

Oxygen potential and thermal conductivity of (U,Pu) mixed oxides

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Abstract

(U,Pu) mixed oxides, $(U_{1-y}Pu_y)O_{2-x}$, with $y = 0.21$ and 0.28 are being considered as fuels for the Prototype Fast Breeder Reactor (PFBR) in India. The use of urania–plutonia solid solutions in PFBR calls for accurate measurement of physicochemical properties of these materials. Hence, in the present study, oxygen potentials of $(U_{1-y}Pu_y)O_{2-x}$, with $y = 0.21$ and 0.28 were measured over the temperature range 1073–1473 K covering an oxygen potential range of -550 to -300 kJ mol⁻¹ (O/M ratio from 1.96 to 2.000) by employing a H₂/H₂O gas equilibration technique followed by solid electrolyte EMF measurement. $(U_{1-y}Pu_y)O_{2-x}$, with $y = 0.40$ is being used in the Fast Breeder Test Reactor (FBTR) in India to test the behaviour of fuels with high plutonium content. However, data on the oxygen potential as well as thermal conductivity of the mixed oxides with high plutonium content are scanty. Hence, the thermal diffusivity of $(U_{1-y}Pu_y)O_2$, with $y = 0.21, 0.28$ and 0.40 was measured and the results of the measurements are reported.

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1. Introduction

(U,Pu) mixed oxides, $(U_{1-y}Pu_y)O_{2-x}$, with $y = 0.21$ and 0.28 are being considered as fuels for the Prototype Fast Breeder Reactor (PFBR). The use of urania–plutonia solid solutions in PFBR calls for the measurement of physicochemical properties of these materials. The behaviour of nuclear fuel materials during irradiation is highly dependent on their physicochemical properties and their variation

with temperature. The intrinsic thermal conductivity of the fuel is affected by the change in the oxygen-to-metal (O/M) ratio of the fuel. The oxygen potential of an oxide fuel material is an important thermochemical property that significantly influences the extent of fuel-clad chemical interaction. It is also a measure of the driving force for the numerous reactions that take place in the fuel during irradiation. It controls (i) the chemical state of fission products and their interaction with the fuel and (ii) the vapour pressure of the mixed oxide inside the fuel pin. In addition, data on the oxygen potential are required for the preparation of fuel with pre-specified O/M ratios and for the interpretation of defect structures. Several investigators have determined the oxygen potentials of (U,Pu) mixed oxides

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[1–12]. The temperature range and compositions over which the oxygen potential had been measured by these investigators are given in Table 1. These measurements were based on thermogravimetric, transpiration or galvanic cell measurements. From Table 1 it is seen that data on the oxygen potentials of mixed oxides with PFBR fuel compositions over the temperature range 1073–1473 K are not available in the literature. Hence, in the present study oxygen potentials of $(U_{1-y}Pu_y)O_{2-x}$, with $y = 0.21$ and 0.28 were measured over the temperature range 1073–1473 K by employing a gas equilibration-EMF measurement technique. $(U_{1-y}Pu_y)O_{2-x}$, with $y = 0.40$ is being used in the Fast Breeder Test Reactor (FBTR) in India to test the behaviour of fuels with high plutonium content. It is in this context that the measurement of the thermal diffusivity of the mixed oxides ($y = 0.21, 0.28$ and 0.40) was taken up in our laboratory.

2. Experimental

2.1. Experimental assembly for oxygen potential measurements

The experimental assembly employed in the present study for oxygen potential measurements of (U,Pu) mixed oxides is similar to the one employed in the measurements of (U,Th) mixed oxides in our laboratory [13]. A schematic diagram of this setup is shown in Fig. 1. Essentially, it consists of a gas mixing setup, an equilibration chamber and an oxygen probe. Gas mixtures with appropriate oxygen partial pressures were obtained by mixing moisture, hydrogen and argon gases in the gas mixing part of the setup. The various H_2O/H_2 ratios were obtained either by passing hydrogen/argon-hydrogen mixtures through a refrigerated water column maintained at a constant temperature using a proportional integral derivative (PID) temperature controller, or by passing the gas through a column containing a mixture of oxalic acid dihydrate and anhydrous oxalic acid. The temperature of the refrigeration unit was maintained within ± 1 K. The flow rates of the gases were adjusted using mass flow controllers (supplied by M/s Unit Instruments Inc., USA).

The equilibration chamber was placed in a resistance wire-wound, horizontal tubular furnace. The temperature of the furnace was controlled within ± 2 K using a PID temperature controller. A recrystallised alumina tube was used as the work-tube.

Table 1
Oxygen potential of $(U_{1-y}Pu_y)O_{2-x}$ reported in the literature

Value of y in $(U_{1-y}Pu_y)O_{2-x}$	O/M ratio ($2-x$)	Temperature range (K)	Technique	References
0.11 and 0.30	1.87–2.08	1023–1373	Thermogravimetry and EMF	Markin and Melver [1]
0.1 and 0.4	1.9–2.0	1173–1373	Thermogravimetry and EMF	Woodley [2,3]
0.25	1.94–2.028	1073–1273	Thermogravimetry and EMF	Woodley and Adamson [4,5]
0.15 and 0.31	Hyperstoichiometry	1518, 1623 and 1823	Transpiration	Chilton and Kirkham [6]
0.1 and 0.2	1.99–1.999	1273–1723	Thermogravimetry	Sorensen [7]
0.2	1.92–1.98	2150–2550	Transpiration	Tetenbaum [8]
0.2	1.92–1.98	1273–1973	Gas equilibration and chemical analysis	Javed [9,10]
0.23 and 0.15	1.9984–2.00	1523–1823	Thermogravimetry	Edwards, Wood and Chilton [11]
0.23	1.995–2.02	1523–1823	Thermogravimetry	Chilton and Edwards [12]
0.31	1.995–2.05	1815	Thermogravimetry	Chilton and Edwards [12]
0.21 and 0.28	1.97–2.000	1073–1473	EMF measurement	Present study

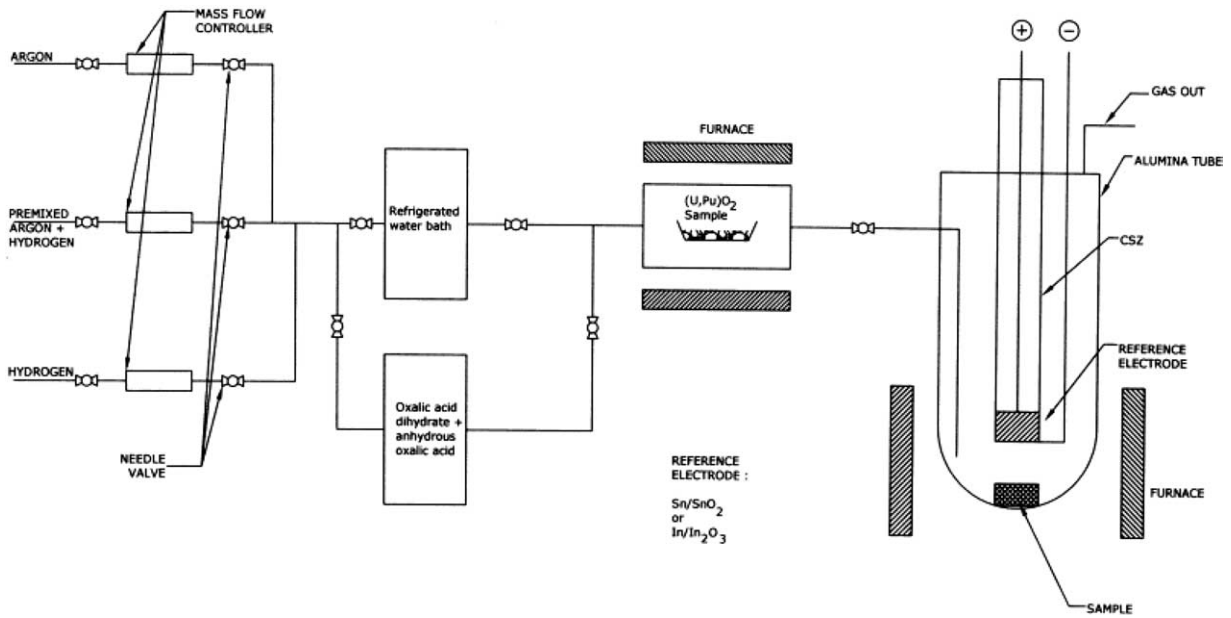


Fig. 1. Schematic diagram of the experimental assembly.

The sample was contained in a recrystallised alumina boat and placed in the uniform zone of the furnace. The gaseous mixture of known H_2O/H_2 ratio was passed over the mixed oxide samples for equilibration.

The oxygen potential of the gas mixture exiting the equilibration chamber was determined using an oxygen probe. The solid electrolyte employed in the probe was calcia stabilized zirconia (CSZ) having a composition of ZrO_2 -11 mol% CaO. The CSZ tube had the dimensions of 13 mm OD, 9 mm ID and 250 mm long. About 40 mm height of the outer end of the thimble was coated with platinum paste and fired at 1073 K for 1 h in air to obtain a porous platinum film. The continuity of the platinum coating on the surface was checked by resistance measurements. The reference electrode In/In_2O_3 mixture was prepared by mixing In and In_2O_3 in the weight ratio of 6:1. This mixture was loaded into the CSZ tube up to 40 mm length. After sealing the reference electrode inside the CSZ tube under high-pure argon cover, the electrode was equilibrated at 723 K for 1 h. A tungsten wire was used as the inner lead. An alumina insulator was inserted over the tungsten lead. The inner chamber was sealed using Torrseal. A Pt–Rh thermocouple was used for the temperature measurements. The oxygen probe was housed inside an alumina tube. The EMF across the solid electrolyte

was measured by a high impedance millivoltmeter connecting the two electrodes. The probe was housed in a separate furnace held at the optimum temperature, namely 773 K.

2.2. Method of measurement

In a typical equilibration experiment, the gas mixture having a known oxygen potential was passed over the mixed oxide sample. The attainment of equilibrium and the actual oxygen potential realized in the gas mixture were determined using the oxygen probe. The O/M values of the equilibrated samples were calculated from the weight change with respect to the reference-state using the following expression:

$$O/M = 2 \pm x = 2 \pm \{[M]/16\} \times \{\Delta W/W\} \quad (1)$$

where W is the sample weight at $O/M = 2.000$, ΔW is the weight change relative to the stoichiometric sample weight and $[M]$ the molecular weight of $(U_{1-y},Pu_y)O_{2.000}$.

2.3. Errors in measurement

In this study, the uncertainty in the temperature measurement is ± 2 K for each individual data point. The maximum error in the measurement of EMF is $\pm 1\%$. This estimate is based on the repeated

measurements using standard gas mixtures. At temperatures 1073–1473 K, these uncertainties would lead to an overall error of $\pm 2 \text{ kJ mol}^{-1}$. Considering the accuracy of the balance ($\approx 10 \mu\text{g}$) and the precision of weight measurements, the cumulative error of the weight measurements is $\pm \approx 100 \mu\text{g}$. This is equivalent to a maximum error of ± 0.001 in O/M.

2.4. Thermal diffusivity measurements

Three mixed oxides, namely, $(\text{U}_{0.79}\text{Pu}_{0.21})\text{O}_{2-x}$, $(\text{U}_{0.72}\text{Pu}_{0.28})\text{O}_{2-x}$ and $(\text{U}_{0.6}\text{Pu}_{0.4})\text{O}_{2-x}$, were prepared by the sol-gel route (at Radiometallurgy Division, Bhabha Atomic Research Centre, India), followed by compaction of the microspheres into pellets and sintering them at 1873 K under flowing argon-hydrogen gas mixture. The thermal diffusivity of these fuel materials was measured by the laser flash technique. Details of the method of measurement are given in Ref. [14]. The sample holder, furnace and detector assembly were enclosed in a glove box filled with high purity argon. The furnace, housed inside the glove box, was controlled by a proportional-integral-derivative temperature controller. A platinum-30%rhodium/platinum-6% rhodium thermocouple was used for monitoring and controlling the temperature of the furnace. The specimens were pellets of 1.1–1.3 mm thickness and 10–12 mm diameter. The sample was loaded in the sample holder and placed in the uniform temperature zone of the furnace. High purity argon gas was passed over the sample throughout the course of measurements. The argon gas was purified by passing it through a purification system containing a zirconium sponge at 973 K. The laser flash experiments were conducted after ensuring that the sample attained the given set temperature. The thermal diffusivity of the mixed oxides was measured over the temperature 923–1773 K.

3. Results and discussion

3.1. Oxygen potential

Figs. 2 and 3 show the oxygen potentials of $(\text{U}_{0.79}\text{Pu}_{0.21})\text{O}_{2-x}$ and $(\text{U}_{0.71}\text{Pu}_{0.28})\text{O}_{2-x}$ respectively, measured in this study. In general, the oxygen potential increases with increase in temperature at a given O/M and plutonia content of the mixed oxide. Similarly, the oxygen potential increases with increase in plutonia content of the mixed oxide at a given temperature and O/M. Very low oxygen poten-

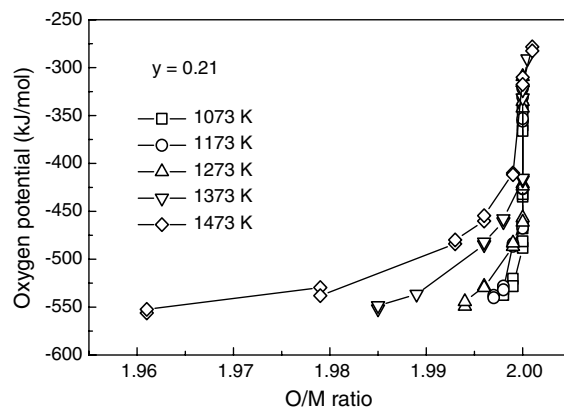


Fig. 2. Oxygen potential of $(\text{U}_{0.79}\text{Pu}_{0.21})\text{O}_{2-x}$.

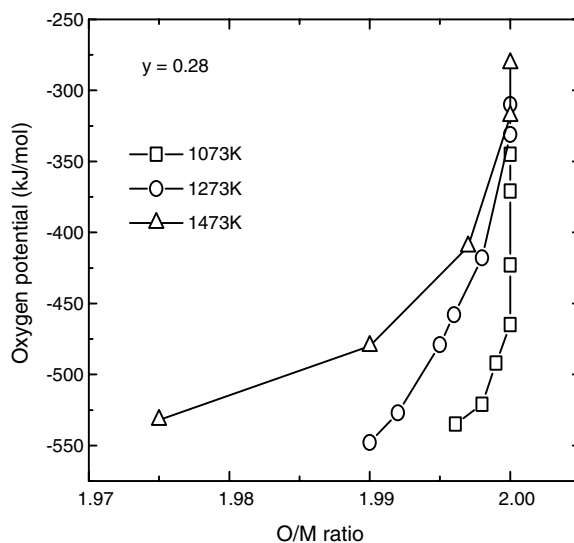


Fig. 3. Oxygen potential of $(\text{U}_{0.72}\text{Pu}_{0.28})\text{O}_{2-x}$.

tials are required to reduce O/M of a given sample at lower temperatures. Sorensen [7] measured the oxygen potential of $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_{2\pm x}$ over the temperature range 1273–1723 K. He had reported that his results were in good agreement with the results reported by Woodley [2–4] and Markin and McIver [1]. Fig. 4 compares the results obtained in this study with those reported by Woodley [2–4] for $(\text{U}_{0.75}\text{Pu}_{0.25})\text{O}_{2\pm x}$ at temperatures between 1173 and 1373 K. Fig. 5 compares the oxygen potentials of mixed oxides at 1273 K with various plutonia content. Comparing the oxygen potential of $(\text{U}_{0.79}\text{Pu}_{0.21})\text{O}_{2-x}$ (present study) with $(\text{U}_{0.75}\text{Pu}_{0.25})\text{O}_{2-x}$ (Woodley [4]) and $(\text{U}_{0.72}\text{Pu}_{0.28})\text{O}_{2-x}$ (present study) with $(\text{U}_{0.6}\text{Pu}_{0.4})\text{O}_{2-x}$ (Woodley [3]), it is observed that the values of oxygen potential measured in the

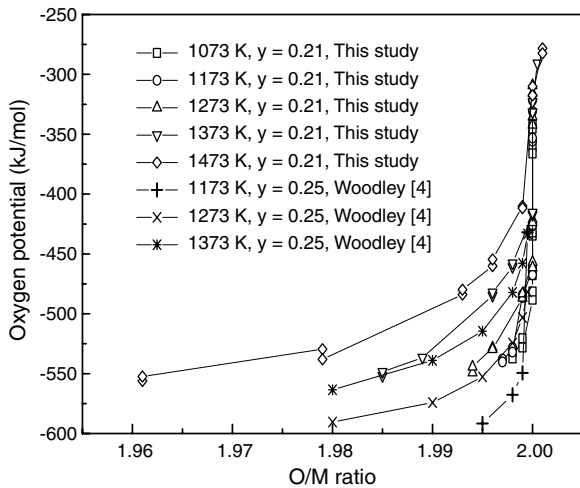


Fig. 4. Comparison of measured oxygen potentials with literature values.

present study are more positive (Fig. 5) than the values reported by Woodley [3,4] at O/M values close to 2.000. The reason is the insufficient accuracy of the O/M ratio measurement. However, in the present study, relatively more experimental measurements were carried out at O/M values closer to 2.000 as compared to the number of measurements by Woodley [2–4]. The present results are in reasonably good agreement (within the experimental uncertainties) with the results reported by Woodley [2–4] at lower O/M values (≤ 1.98). Most of the other results reported in the literature could not be compared with the results reported in this study because of the difference in temperature of measurement and the difference in composition and O/M of the mixed oxide samples.

3.2. Thermal conductivity

The method of thermal diffusivity measurement by laser flash technique, employed in the present study, was validated by measuring the thermal diffusivity of stainless steel (SS 304) standards. The measured values were found to be in good agreement with the values reported in the literature [14]. Results of the thermal diffusivity measurements on $(U_{1-y}Pu_y)O_2$ with $y = 0.21$ (Fuel A, O/M = 2.0, density: 1062 kg m^{-3}), 0.28 (Fuel B, O/M = 2.0, density: 1064 kg m^{-3}) and 0.40 (Fuel C, O/M = 2.0, density: 1077 kg m^{-3}) with are given in Table 2. Thermal conductivity values for these oxide fuels were obtained as a product of thermal diffusivity, heat capacity and density. Heat capacity values required for the computation of thermal conductivity were obtained from the measurements carried out in our laboratory [15]. The density of all the

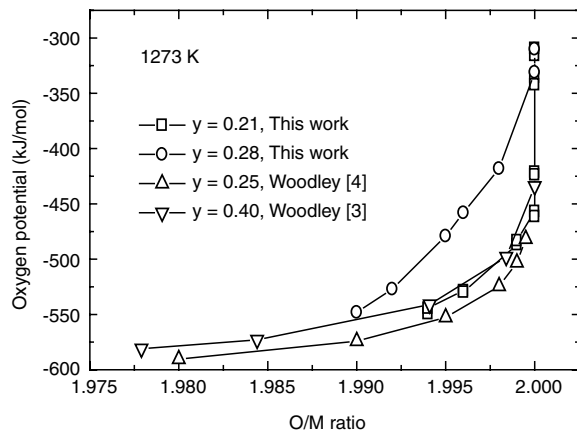


Fig. 5. Comparison of the oxygen potentials of mixed oxides at 1273 K with various plutonia content.

Table 2

Thermal diffusivity and thermal conductivity values obtained for the oxide fuels (Fuel A: $(U_{0.79}Pu_{0.21})O_2$, Fuel B: $(U_{0.72}Pu_{0.28})O_2$, Fuel C: $(U_{0.60}Pu_{0.40})O_2$)

Temperature (K) <i>T</i>	Thermal diffusivity ($10^{-6} \text{ m}^2 \text{ s}^{-1}$)			Heat capacity ($\text{J K}^{-1} \text{ kg}^{-1}$)			Thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)		
	Fuel A	Fuel B	Fuel C	Fuel A	Fuel B	Fuel C	Fuel A	Fuel B	Fuel C
673	1.739	–	1.060	300.9	303.6	306.1	5.57	–	3.47
773	1.610	1.160	0.878	307.3	310.7	313.6	5.26	3.84	2.94
873	1.490	1.117	0.748	312.7	316.9	320.0	4.95	3.77	2.56
973	1.370	1.001	0.693	317.3	322.5	325.8	4.61	3.44	2.41
1073	1.200	0.940	0.662	321.4	327.7	331.2	4.09	3.28	2.34
1173	1.120	0.954	0.656	325.3	332.6	336.4	3.86	3.38	2.36
1273	1.010	0.865	0.601	329.0	337.4	341.3	3.52	3.11	2.19
1373	–	0.844	0.606	332.5	342.0	346.2	–	3.07	2.24
1473	0.848	0.791	0.599	336.1	346.5	350.9	3.02	2.92	2.24

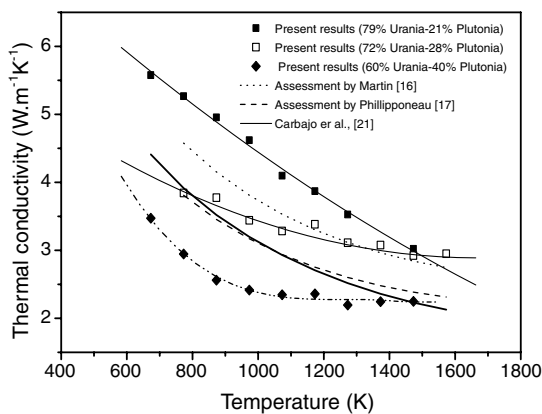


Fig. 6. Thermal conductivity of (U,Pu) mixed oxides with 96% TD.

pellets is about 96% TD. The measured thermal conductivity values are shown in Fig. 6. The trend of the conductivity curves is similar to that of the diffusivity curves. It is seen that the thermal conductivity is sensitive to plutonium content and decreases with increase in the plutonium content at a given temperature. The 40% plutonia fuel has the lowest thermal conductivity of all the three compositions. The general view expressed in the assessments [16,17] that the thermal conductivity of urania–plutonia solid solutions with 15–30% plutonia content is insensitive to plutonium content is debatable, and the present results show that the thermal conductivity does vary with plutonium content. Martin [16] and Phillipponneau [17] have assessed the thermal conductivity of the mixed oxide fuels taking into account several investigations [18–20]. It is seen that the thermal conductivity values (for mixed oxides with 15–30% plutonia content) assessed by Martin [16] lie between the values corresponding to fuels A and B. According to the assessment by Carbajo et al. [21] which assumes that the thermal conductivity does not depend on the plutonium content, the thermal conductivity values (for mixed oxides with 15–30% plutonia content) lie between the values corresponding to 28% and 40% plutonium containing fuel compositions. It is possible that the thermal conductivity of (U,Pu) mixed oxides decreases with increasing plutonia content higher than 30%. No experimental results in the

high plutonium mixed oxides were hitherto available. Hence comparisons are not possible.

4. Conclusion

Oxygen potentials of (U,Pu) mixed oxides, $(U_{1-y}Pu_y)O_{2-x}$, with $y = 0.21$ and 0.28 were measured over the temperature range 1073–1473 K by employing a gas equilibration technique and covered an O/M ratio from 1.96 to 2.000. The oxygen potentials of the mixed oxides depend strongly on plutonium content and temperature. The thermal conductivity of the mixed oxides with 21%, 28% and 40% plutonia measured in this study indicate that the thermal conductivity of mixed oxides is sensitive to the plutonia content.

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