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Oxygen chemical diffusion in hypo-stoichiometric MOX

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ABSTRACT

Kinetics of the oxygen-to-metal ratio change in $(U_{0.8}Pu_{0.2})O_{2-x}$ and $(U_{0.7}Pu_{0.3})O_{2-x}$ was evaluated in the temperature range of 1523–1623 K using a thermo-gravimetric technique. The oxygen chemical diffusion coefficients were decided as a function of temperature from the kinetics of the reduction process under a hypo-stoichiometric composition. The diffusion coefficient of $(U_{0.7}Pu_{0.3})O_{2-x}$ was smaller than that of $(U_{0.8}Pu_{0.2})O_{2-x}$. No strong dependence was observed for the diffusion coefficient on the O/M variation of samples.

1. Introduction

Plutonium and uranium mixed oxide (MOX) has been developed for use as fuel for fast reactors. It is well-known that MOX having a fluorite structure is an oxygen non-stoichiometric compound which is stable in regions of both hyper- and hypo-stoichiometric compositions [1,2]. The oxygen-to-metal (O/M) ratio of MOX fuel is an important parameter to control its irradiation behavior (e.g. fuel and cladding chemical interaction) as well as sintering behavior in the fabrication process of fuel pellets.

In general, O/M ratios of pellets are controlled during sintering. To adjust the O/M ratio with precision, it is essential to know the oxygen potentials ($\Delta\overline{G}_{O_2}$) and oxygen chemical diffusion coefficients in MOX. Oxygen potentials of MOX depend strongly on O/M ratio and many studies [3–7] on their oxygen potentials have been reported. The authors [8,9] have also measured them with good accuracy as a function of O/M ratio and temperature. In addition to sintering behaviors, oxygen potential is an important parameter controlling the chemical reactions in operating fuel pins. Oxygen diffusion coefficient of MOX is another essential parameter to understand dynamical behavior of oxygen in fuel pellets.

The O/M ratio of MOX pellets is adjusted by reduction during sintering which is carried out in a mixed atmosphere of hydrogen and inert gas; their ratio affects sintering behavior [10–12]. Therefore, the kinetics of the reduction process is important to adjust the O/M ratio and the microstructure of the MOX pellets, and hence the kinetics of O/M change in the MOX has been reported [13–17]. Additionally, the oxygen chemical diffusion coefficients were obtained from the O/M data on the oxidation process of the $(U_{0.8}Pu_{0.2})O_{2-x}$. In this work, the kinetics of the O/M ratio change in $(U_{0.8}Pu_{0.2})O_{2-x}$ and $(U_{0.7}Pu_{0.3})O_{2-x}$ was investigated for the redox process using a thermo-gravimetric technique.

2. Experimental

2.1. Sample preparation

Two batch of MOX powders with 20%Pu and 30%Pu contents, respectively, were prepared by a direct microwave heating denitration process. Each batch of powder was pressed and sintered at 1873 K for 3 h in an atmosphere of Ar/5% H_2 mixed gas with added moisture. This resulted in needle-like samples which were about 1.4 mm in diameter and 5.7–7.2 mm in length, weighed about 120 mg each and had 87.8–92.9% TD.

2.2. Apparatus and experimental technique

Measurements of changing rate of O/M ratio were carried out by a thermo-gravimetric technique at temperatures of 1523, 1573 and 1623 K. The thermo-gravimetry (TG) which utilizes a horizontal differential type balance is able to measure the weight change of ±1 μg which corresponds to the O/M change of ±0.0002. Details of the apparatus were reported previously [8,9]. The oxygen partial pressure in the atmosphere was changed rapidly by changing the ratio of hydrogen partial pressure to moisture partial pressure (P_{H_2}/P_{H_2O}) and the change of sample weight was measured as a function of time.

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3. Results and discussion

Fig. 1(a) and (b) shows the measurement results of reduction process and oxidation process in the range of hypo-stoichiometric composition. As shown in Fig. 1(a), O/M ratios in the reduction process attains equilibrium with the atmosphere after about 0.4 h and 0.5 h in $(U_{0.8}Pu_{0.2})O_{2-x}$ and $(U_{0.7}Pu_{0.3})O_{2-x}$, respectively. And the time to reach equilibrium is almost the same regardless of the initial O/M ratio in each sample. On the other hand, the O/M ratio in the oxidation process varies linearly with time, and the slope is the same regardless of Pu content and initial O/M ratio. These measurement results show that the mechanisms of the O/M ratio changes in the reduction and the oxidation process are distinctly different.

The average concentration $\bar{c}$ of an infinite cylindrical sample of radius r_0 is given by Eq. (1) when the change is dominated by chemical diffusion [18]:

$$F = \frac{\bar{c} - c_f}{c_i - c_f} = \sum_{\nu=1}^{\infty} \frac{4}{\xi_\nu^2} \exp\left(-\frac{\xi_\nu^2 \tilde{D} t}{r_0^2}\right). \tag{1}$$

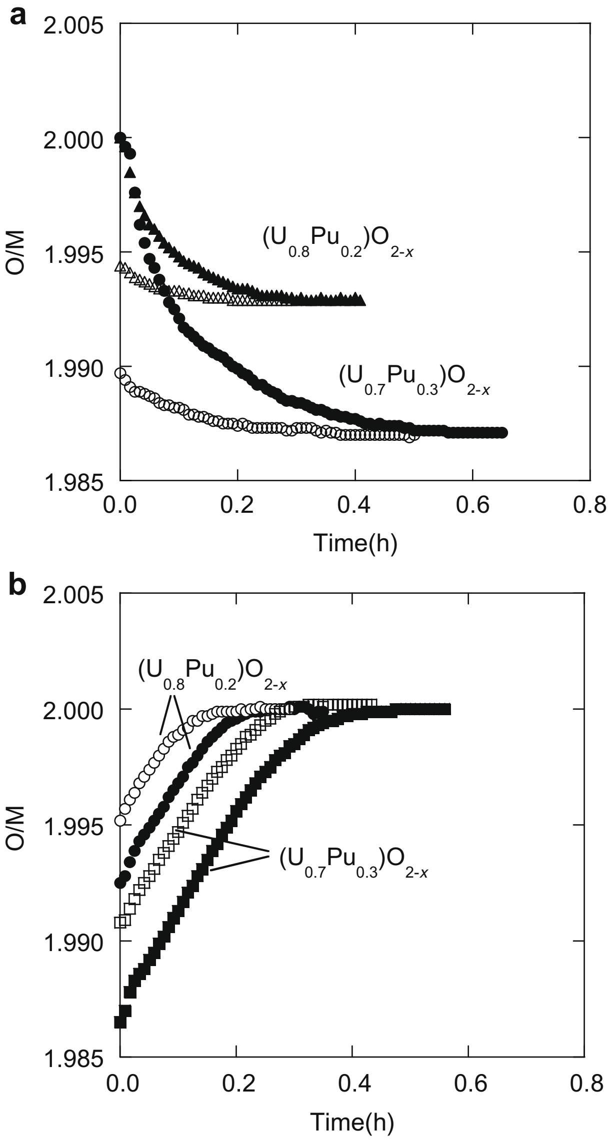

Fig. 1. Kinetics of the (a) reduction process and (b) oxidation process in $(Pu_{0.2}U_{0.8})O_{2-x}$ and $(Pu_{0.3}U_{0.7})O_{2-x}$ at 1573 K as a function of time.

Here c_i, c_f, t and ξ_ν are the initial concentration, the final concentration, time and the roots of the equation $J_0(x) = 0$, respectively, where $J_0(x)$ is the Bessel function of zero order. The measurement data shown in Fig. 1 were analyzed using Eq. (1), since the infinite cylinder is a good approximation for the present needle-like samples. As seen in Fig. 2, it is clear that Eq. (1) represents the curves of the reduction process very well. The variation of the final value is the same for the same time regardless of the initial O/M ratio in each sample of $(U_{0.8}Pu_{0.2})O_{2-x}$ and $(U_{0.7}Pu_{0.3})O_{2-x}$. This result shows that the oxygen chemical diffusion coefficient has little relevance to O/M variation. The oxygen chemical diffusion coefficients $\tilde{D}$ of hypo-stoichiometric MOX with 20%Pu and 30%Pu are estimated to be 3.2×10^{-6} and $1.6 \times 10^{-6}\ \mathrm{cm^2\ s^{-1}}$, respectively, from the results of reduction curves at 1573 K. The oxygen chemical diffusion coefficient in $(U_{0.8}Pu_{0.2})O_{2-x}$ is larger than that in $(U_{0.7}Pu_{0.3})O_{2-x}$. On the other hand, the measurement results in oxidation process cannot be reproduced by Eq. (1). The oxidation process might be dominated by reaction of zero order such as a reaction on the surface, because the oxidation varies linearly at a constant rate with time.

The oxygen chemical diffusion coefficients obtained are listed in Table 1. The oxygen chemical diffusion coefficients of $(U_{0.8}Pu_{0.2})O_{2-x}$ and $(U_{0.7}Pu_{0.3})O_{2-x}$ are expressed by Eqs. (2) and (3) and plotted in Fig. 3 as a function of reciprocal temperature:

$$\ln \tilde{D} = \left(-\frac{60 \times 10^3}{RT}\right) + \ln(3.03 \times 10^{-4}) \quad \text{for} \quad (U_{0.8}Pu_{0.2})O_{2-x}, \tag{2}$$

$$\ln \tilde{D} = \left(-\frac{88 \times 10^3}{RT}\right) + \ln(1.57 \times 10^{-3}) \quad \text{for} \quad (U_{0.7}Pu_{0.3})O_{2-x}. \tag{3}$$

Eqs. (2) and (3) give activation energies of $(U_{0.8}Pu_{0.2})O_{2-x}$ and $(U_{0.7}Pu_{0.3})O_{2-x}$ as 60 and 88 kJ mol^{-1}, respectively. Data from other works [13–15,19] are also plotted in Fig. 3 and they are larger than the presently obtained coefficients. In the previous reports, the oxygen chemical diffusion coefficients were determined from kinetics of the oxidation process observed by placing samples in an atmosphere of CO_2/CO heated to the test temperatures. Such experimental conditions are difficult to control and that may affect the experimental results. Additionally, the oxidation process does not follow the model of oxygen chemical diffusion as described above. It might be said that the present data are more reliable compared to the other published data. In this paper, the effects of grain

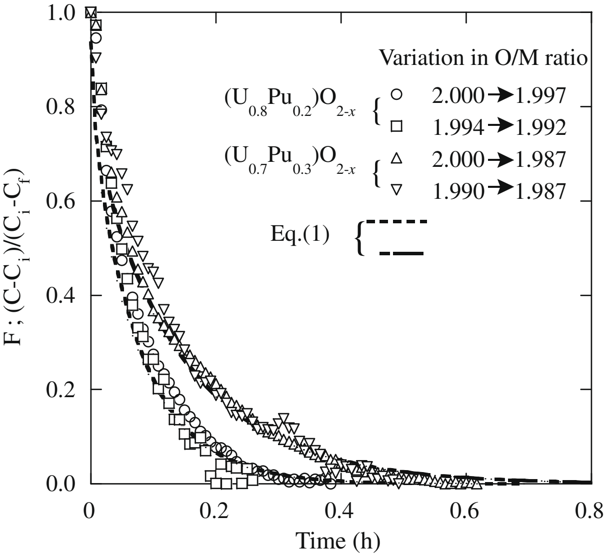

Fig. 2. Changing rate of O/M ratio, F, analyzed by Eq. (1) as a function of time.

Table 1
Oxygen chemical diffusion coefficients in (U,Pu)O_{2-x}.

Pu content (%)	Temperature (K)	O/M		$\tilde{D}$ (cm^2 s^{-1})
		Initial	Final	
20%Pu	1523	2.000	1.994	2.9×10^{-6}
	1573	2.000	1.992	2.9×10^{-6}
	1573	1.994	1.992	3.2×10^{-6}
	1573	1.996	1.993	2.9×10^{-6}
	1573	2.000	1.992	3.3×10^{-6}
	1573	2.000	1.997	3.2×10^{-6}
	1573	2.000	1.994	3.3×10^{-6}
	1573	2.000	1.992	3.0×10^{-6}
	1623	2.000	1.990	3.2×10^{-6}
	1623	1.999	1.990	3.8×10^{-6}
	1623	1.999	1.998	2.6×10^{-6}
	1623	2.000	1.999	3.4×10^{-6}
	1623	1.998	1.997	2.6×10^{-6}
	1623	1.999	1.995	3.6×10^{-6}
30%Pu	1523	2.000	1.992	1.4×10^{-6}
	1523	2.000	1.992	1.5×10^{-6}
	1573	2.000	1.985	1.2×10^{-6}
	1573	2.000	1.987	1.6×10^{-6}
	1573	2.000	1.991	1.8×10^{-6}
	1573	2.000	1.989	1.8×10^{-6}
	1573	1.990	1.987	1.6×10^{-6}
	1623	2.000	1.979	2.5×10^{-6}
	1623	2.000	1.988	2.0×10^{-6}
	1623	1.988	1.984	2.2×10^{-6}

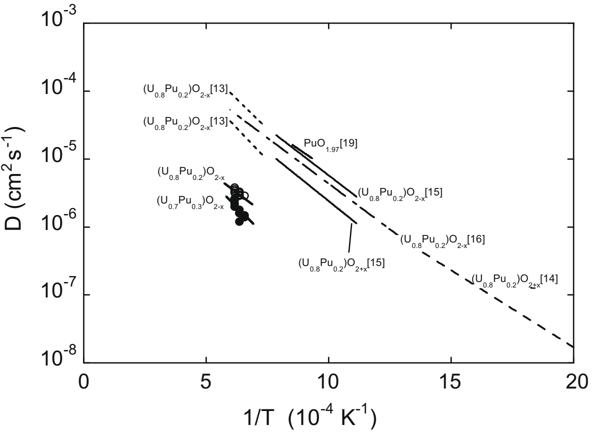

Fig. 3. Comparison of literature oxygen chemical diffusion coefficients and coefficients obtained in this work as plotted in an Arrhenius diagram: ○, $(U_{0.8}Pu_{0.2})O_{2-x}$ and ●, $(U_{0.7}Pu_{0.3})O_{2-x}$.

size and sample density on the oxygen chemical diffusion were not considered. To improve understanding of the kinetics of oxygen in MOX, these effects need to be further explored.

It is well-known that the diffusion coefficient is closely related to the type of the lattice defect [20]. In previous works [8,9,21–22], the lattice defects of hypo-stoichiometric MOX were reported to change its type with variation of O/M ratio and Pu content. The authors [23] evaluated the defect types of $(U_{0.8}Pu_{0.2})O_{2-x}$ and $(U_{0.7}Pu_{0.3})O_{2-x}$ from the measured data of oxygen potentials based on lattice defect chemistry, and reported $x \propto P_{O_2}^{-1/4}$ and $x \propto P_{O_2}^{-1/3}$ in $(U_{0.8}Pu_{0.2})O_{2-x}$ and $(U_{0.7}Pu_{0.3})O_{2-x}$, respectively. The difference in the diffusion coefficients might be explained by the difference in the lattice defect types for $(U_{0.8}Pu_{0.2})O_{2-x}$ and $(U_{0.7}Pu_{0.3})O_{2-x}$.

In the case of MO_{2-x}, the chemical diffusion coefficient $\tilde{D}$ can be expressed in terms of defect diffusion coefficients of anions D^* as follows:

$$\tilde{D} = \frac{1}{2}\frac{C_M}{C_O}\frac{\partial \log P_{O2}}{\partial \log x}D^* = \frac{1}{4}\frac{\partial \log P_{O_2}}{\partial \log x}D^*, \tag{4}$$

where C_M and C_O are the concentrations of metal and oxygen, respectively. The D^* in (U,Pu)O_{2-x} were estimated from $\tilde{D}$ obtained in this work assuming $\frac{\partial \log P_{O_2}}{\partial \log x} = 4$ and 3, respectively, for $(U_{0.8}Pu_{0.2})O_{2-x}$ and $(U_{0.7}Pu_{0.3})O_{2-x}$ which were reported previously [24]. These data are plotted in Fig. 4 together with those of UO_{2-x} and PuO_{2-x} reported before [24–26]. Matsui and Naito [27] reported D^* values in (Th,U)O_{2+x} solid solution and they increased with an increase of U content. The D^* values in (U,Pu)O_{2-x}, which were obtained from the measured $\tilde{D}$, also vary linearly with increasing Pu content and are consistent with other data.

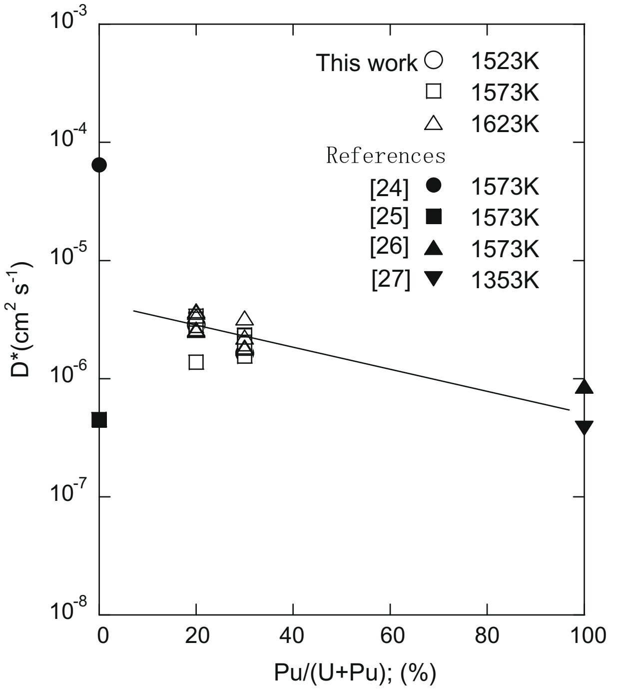

Fig. 4. Variation of the defect diffusion coefficient with Pu content.

4. Conclusion

The kinetics of the reduction process of $(U_{0.8}Pu_{0.2})O_{2-x}$ and $(U_{0.7}Pu_{0.3})O_{2-x}$ was measured by thermo-gravimetry. The oxygen chemical diffusion coefficients $\tilde{D}$ were estimated from the reduction curves. It was concluded that the oxygen chemical diffusion coefficient in $(U_{0.7}Pu_{0.3})O_{2-x}$ was smaller than that of $(U_{0.8}Pu_{0.2})O_{2-x}$. The diffusion coefficient did not depend strongly on the O/M variation of samples. Furthermore the defect diffusion coefficient D^* of $(U_{1-y}Pu_y)O_{2-x}$ was estimated from the oxygen chemical diffusion coefficients measured in this work. The D^* values decreased slightly with increasing Pu content.

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