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Oxygen Potentials and Defect Chemistry in Nonstoichiometric (U,Pu)O$_2$

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1. Introduction

Nuclear reactors have been developed to secure stable long-term energy supply. Light water reactors (LWRs) have been operated on a commercial basis in many countries. In LWRs, uranium oxide is used as a fuel. Plutonium which is another element that can be used for generating nuclear energy is produced by a nuclear reaction during burning of uranium oxide fuel and it is extracted from spent fuel when they are reprocessed. Uranium and plutonium mixed oxide s (MOX) fuels containing Pu of less than and more than 15% have been developed for LWRs and fast reactors, respectively. These oxides are fabricated into pellets by powder metallurgy. In the pellet production process, dimensions, density and oxygen-to-metal (O/M) ratio of the pellets are managed as important fuel specifications. The O/M ratio significantly affects various physical properties. Therefore it is essential to understand the O/M ratio dependence on physical properties for analyzing irradiation behavior.

Uranium and plutonium mixed oxide (U,Pu)O$_2$, which is used in nuclear fuels, is a substitutional solid solution compound having the CaF$_2$ type fluorite structure as shown in Fig.1 (Markin & Street, 1967; Sari et al., 1970; Kato & Konashi, 2009). (U,Pu)O$_2$ is stable in a wide range region of hyper- and hypo-stoichiometric compositions. The O/M ratio in nonstoichiometric (U,Pu)O$_2$ is dominated by the numbers of oxygen vacancies and interstitial oxygen atoms. The stoichiometry of (U,Pu)O$_2$ significantly affects various physical properties such as lattice parameter, melting temperature, and thermal conductivity. (Kato et al., 2011a) Therefore many studies on O/M ratio dependence of oxygen potential have been carried out by various methods. The oxygen potential of (U,Pu)O$_2$ drastically changes with a slight O/M change in the near stoichiometric region. Such drastic change may cause a large uncertainty in oxygen potential measurements, and the measured data may be scattered in a range of more than ±100 kJ/mol.

Oxygen potentials have been measured by various methods including the E.M.F. and the gas equilibrium method using thermo-gravimetric measurements. The E.M.F. method cannot be applied to measurements above 1473 K temperature, and it is difficult to use it to determine slight O/M changes in the near stoichiometric region. In the thermo-gravimetric measurements, various gas mixtures like CO/CO$_2$ and H$_2$O/H$_2$ are employed for controlling the oxygen potential. The oxygen potential region control depends on the kind of gases used for the measurements. So, it is crucial to understand the relationships among

the used gas types, oxygen potential and O/M ratio. Furthermore, for the thermo-gravimetric measurements as well, it is very difficult to determine the stoichiometric composition in the high temperature region because of the O/M ratio continuous variation for the near stoichiometric composition.

In previous studies (Kato et al., 2009a, 2011b 2011c), the stoichiometric compositions in $(U,Pu)O_2$ have been determined based on defect chemistry. The relationship between oxygen partial pressure and deviation x from stoichiometric composition has been analyzed in non-stoichiometric oxides. Kosuge (1993) used statistical thermodynamics considerations for description of non-stoichiometric compounds, and Karen (2006) reported a point-defect scheme for them. Recently their methods have been applied for nonstoichiometric $(U,Pu)O_2$, and experimental data, accurately measured in the near stoichiometric region, were analyzed as a function of temperature. In this report the measurement data and the measurement technique were reviewed and analysis results based on defect chemistry were summarized.
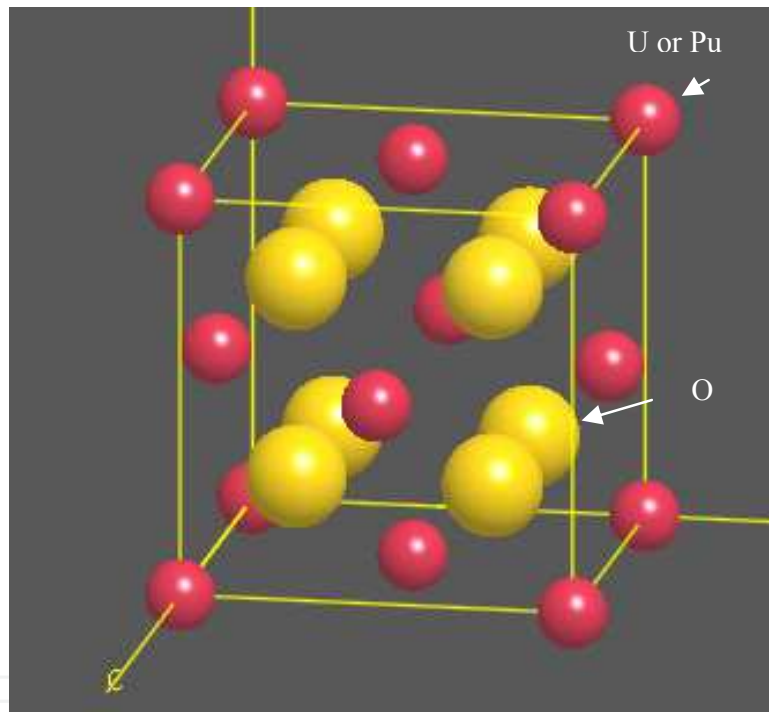

Fig. 1. CaF_2 type fluorite structure

2. Experimental data of oxygen potential in $(U,Pu)O_2$

The measurement data of $(U,Pu)O_2$ are listed in Table 1. The relationships between oxygen potential and O/M ratio were obtained as functions of temperature and Pu content. Almost all data that were measured in the 1960's and 1970's had large uncertainty. Recently Kato et al. (2005, 2009b, 2011b, 2011c) accurately obtained a large number of data in $(U,Pu)O_2$ by in-situ analysis. Fig.2 shows the measurement data as functions of O/M ratio and Pu content. The data were measured in both regions of hyper- and hypo-stoichiometric compositions and they increased with Pu content. Fig.3 shows the oxygen potential $\Delta \bar{G}_{O_2}$ of $(U_{0.8}Pu_{0.2})O_{2\pm x}$. The oxygen potential is calculated by eqs.(1)-(2).

| References	Pu (%)	O/M	Temp. (K)	Data points
Woodley, 1981	10	1.96-2.00	1273-1473	17
Sørensen,1976	10	1.98-1.99	1222-1674	12
Markin & McIver, 1965	11	1.95-2.08	1073-1373	45
Kato et al., 2011b	12	1.988-2.0408	1673-1873	76
Chilton & Kirkham, 1976	15	2.002-2.106	1518-1823	24
Javed, 1973	20	1.920-1.989	1273-1973	20
Sørensen,1976	20	1.99-2.00	1359-1674	17
Mari et al., 1977	20	1.96-1.99	757-1276	24
Tetenbaum, 1974	20	1.92-1.96	2150-2550	25
Kato et al., 2009b,2011c	20	1.979-2.0088	1473-1873	105
Vasudeva Rao et al., 2006	21	1.964-2.00	1073-1473	53
Chilton & Edwards, 1980	23	1.980-2.030	1523-1822	114
Woodley &Adamson, 1985	25	1.90-2.00	1222-1674	68
Vasudeva Rao et al., 2006	28	1.975-2.00	1073-1473	19
Markin & McIver, 1965	30	1.86-2.06	1073-1373	39
Kato et al., 2005, 2011c	30	1.964-2.028	1273-1873	153
Chilton & Kirkham, 1976	31	1.99-2.07	1518-1823	52
Woodley, 1981	40	1.90-2.00	1273-1473	23

Table 1. Measurement data of (U,Pu)O₂
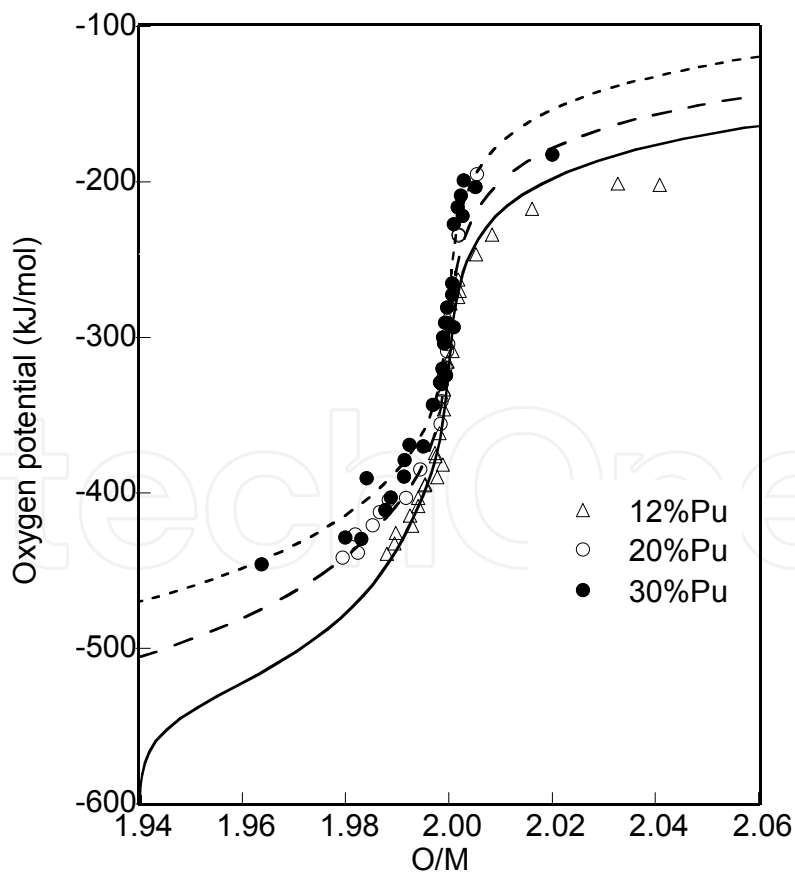
Fig. 2. Oxygen potential at 1873 K as function of Pu content and O/M ratio (Kato et al., 2009b, 2011c)

$$\Delta \overline{G}_{O_2} = RT \ln P_{o_2} \tag{1}$$

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

Here R is the gas constant (8.3145 J/K/mol), T is absolute temperature $\Delta \overline{H}_{O_2}$ is partial molecular enthalpy of O_2 and $\Delta \overline{S}_{O_2}$ is partial molecular entropy of O_2. Eq.(2) predicts that the oxygen potential varies in a linear manner as a function of temperature. The data, however, have an inflection point at hypo-stoichiometric composition of 2.00>O/M>1.95 as shown in Fig.3. This change is consistently explained based on defect chemistry as mentioned later.
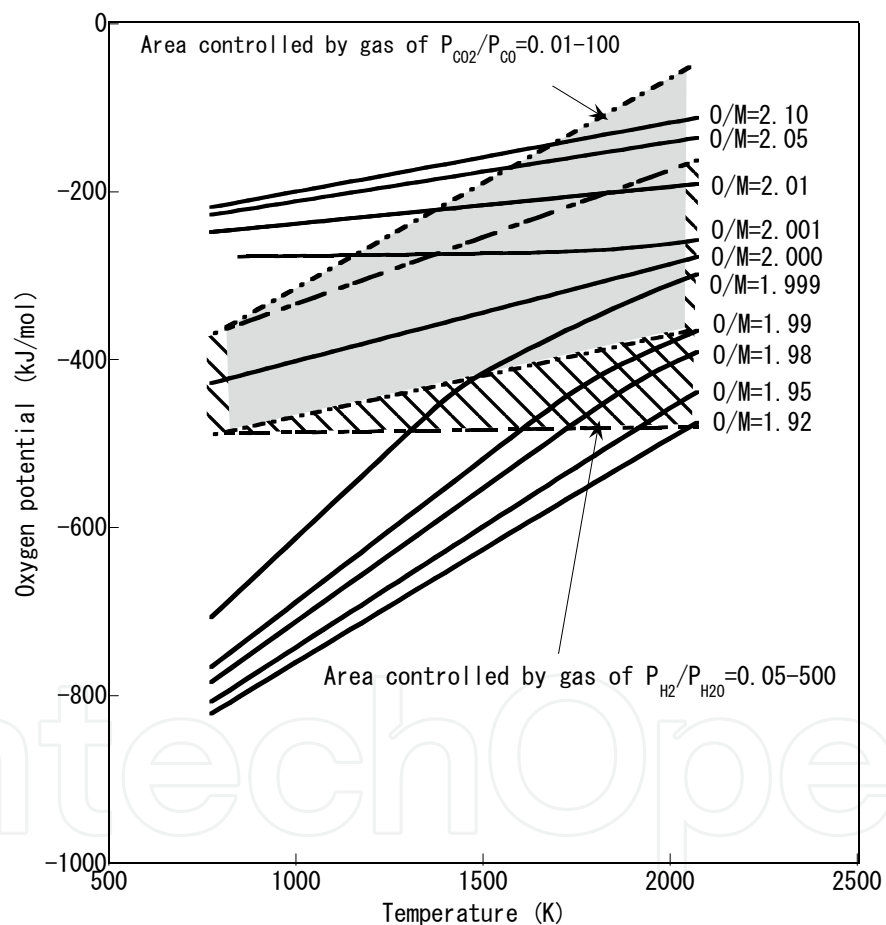

Fig. 3. Oxygen potential of $(U_{0.8}Pu_{0.2})O_{2\pm x}$

3. Measurement techniques

The measurements in previous studies were carried out by the E.M.F. and gas equilibrium methods. The former can accurately measure oxygen potentials, but the measurement data are only limited to a temperature range between 1123 K and 1423 K. Besides, it is

difficult to determine the O/M ratio for the near stoichiometric composition. In the gas equilibrium method, a thermo-gravimeter is employed, which can measure a small deviation of the O/M ratio. Here, the measurement technique by the gas equilibrium method is explained. A thermo-gravimetry and differential thermal analysis system (TG-DTA) was put in glove box and used to measure oxygen potential (Kato et al., 2005, 2009b, 2011b, 2011c). The oxygen partial pressure of the flowing gas was monitored at the inlet and outlet of the apparatus using stabilized zirconia oxygen sensors. Gas mixtures of H_2/H_2O and CO/CO_2 were used for controlling the measurement atmosphere. The oxygen partial pressures are determined by the reactions of eqs.(3) and (4) in each gas system.

$$CO + 1/2\ O_2 \leftrightarrow CO_2 \tag{3}$$

$$\overline{\varDelta S}_{O_2} \leftrightarrow H_2O \tag{4}$$

The regions controlled by both gas mixtures are shown by shaded and gray areas, respectively, in Fig.3. The H_2/H_2O mixture gives control at lower oxygen potential. Previously, Kato et al. (2011b, 2011c) used the H_2/H_2O mixture to measure hyper- and hypo-stoichiometric (U,Pu)O₂. Considering the reaction of eq.(4), the equilibrium may be expressed by a free energy of formation, $\varDelta G_f$, given by eqs.(5) and (6).

$$\Delta G_f = -RT \cdot \ln \frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}^{1/2}} \tag{5}$$

$$\Delta G_f = -246440 + 54.8 \cdot T \tag{6}$$

The P_{o_2} values in the flowing gas from the measurement apparatus were monitored at 973 K with the stabilized zirconia sensors at the inlet and the outlet. The ratio of P_{H_2}/P_{H_2O} at the outlet sensor can be determined by eqs.(5) and (6), and P_{o_2} at measurement temperatures was calculated under the assumption that the ratio of P_{H_2}/P_{H_2O} at the sensor position was the same at any sampling position. Therefore, the oxygen potential can be determined by controlling the ratio of P_{H_2}/P_{H_2O} in the flowing gas.

4. Statistical thermodynamics of point defects

The relation between x and P_{o_2} in non-stoichiometric compounds was analyzed based on statistical thermodynamics of point defects in a previous report (Kosuge, 1993) and eq.(7) was derived.

$$\frac{P_{o_2}(x)}{P_{o_2}(0)} = 1 + \frac{x^2 + x\sqrt{x^2 + 4C^2}}{2C^2} \tag{7}$$

Here $P_{o_2}(0)$ represents P_{o_2} at the stoichiometric composition and C is the intrinsic fraction of defects. Eq.(7) can be applied in the near stoichiometric region. Data for (U,Pu)O₂ in the near stoichiometric region have been obtained by Kato et al. (2011b, 2011c). Curves of

$P_{o_2}(0)/P_{o_2}(x)$ versus x are shown in Fig.4. Eq. (7) was a least square fit using the experimental x and $P_{O2}(x)$ as a parameter of temperature and the relationship between x and P$_{O2}$(x) was determined. The $P_{O2}(x)$ and C were evaluated from Fig.4; they are shown in Table 2. Temperature dependence on oxygen potential is given by eq. (2). Therefore, oxygen potential of stoichiometric $(U_{0.8}Pu_{0.2})O_2$ was obtained from the data in Table 1 according to the following equation.

$$\Delta \overline{G}_{O_2} = -517.5 \times 10^3 + 116.5 \cdot T \tag{8}$$

Eq.(8) shows that $\Delta \overline{H}_{O_2}$ and $\Delta \overline{S}_{O_2}$ at stoichiometric composition are -517.5 kJ/mol and 116.5 J/mol/K, respectively. Kato et al. (2011c) summarized their data in MOX containing 12, 20 and 30% Pu. The $\Delta \overline{H}_{O_2}$ values were almost the same and the $\Delta \overline{S}_{O_2}$ values decreased with Pu content. In the present work the oxygen potential of $(U_{1-y}Pu_y)O_{2.00}$ dependence on Pu content was estimated by eq.(9).

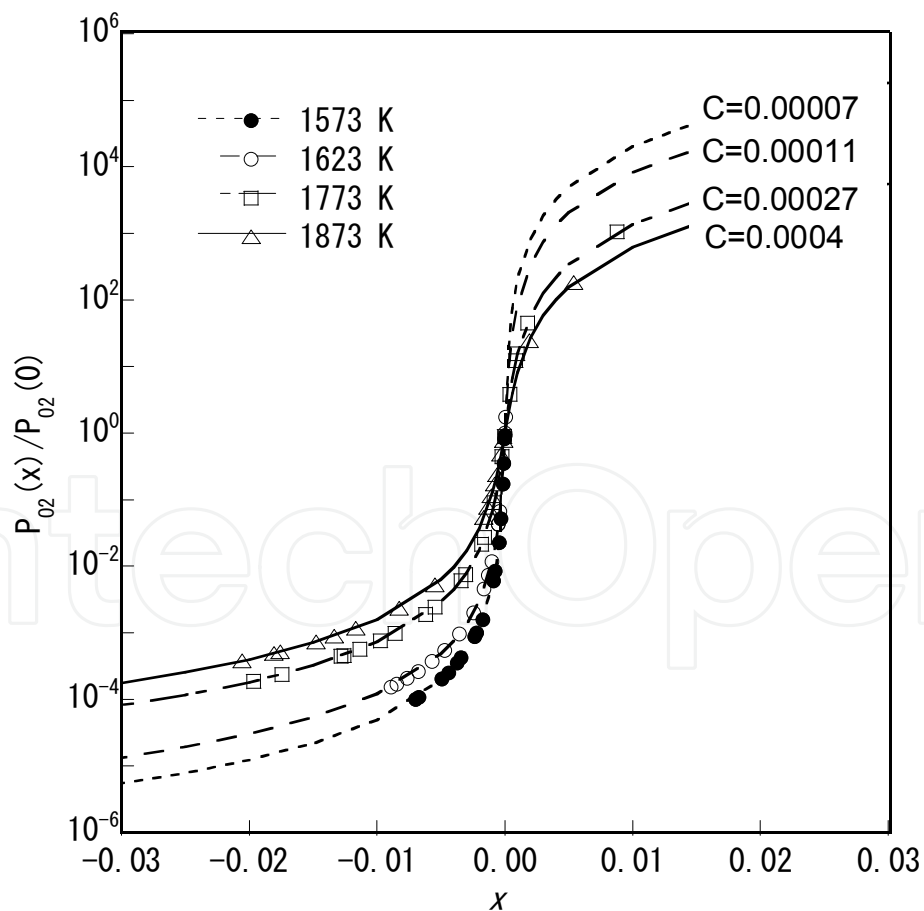$$\Delta \overline{G}_{O_2} = -521.2 \times 10^3 - (117.8 \cdot y + 92.1) \cdot T \tag{9}$$

Fig. 4. Curves of $P_{o_2}(0)/P_{o_2}(x)$ versus x in ($U_{0.8}Pu_{0.2})O_{2\pm x}$

Temperature (K)	$P_{o_2}(0)$ (atm)	C
1573	7.93E-12	0.00007
1623	2.68E-11	0.00011
1773	6.88E-10	0.00027
1873	4.48E-09	0.00040

Table 2. $P_{o_2}(0)$ and C in $(U_{0.8}Pu_{0.2})O_2$

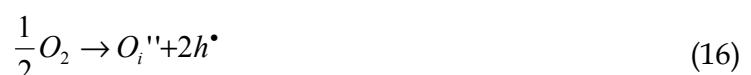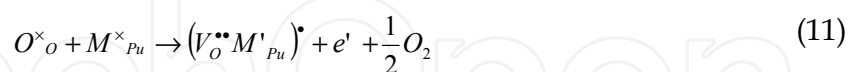The intrinsic fraction of defects C may be described by the following equation:

$$C = A \cdot \exp\left(-\frac{E}{2\kappa T}\right) \tag{10}$$

where E is the formation energy for intrinsic ionization, A is a constant and κ is the Boltzmann constant. E was estimated to be 2.9 eV from the relationship between C and $1/T$. The value of E predicts the band gap energy. The band gap energies of UO₂ andPuO₂ were reported to be 2.7 and 2.5 eV, respectively (Nakamura & Fujino, 1986; Naito et al., 1980). The value of E in this work was slightly higher compared with other data.

5. Defect equilibria — Kröger-Vink diagram

The nonstoichiometry of various compounds has been analyzed using Kröger - Vink diagrams (Kröger & Vink, 1957; Kofstad, 1972; Sørensen, 1981; Karen, 2009). In this section, the notation of Kröger - Vink was used. (Kröger & Vink, 1957) Deviation x in $(U,Pu)O_{2\pm x}$ is proportional to $P_{o_2}^{\pm 1/n}$, where n is a characteristic number identifying the defect (Kofstad, 1972; Sørensen, 1981). Relationships between x and P_{o_2} in $(U_{0.8}Pu_{0.2})O_{2\pm x}$ were analyzed, and are shown in Fig.5. The slopes of $n=-4$, and -2 were observed in hypo-stoichiometric MOX, and that of $n=+2$ was observed in hyper-stoichiometric MOX. It was reported that $n=-4$ changed to $n=-3$ for $(U_{0.7}Pu_{0.3})O_{2\pm x}$.

Then, defect reactions of eqs. (11)-(16) are considered for defect equilibria in $(U_{0.8}Pu_{0.2})O_{2\pm x}$.
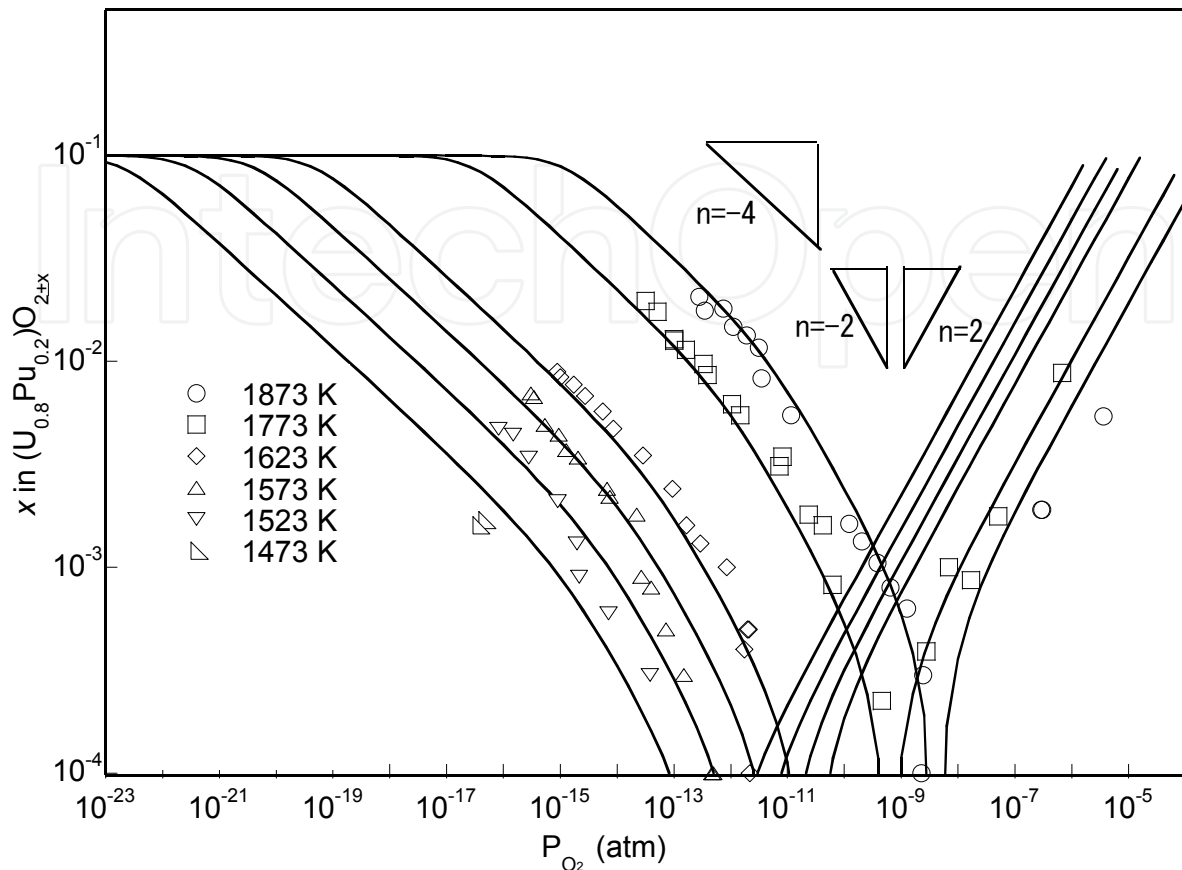
$$O^{\times}_{O} + M^{\times}_{Pu} \rightarrow \left(V^{\bullet\bullet}_{O} M'_{Pu}\right)^{\bullet} + e' + \frac{1}{2}O_2 \tag{11}$$

$$2O^{\times}_{O} + O_2 \rightarrow \left(2O^{a}_{i} 2O^{b}_{i} 2V^{\bullet\bullet}_{O}\right)' + h^{\bullet} \tag{12}$$

$$Nill \rightarrow e' + h^{\bullet} \tag{13}$$

$$O^{\times}_{O} \rightarrow V^{\bullet\bullet}_{O} + O_i'' \tag{14}$$

$$O^{\times}_{O} \rightarrow V^{\bullet\bullet}_{O} + 2e' + \frac{1}{2}O_2 \tag{15}$$

$$\frac{1}{2}O_2 \rightarrow O_i'' + 2h^{\bullet} \tag{16}$$

Fig. 5. The P_{O_2} versus x in $(U_{0.8}Pu_{0.2})O_{2\pm x}$

The equibrium constants in the defect reactions (11)-(16) are described as Eqs.(17)-(22), respectively.

$$K_{Re} = \left[\left(V_O^{\bullet\bullet}Pu'\right)^{\bullet}\right]\left[Pu'\right]P_{O_2}^{1/2} \tag{17}$$

$$K_{Ox} = \left[\left(2O_i^a 2O_i^b 2V_O^{\bullet\bullet}\right)'\right]\left[h^{\bullet}\right]P_{O_2}^{-1} \tag{18}$$

$$K_i = \left[h^{\bullet}\right]\left[e'\right] \tag{19}$$

$$K_F = \left[V_O^{\bullet\bullet}\right]\left[O_i''\right] \tag{20}$$

$$K_{Vo} = \left[V_O^{\bullet\bullet}\right]\left[e'\right]^2 P_{O_2}^{1/2} \tag{21}$$

$$K_{Oi} = \left[O_i''\right]\left[h^{\bullet}\right]^2 P_{O_2}^{-1/2} \tag{22}$$

Two types of diagrams were proposed depending on the dominant defects of the near stoichiometric region; these are Frenkel defects or intrinsic defects.

Region I: Near stoichiometric region

In the case of $(U,Pu)O_{2\pm x}$, it was reported that intrinsic ionization of eq.(13) is dominant in the near stoichiometric region. So, eq.(20) can be written as

$$[h^\bullet] = [e'] = K_i^{1/2}. \tag{23}$$

When inserting eq.(23) into eqs.(21) and (22), $[V_O^{\bullet\bullet}]$ and $[O_i'']$ are given by eqs.(24) and (25).

$$[V_O^{\bullet\bullet}] = \frac{K_{Vo}}{[e']^2} P_{O_2}^{-1/2} = \frac{K_{Vo}}{K_i} P_{O_2}^{-1/2} \tag{24}$$

$$[O_i''] = \frac{K_{Oi}}{[h^\bullet]^2} P_{O_2}^{1/2} = \frac{K_{Oi}}{K_i} P_{O_2}^{1/2} \tag{25}$$

If the deviation x is given by

$$x = [V_O^{\bullet\bullet}] \quad or \quad [O_i''], \tag{26}$$

the value of n is +2 and -2 in the near stoichiometric region, which is consistent with the relationship shown in Fig.5.

Region II: Reducing region

In the defect reaction of eq.(11), the electro-neutrality condition is given by

$$[(V_O^{\bullet\bullet}Pu')^\bullet] = [e']. \tag{27}$$

When inserting eq.(27) into eq.(17), $[V_O^{\bullet\bullet}]$ can be written by

$$[V_O^{\bullet\bullet}] = [(V_O^{\bullet\bullet}Pu')^\bullet] = K_{Re}^{1/2} P_{O_2}^{-1/4}. \tag{28}$$

The value of n is derived as -4.

Region III: Oxidizing region

In the defect reaction of eq.(12), the electro-neutrality condition is given by

$$\left[\left(2O_i^a 2O_i^b 2V_O^{\bullet\bullet}\right)'\right] = [h^\bullet]. \tag{29}$$

When inserting eq.(29) into eq.(18), $[O_i'']$ can be written by

$$[O_i''] = 2\left[\left(2O_i^a 2O_i^b 2V_O^{\bullet\bullet}\right)'\right] = 2K_{Oi}^{1/2} P_{O_2}^{1/2} \tag{30}$$

The value of n is derived as +2.

The measured data shown in Fig.5 were fitted by eqs.(24), (25), (29) and (30), and the equilibrium constants were estimated as a function of temperatures. Eqs.(31)-(34) were obtained from the relationship between equilibrium constants and $1/T$.

$$K' = \frac{K_{Vo}}{K_i} = 493.4 \exp\left(\frac{-372.0 \times 10^3}{RT}\right) \tag{31}$$

$$K'' = \frac{K_{Oi}}{K_i} = 5.095 \times 10^{-5} \exp\left(\frac{175.6 \times 10^3}{RT}\right) \tag{32}$$

$$K_{Re} = 80420 \exp\left(\frac{-515.0 \times 10^3}{RT}\right) \tag{33}$$

$$K_{Ox} = 4.14 \times 10^{-8} \exp\left(\frac{291.0 \times 10^3}{RT}\right) \tag{34}$$

Eqs. (24), (25), (29), (30) and (31)-(34) could represent the Kröger - Vink diagram as shown in Fig.6. The calculation results were consistent with the measured data. In addition, the equilibrium constants, K_i, K_F, K_{Vo} and K_{Oi}, were obtained as eqs.(35)-(38).

$$K_i = 106400 \exp\left(\frac{-286.0.0 \times 10^3}{RT}\right) \tag{35}$$

$$K_F = 0.2006 \exp\left(\frac{-226.5 \times 10^3}{RT}\right) \tag{36}$$

$$K_{Vo} = 5.248 \times 10^7 \exp\left(\frac{-658.0 \times 10^3}{RT}\right) \tag{37}$$

$$K_{Oi} = 4.41 \times 10^{-3} \exp\left(\frac{5.0 \times 10^3}{RT}\right) \tag{38}$$

Eqs.(35)-(38) can predict the transformation energy of defects. The predicted values are shown in Table 3 and they had close agreement with other data.

The O/M ratio of $(U,Pu)O_2$ is an important parameter for development of nuclear fuels. So, it is essential to know the O/M ratio as functions of temperature and oxygen potential. If deviation x is equivalent to $\left[V_O^{\bullet\bullet}\right]$ and $\left[O_i''\right]$, the O/M ratio can be written by

$$\text{O/M} = 2.00 - \left[V_O^{\bullet\bullet}\right] + \left[O_i''\right]. \tag{39}$$

In the hypo-stoichiometric region, $\left[V_O^{\bullet\bullet}\right]$ is described by eqs.(24) and (28). In addition, it is assumed that $\left[V_O^{\bullet\bullet}\right]$ is limited by eq.(40) because the valence of Pu is +3.

$$\left[V_O^{\bullet\bullet}\right] = 0.01. \tag{40}$$

Therefore, $\left[V_O^{\bullet\bullet}\right]$ is estimated by the following equation using eqs.(24), (28) and (40).

$$\left[V_O^{\bullet\bullet}\right] = \left[\left(\frac{K_{Vo}}{K_i} P_{O_2}^{-1/2}\right)^{-3} + \left(K_{Re}^{1/2} P_{O_2}^{-1/4}\right)^{-3} + (0.01)^{-3}\right]^{-1/3} \tag{41}$$

$\left[O_i''\right]$ is estimated by the following equation using eqs.(25).

$$[O_i''] = \left[\left(\frac{K_{Oi}}{K_i}P_{O_2}^{1/2}\right)^{-2} + \left(2K_{Oi}^{1/2}P_{O_2}^{1/2}\right)^{-2}\right]^{-1/2} \tag{42}$$
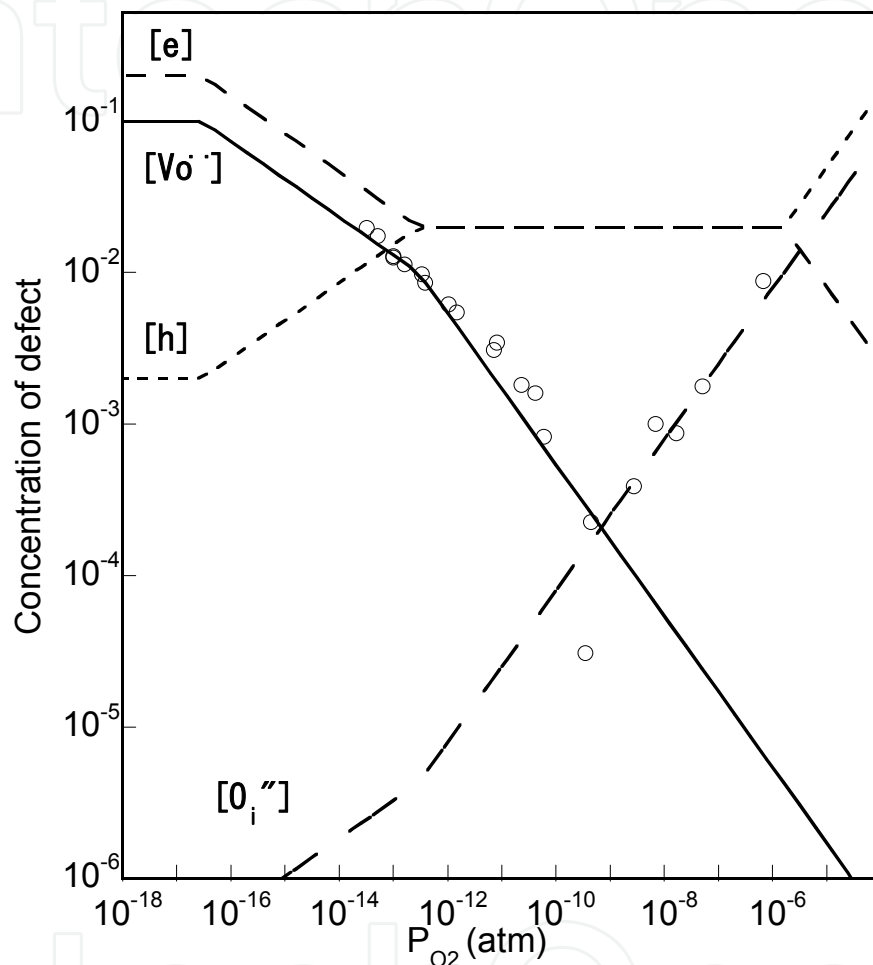

Fig. 6. Calculation results of defect concentration at 1773 K in $(U_{0.8}Pu_{0.2})O_{2\pm x}$

When inserting eqs.(38) and (39) into eq.(36), the O/M ratio can be represented. The calculation results are shown in Fig.5; lines as functions of temperature and oxygen partial pressure were in good agreement with the experimental data. The figure shows that the dominate defect changed with temperature in hypo-stoichiometric oxide with constant O/M ratio. So, two forms of eq.(2) were obtained, and the curve of the temperature dependence of the oxygen potential had a flexion point as shown in Fig 3.

In the reducing region, the relationship of n changed from -4 to -3 with Pu content. The n=-3 was observed in $(U_{0.7}Pu_{0.3})O_{2-x}$. In this region, the defect reaction of (43) was assumed for describing the Kröger – Vink diagram. The defect concentration was given by eq.(44) and the relationship of n=-3 was obtained.

$$2O^{\times}{}_{O} + 2M^{\times}{}_{Pu} \rightarrow \left(2V_{O}^{\bullet\bullet} 2M'_{Pu}\right)^{\bullet} + 2e' + \frac{1}{2}O_2 \tag{43}$$
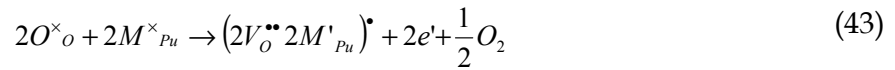
$$\left[V_{O}^{\bullet\bullet}\right] = 2\left[\left(2V_{O}^{\bullet\bullet} 2Pu'\right)^{\bullet\bullet}\right] = (2K_{Re})^{1/3} P_{o_2}^{-1/3} \tag{44}$$

Defect reaction	Material	Transformation energy of defect (eV)	References
$Nill \rightarrow e' + h^{\bullet}$	MOX	3.0	This work
	UO$_2$	2.1	Nakamura & Fujino, 1986
	PuO$_2$	2.5	Stan & Cristea, 2005
$O_{O}^{\times} \rightarrow V_{O}^{\bullet\bullet} + O_i''$	MOX	2.3	This work
	UO$_2$	5.3	Nakamura & Fujino, 1986
$O_{O}^{\times} \rightarrow V_{O}^{\bullet\bullet} + 2e' + \frac{1}{2}O_2$	MOX	6.8	This work
	PuO$_2$	4.8	Stan & Cristea, 2005
$\frac{1}{2}O_2 \rightarrow O_i'' + 2h^{\bullet}$	MOX	-0.05	This work
	UO$_2$	-0.2	Nakamura & Fujino, 1986
$O_{O}^{\times} + Pu^{\times} \rightarrow \left(V_{O}^{\bullet\bullet} Pu'\right)^{\bullet} + Pu' + \frac{1}{2}O_2$	MOX	5.3	This work
$2O_{O}^{\times} + O_2 \rightarrow \left(2O_i^a 2O_i^b 2V_{O}^{\bullet\bullet}\right)' + U^{\bullet}$	MOX	-3.0	This work
	UO$_2$	-2.6	Nakamura & Fujino, 1986

Table 3. Comparison of transformation energy of defects

6. Application to O/M control

The O/M ratio is one of the most important parameters in controlling a reactor using (U,Pu)O$_2$ nuclear fuels. The fuels are used in the hypo-stoichiometric composition range to control the fuel and cladding chemical interaction. The O/M ratio is adjusted in a sintering process which is carried out in an Ar/H$_2$ gas mixture atmosphere. In this atmosphere, the oxygen potential is determined by eqs. (1), (5) and (6). According to the equations, the oxygen partial pressure is determined by controlling the P_{H_2} / P_{H_2O} ratio and temperature.

The O/M ratios of (U,Pu)O$_2$ are represented by the derived eqs.(36), (38) and (39) and are shown in Fig.7 as functions of P_{H_2} / P_{H_2O} and temperatures. In the low temperature region of less than 1000 K, the O/M ratio is almost 2.0, despite P_{H_2} / P_{H_2O} ratio in the atmosphere. In this temperature range, it is almost impossible to adjust to a hypo-stoichiometric composition in the H$_2$/H$_2$O gas atmosphere. In the higher temperature range, the O/M ratio decreases with increasing P_{H_2} / P_{H_2O} ratio. The O/M ratio approaches 1.65 and remains at almost 2.00 at 1973 K in the atmosphere of $P_{H_2} / P_{H_2O} = 200$ and $P_{H_2} / P_{H_2O} = 2$, respectively. The (U,Pu)O$_2$ fuels with various O/M ratios may be produced using the relationships of Fig.7.

However, the O/M ratio increases during the cooling process after the sintering. So, control of cooling rate may be needed to obtain low O/M fuel. Furthermore, the kinetics evaluation of O/M change is essential to get adjustment to an accurate O/M ratio.
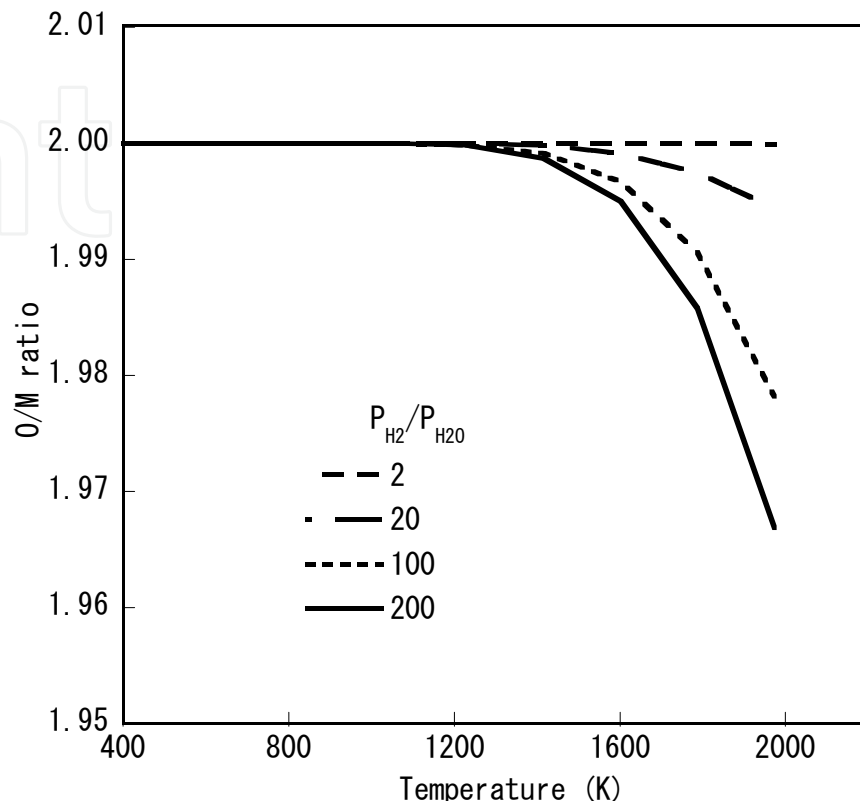

Fig. 7. O/M variation of $(U_{0.8}Pu_{0.2})O_{2\pm x}$ as a function of P_{H_2}/P_{H_2O}

7. Summary

In (U,Pu)O₂ the oxygen nonstoichiometry significantly affects various physical properties, so it is essential to know the oxygen potential as functions of O/M ratio and temperatures for development of nuclear fuels. Many studies on oxygen potential have been carried out. However, the data are scattered because of the difficulty of measurement.

Recently, data were accurately measured by the gas equilibrium method using thermogravimetry. The data were analysed based on defect chemistry. The O/M ratio varies continuously with changing oxygen potential for the near stoichiometric composition, so it is very difficult to determine the stoichiometric composition in experiments. The stoichiometric composition was determined by analysis of statistical thermodynamics of point defects. The analysis results predicted the band gap energy of 2.9 eV. Additionally, the data were analyzed by a Kröger - Vink diagram. The defect reactions were assumed from experimental data, concentrations of defects were evaluated as functions of temperature and oxygen partial pressure, and the equation for the O/M ratio was derived. The derived equation can represent the O/M ratio as functions of temperature and P_{H_2}/P_{H_2O} and can be applied for the sintering process to adjust the O/M ratio.

In the development of nuclear fuels, it is also important to understand the oxygen potential dependence on Pu, Am and Np contents. Pu content is known to increase the oxygen potential. Several groups have investigated the effect of Am and Np addition in $(U,Pu)O_2$ (Kato et al., 2009;Nakamichi et al., 2011). They found that the addition of Am caused the oxygen potential to increase, but Np addition did not affect the oxygen potential. The derived equation for O/M ratio will be extended to represent the O/M ratio dependence on Pu and Am contents in future fuels.

8. Acknowledgement

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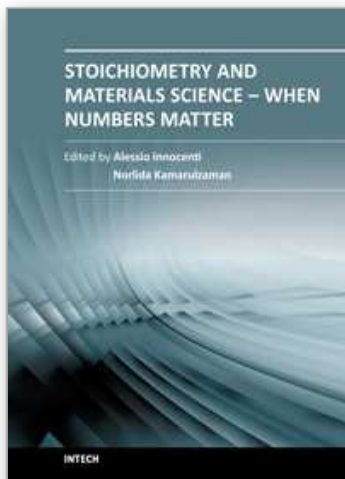
Stoichiometry and Materials Science - When Numbers Matter

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The aim of this book is to provide an overview on the importance of stoichiometry in the materials science field. It presents a collection of selected research articles and reviews providing up-to-date information related to stoichiometry at various levels. Being materials science an interdisciplinary area, the book has been divided in multiple sections, each for a specific field of applications. The first two sections introduce the role of stoichiometry in nanotechnology and defect chemistry, providing examples of state-of-the-art technologies. Section three and four are focused on intermetallic compounds and metal oxides. Section five describes the importance of stoichiometry in electrochemical applications. In section six new strategies for solid phase synthesis are reported, while a cross sectional approach to the influence of stoichiometry in energy production is the topic of the last section. Though specifically addressed to readers with a background in physical science, I believe this book will be of interest to researchers working in materials science, engineering and technology.

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