygen into the sample was very small.

4. Discussions

The chemical diffusion coefficients of oxygen in $(Th_{1-y}, U_y)O_{2+x}$ solid solution were found to be independent on the oxygen partial pressure corre-

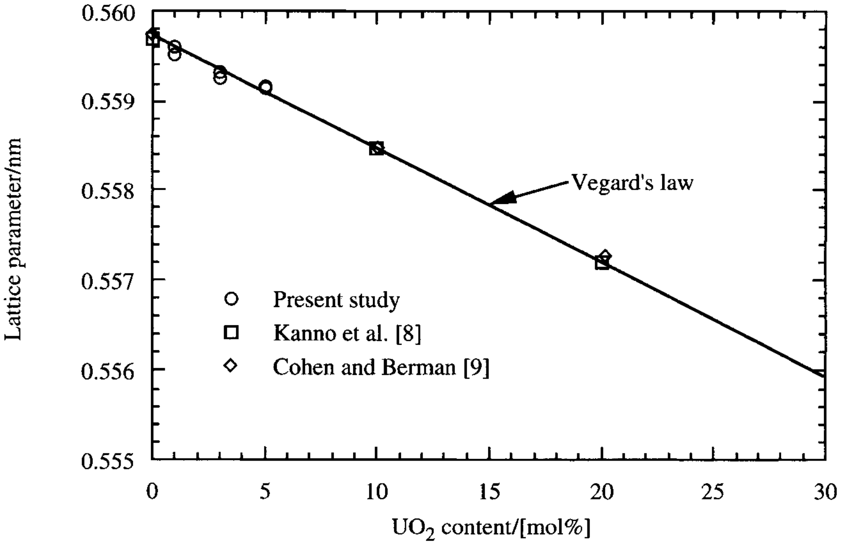

Fig. 6. Lattice parameter as a function of UO_2 content for the thoria–urania system.

sponding to each atmosphere. This result is shown in Fig. 4. The dependence of oxygen partial pressure on chemical or self-diffusion coefficients of oxygen in $(Th_{1-y}, U_y)O_{2+x}$ solid solution was not investigated so far. However, some experiments concerning the effect of oxygen partial pressure have been performed for UO_{2+x} [10–12] and $(Pu, U)O_{2+x}$ [13] solid solution. According to these previous studies, self-diffusion coefficient was strongly dependent on the stoichiometry deviation x, nevertheless chemical diffusion coefficient was insensitive on the value of O/M without the large x region ($x >$ ca. 0.1). This result can be interpreted, using the thermodynamic relation between chemical diffusion coefficient and self-diffusion one. The thermodynamic relation is discussed in latter. In the present study, we measured the chemical diffusion coefficient in the stoichiometry deviation less than ca. 0.026. Therefore, assuming the similar thermodynamic relation for the $(Th_{1-y}, U_y)O_{2+x}$ solid solution, our result with the chemical diffusion coefficient is insensitive on the oxygen partial pressure, can be understood.

The activation energies obtained in the present study were 71.0, 88.3 and 99.6 kJ/mol for uranium content $y = 0.05$, 0.03 and 0.01, respectively. The activation energies of oxygen diffusion coefficients for various oxides are listed in Table 1 [5,6,10,13–18]. These values are obtained based on the experimental data, which are in good agreement with our results. Therefore, it indicates that similar diffusion mechanism exists among these oxides. For the hyperstoichiometric UO_{2+x}, the oxygen diffusion mechanism as well as the defect structure has been studied in detail. In general, the defect model (2:2:2 structure) proposed by Willis is believed at present, which consists of oxygen vacancies at the normal lattice sites and two kinds of interstitial oxygens in actinide oxides having CaF_2 structure. Matsui and Naito [1] proposed the complex defects which are different in oxygen partial pressure. Colbourn and Mackrodt [19] evaluated the migration energies of both cation and anion in ThO_2. According to their calculations, oxygen migration energy due to interstitialcy mechanism was estimated to be 88.8 kJ/mol. In the present study, the samples were hyperstoichiometric $(Th, U)O_{2+x}$, and oxidation or reduction was performed in the temperature range from 1213 to 1313 K, where the UO_2 contents behaved like impurities in the extrinsic region. As a result, it concluded that oxygen migration in $(Th, U)O_{2+x}$ was due to interstitialcy mechanism in the present experimental conditions.

The magnitude of oxygen activation energy of $(Th_{1-y}, U_y)O_{2+x}$ was found to decrease with uranium content y. Lee [20] showed that the activation energy

Table 1
Activation energies of chemical or self-diffusion coefficient of oxygen

Oxide	Activation energy (kJ/mol)	Oxygen chemical (C) or self (S)-diffusion coefficient	Reference
$(Th_{0.95}, U_{0.05})O_{2+x}$	71.0	C	This work
$(Th_{0.97}, U_{0.03})O_{2+x}$	88.3	C	This work
$(Th_{0.99}, U_{0.01})O_{2+x}$	99.6	C	This work
$(Th_{0.6}, U_{0.4})O_{2+x}$	93.1	C	[5]
$(Th_{0.8}, U_{0.2})O_{2+x}$	66.8	C	[5]
$(Th_{0.3}, U_{0.7})O_{2+x}$	108.0	C	[6]
$(Th_{0.5}, U_{0.5})O_{2+x}$	112.1	C	[6]
$(Th_{0.7}, U_{0.3})O_{2+x}$	107.1	C	[6]
ThO_{2+x}	73.6	S	[14,15]
UO_{2+x}	99.6	S	[10]
UO_{2+x}	100.1–103.5	C	[10]
UO_{2+x}	119.2	C	[16]
UO_{2+x}	86.6	C	[17]
UO_{2+x}	96.7	S	[18]
$(Pu_{0.2}, U_{0.8})O_{2+x}$	72.4	C	[13]

obtained from measurements of the electrical conductivities decreased with uranium content in the range UO_2–$(Th_{0.85}, U_{0.15})O_2$. However, other experiments reported that the activation energy in $(Th_{1-y}, U_y)O_{2+x}$ was not influenced by uranium content y [5,6]. In the present work, we measured the lattice parameter as a function of uranium content. However, it could be interpreted in terms of the strain of lattice structure, because both obtained activation energy and lattice parameter decreased with increasing uranium content.

Considering the valence of uranium ions in the solid solution, our result could be interpreted. The mean valence of uranium ions in $(Th_{1-y}, U_y)O_{2+x}$ is given by

$$V_u = 4 + \frac{2x}{y}. \tag{5}$$

According to this equation, V_u is increasing with decreasing y when x is constant. In other words, the ratio of uranium ions with higher valence, U^{5+} and U^{6+}, to U^{4+} ions increases with the decrease in y. As a result, interaction energy between higher valence uranium ions and interstitial oxygen ions increases, which leads the increase in activation energy of oxygen in $(Th_{1-y}, U_y)O_{2+x}$.

In case of $(Th, U)O_{2+x}$ as well as UO_2, the chemical diffusion coefficient D of oxygen can be expressed by its self-diffusion coefficient in the following way, since cation self-diffusion coefficient in thoria–urania based materials is much smaller than that of oxygen [21,22]:

$$D = \frac{2+x}{2x}\frac{\partial \ln P_{O_2}}{\partial \ln x} D^*, \tag{6}$$

where $\partial \ln P_{O_2}/\partial \ln x$ is the thermodynamic factor, and D^* is the self-diffusion coefficient. This idea is advocated by Lay [16] for hyperstoichiometric uranium oxides. Assuming the probability, which the oxygen can find the defect site, is simply proportional to the uranium content y, the self-diffusion coefficient may be given by

$$D^* = 2y\left(\frac{x}{2+x}\right) D_i^0 \exp\left(-\frac{\Delta H_m}{RT}\right), \tag{7}$$

where D_i^0 is constant, ΔH_m is the migration energy. Introducing Eq. (7) into Eq. (6), the chemical diffusion coefficient is re-written by

$$D = y\left(\frac{\partial \ln P_{O_2}}{\partial \ln x}\right) D_i^0 \exp\left(-\frac{\Delta H_m}{RT}\right). \tag{8}$$

The thermodynamic factor $\partial \ln P_{O_2}/\partial \ln x$ or oxygen potentials of $(Th, U)O_{2+x}$ as well as UO_{2+x} has been investigated by several researchers [2–5]. Aronson and Clayton [4] measured the oxygen pressures in equilibrium with $(Th_{1-y}, U_y)O_{2+x}$ in the range of y from

0.9 to 0.3, and the thermodynamic factor, which increased with decreasing y, was estimated to be approx. 3–4. Ugajin [2] measured the oxygen potential of $(Th_{1-y}, U_y)O_{2+x}$ with y of 0.2 to 0.05, and the thermodynamic factor seemed to be approx. 4–6. The thermodynamic factor calculated based on data obtained by Ugajin was also increasing with the decrease in y. Anthonysamy et al. [3] reported the relation between the oxygen potentials of $(Th_{1-y}, U_y)O_{2+x}$ and uranium content $y > 0.54$. According to their data, the thermodynamic factor was found to be compatible with ca. 6. Matsui and Naito [5] proposed that the thermodynamic factor depends on the defect structure of $(Th, U)O_{2+x}$ or UO_{2+x}. Moreover, this factor depends on the stoichiometry deviation x, and was considered to be a different integer ($n = 2$, 4 and 12) for each defect structure. e.g., the thermodynamic factor of the defect structure (2:2:2 model) proposed by Willis was estimated to be 4, assuming that the charge of the complex defect was -3 with relatively large $x > 0.008$. Fig. 7 shows comparison of the chemical diffusion coefficient of oxygen for $(Th, U)O_{2+x}$ [5] and UO_{2+x} [10]. Inconsistency between experiments was found for the magnitude of chemical diffusion coefficients. However, uranium content dependence was shown in each experiment. We tried to plot the measured D/y values as a function of $1/T$, so that most of the D/y values fell into the narrow band. The following mean values for the fit parameters $(\partial \ln P_{O_2}/\partial \ln x)D_i^0$ and ΔH_m were derived: $(\partial \ln P_{O_2}/\partial \ln x)D_i^0 = 4.40 \times 10^{-6}\ m^2/s$, $\Delta H_m = 87.2$ kJ/mol. The proper D_i^0 value was not calculated for (Th,

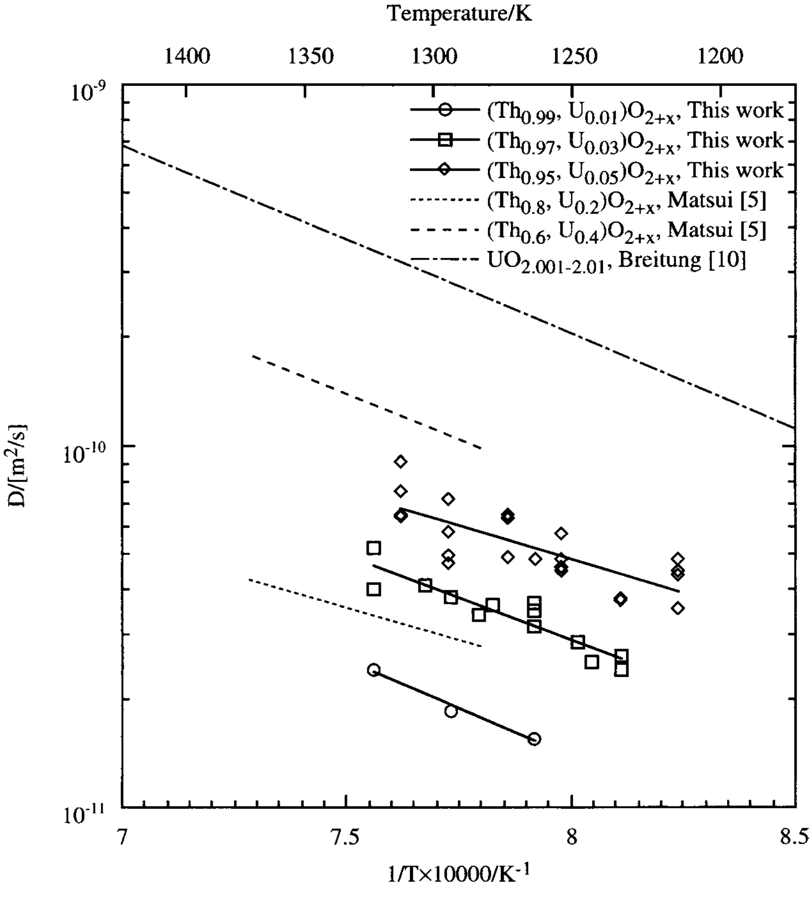

Fig. 7. Comparison of the chemical diffusion coefficients of oxygen for $(Th_{1-y}, U_y)O_{2+x}$ and UO_{2+x}.

U)O_{2+x} so far. Using the D_i^0 value, 6.65×10^{-7} m²/s, for UO_{2+x} [10], the thermodynamic factor thus obtained was 6.61. On the contrary, assuming that the defect structure was 2:2:2 model proposed Willis, i.e., $\partial \ln P_{O_2}/\partial \ln x = 4$, the D_i^0 value was estimated to be 1.10×10^{-6} m²/s. In order to determine the relation among these parameters in the equation of chemical diffusion coefficient, more systematic studies are needed.

5. Conclusion

The chemical diffusion coefficients of oxygen were measured for the $(Th_{1-y}, U_y)O_{2+x}$ with uranium content y of 1, 3 and 5 mol% in the temperature range between 1213 and 1313 K in the controlled N_2/5% H_2, 1% CO/CO_2 and CO_2 atmospheres. The magnitude of activation energies obtained for oxygen diffusion was in god agreement with the migration energy calculated by Colbourn. It could be interpreted in terms of the interstitialcy mechanism. The chemical diffusion coefficients of oxygen in $(Th_{1-y}, U_y)O_{2+x}$ increased with uranium content, and its magnitude was approaching that of the hyperstoichiometric UO_{2+x}. On the contrary, the activation energy for oxygen diffusion decreased slightly with uranium content in the present experimental conditions. It indicated that the interaction energy between the higher valence uranium ions and interstitial oxygen ions increased with decreasing uranium content. Relation between chemical and self-diffusion coefficients could be expressed in terms of uranium content and thermodynamic factor. Both the chemical diffusion coefficient of oxygen and the lattice parameter of $(Th_{1-y}, U_y)O_{2+x}$ were insensitive on the oxygen partial pressure. In the present study, the lattice parameter as a function of uranium content followed Vegard's law, and decreased with uranium content.

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