Thermochimica Acta, 66 (1983) 153–159
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

STUDIES ON THE OXIDATION OF URANIUM–PLUTONIUM OXIDES BY NON-ISOTHERMAL KINETICS

S. SAMPATH and D.M. CHACKRABURTTY

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085 (India)

(Received 7 January 1983)

ABSTRACT

Kinetic data on the oxidation and oxygen chemical diffusion of uranium–plutonium oxides is important in assessing the chemical behaviour of the oxide. The oxidation of uranium–plutonium oxides, both hypostoichiometric [$(U,Pu)O_{2-x}$] and hyperstoichiometric [$(U,Pu)O_{2+x}$], with varying plutonium content, was studied by non-isothermal methods of thermogravimetry. The kinetics of the oxidation were found to be controlled by oxygen chemical diffusion, with activation energies in the range 7–12 kcal mole^{-1} for $(U, Pu)O_{2-x}$, and 15–19 kcal mole^{-1} for $(U, Pu)O_{2+x}$. The effect of variation of plutonium content on the kinetics was negligible.

INTRODUCTION

Uranium–plutonium oxide ($MO_{2\pm x}$, where $M = U + Pu$) exhibits significant non-stoichiometry due to the multiplicity of the oxidation states of uranium and plutonium. The oxygen-to-metal ratio (O/M) of the oxide plays an important role in the chemical behaviour of the oxide since changes in O/M can lead to variations in the oxygen chemical potential ($\Delta\overline{G}/O_2$), and in fact considerable changes in O/M can occur during fabrication, storage or irradiation.

The variations in O/M are essentially associated with oxygen diffusion, since cation diffusion rates are very low. Kinetic data on the oxidation and oxygen chemical diffusion of $(U,Pu)O_{2\pm x}$ of varying plutonium content are lacking, and it is only recently that some work has been reported using thermogravimetry and dilatometry [1–4].

Although isothermal methods are simple they are time consuming; also, when the amount of reactant material available is limited, it is desirable to obtain maximum information from a single kinetic experiment. This has led to considerable work on the development of methods based on non-isothermal and quasi-isothermal experiments [5,6]. In this paper, we report on the kinetics of the oxidation of

$$U_{1-y}Pu_yO_{2.0} \rightarrow U_{1-y}Pu_yO_{2+x}$$

($y = 0.05$, 0.3 or 0.75) under non-isothermal and quasi-isothermal conditions.

EXPERIMENTAL

The samples used were sintered uranium–plutonium mixed oxide pellets, 4 mm in diameter. Thermogravimetric analyses of the samples were carried out using a Mettler thermoanalyser with a balance precision of ±0.01 mg and a programmable temperature control giving the temperature within ±0.5°C of the set value. The oxides were equilibrated in an atmosphere of moist argon/hydrogen at 800°C to convert them to $MO_{2.00}$ [7] before being heated at the desired rate of heating up to 1000°C. For quasi-isothermal experiments, the sample was heated at the rate of 4°C min^{-1} until rate of weight gain was significant and then alternate isothermals and polythermals were run keeping the limits of dw/dt manually in the desired range.

RESULTS AND DISCUSSION

The method followed for non-isothermal kinetics was that of Satava and Skvara [8]. The form of $f(\alpha)$ used was $(1-\alpha)\ \ln(1-\alpha) + \alpha$. This form is recommended for diffusion control as the rate-determining step for cylindri-

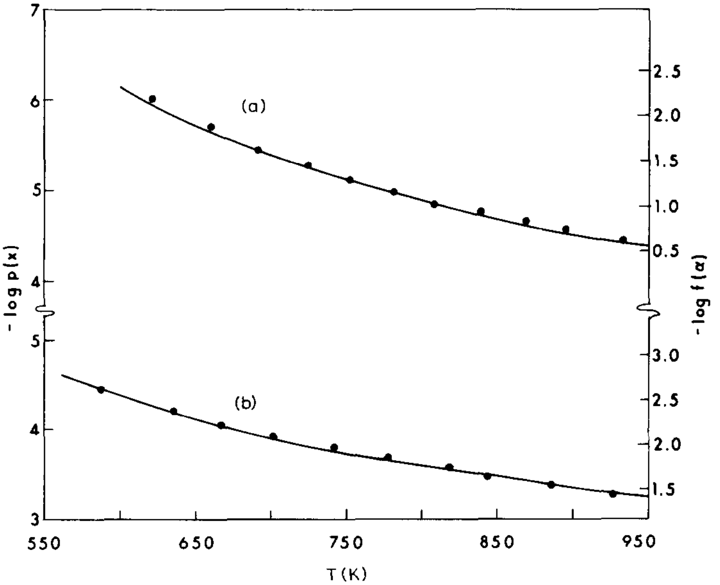

Fig. 1. Non-isothermal kinetic curve-fit for $U_{1-y}Pu_yO_{2-x} \rightarrow U_{1-y}Pu_yO_{2.00}$. (a) $y = 0.3$, $E = 11$ kcal $mole^{-1}$; (b) $y = 0.75$, $E = 7$ kcal $mole^{-1}$.

cal specimens and has been used by us in our earlier work on the isothermal oxidation of MO_{2-x} to $MO_{2.00}$. Values of $\log[p(x)]$ were calculated for activation energies from 5 kcal mole^{-1} up to 30 kcal mole^{-1} in steps of 2 kcal [5] for the temperature range 500–1000 K, and plotted against T for various values of E on transparent paper. Experimental α values were obtained from the weight gain, X_t/X_∞, where X_t = the quantity of oxygen diffused into the pellet in time t, and X_∞ = the corresponding amount after infinite time. Values of α were converted to $\log[f(\alpha)]$ for the chosen function and were plotted against experimental T values using the same scales used for $-\log[p(x)]$ vs. T plots. The transparent plot is superimposed with the T scales, matched, and the two curves are moved relative to one another in the y direction until the $-\log[f(\alpha)] - T$ curve matches one of the $-\log[p(x)] - T$ curves. The displacement in the Y scales required for matching is the value of B in the expression

$$\log[f(\alpha)] - \log(p(x)) = \log\frac{AE}{R\phi} = B$$

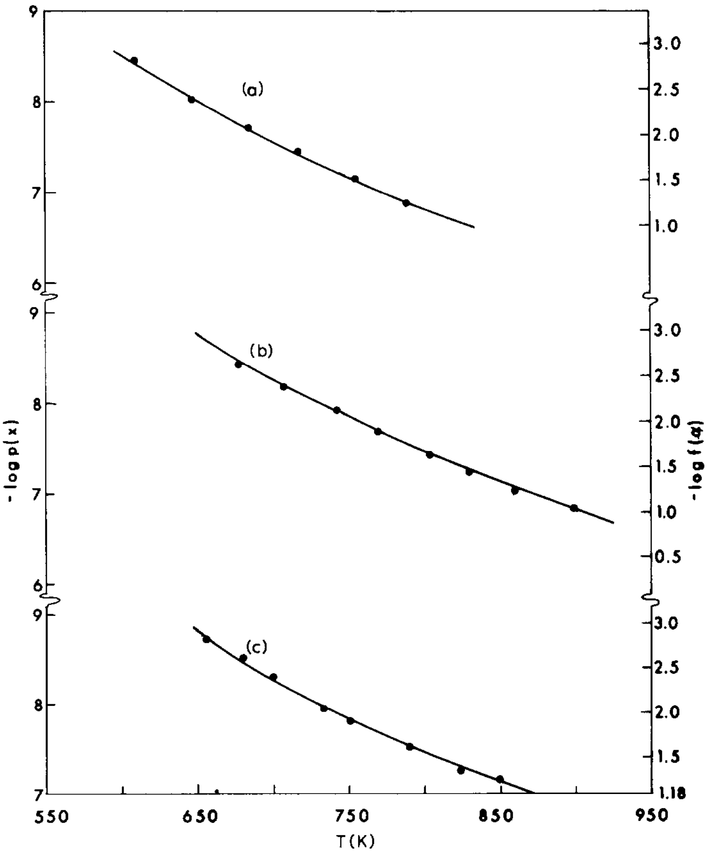

Fig. 2. Non-isothermal kinetic curve-fit for $U_{1-y}Pu_yO_{2.00} \rightarrow U_{1-y}Pu_yO_{2+x}$. (a) $y = 0.05$, $E = 17$ kcal mole^{-1}; (b) $y = 0.3$, $E = 19$ kcal mole^{-1}; (c) $y = 0.75$, $E = 19$ kcal mole^{-1}.

TABLE 1

Kinetic data on (U, Pu)$O_{2\pm x}$ oxidation by non-isothermal TG

Composition	Initial O/M	Initial wt. (g)	Heating rate (°C min^{-1})	Activation energy (kcal $mole^{-1}$)	B	log$A$
$U_{0.25}Pu_{0.75}O_{2-x}$	1.935	1.2402	25	7	1.84	2.09
$U_{0.7}Pu_{0.3}O_{2-x}$	1.964	0.8506	10	11	3.84	0.68
$U_{0.25}Pu_{0.75}O_{2+x}$	2.00	0.8218	6	19	6.86	1.88
$U_{0.7}Pu_{0.3}O_{2+x}$	2.00	0.225	10	19	6.8	2.04
$U_{0.95}Pu_{0.05}O_{2+x}$	2.00	0.901	6	17	6.64	1.71

where ϕ = rate of heating employed. Once B and E are known, the value of A can be calculated.

This method was first attempted for the oxidation of MO_{2-x} to $MO_{2.00}$ with [Pu]/[U + Pu] = 0.75 and 0.3 for which activation energy data have been reported by us earlier using isothermal methods. Figure 1 shows plots of $-\log[p(x)]$ vs. T calculated for activation energies of 7 and 11 kcal $mole^{-1}$. The points shown in the figure represent values of $-\log[f(\alpha)]$ vs. T obtained by us for the oxidation of MO_{2-x} to $MO_{2.00}$. The curve-fits show an activation energy of 7 kcal $mole^{-1}$ for the oxidation of

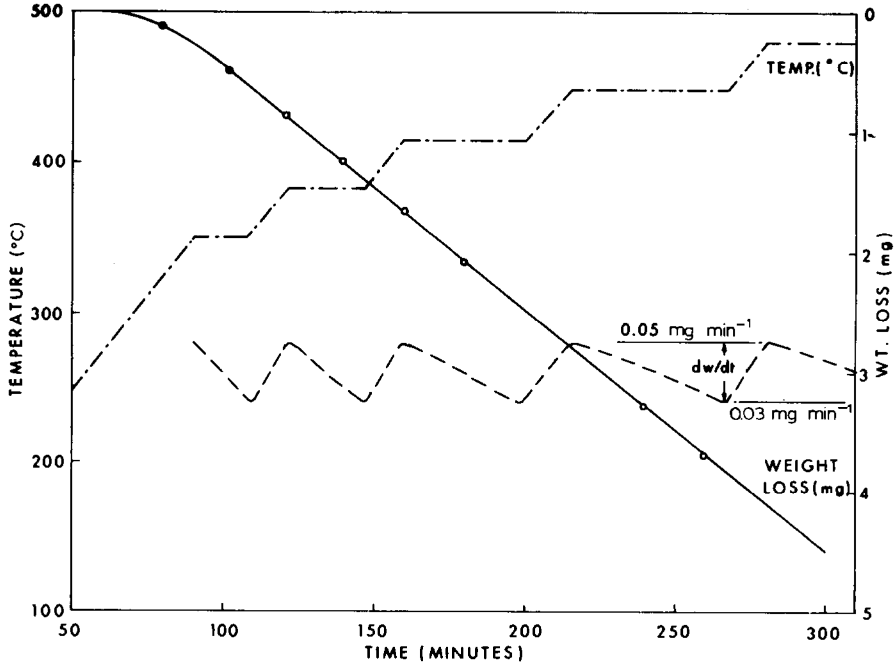

Fig. 3. Quasi-isothermal curves for $U_{0.25}Pu_{0.75}O_{2.00} \rightarrow U_{0.25}Pu_{0.75}O_{2+x}$.

TABLE 2

Activation energy data on $U_{1-y}Pu_yO_{2-x}$

Diam. of cylindrical pellets (mm)	y	Method	Temp. range (K)	Activation energy (kcal mole^{-1})	Ref.
6	1	Isothermal dilatometry and TG	700–1300	11	1
4	0.75	Isothermal TG	800–1300	7	4
		Non-isothermal TG	500–1000	7	Present work
4	0.3	Isothermal TG	800–1300	12	4
		Non-isothermal TG	500–1000	11	Present work
6	0.2	Isothermal dilatometry	900–1300	12	2
5	0.2	Isothermal TG	1373–1673	16	3

$U_{0.25}Pu_{0.75}O_{2-x}$ and 11 kcal mole^{-1} for the oxidation of $U_{0.7}Pu_{0.3}O_{2-x}$ to $MO_{2.00}$, and these values are in excellent agreement with our earlier reported values of 7.4 and 12 k cal mole^{-1} obtained by isothermal methods, thereby showing the applicability of the non-isothermal method.

This method was followed for the oxidation of $MO_{2.00}$ to MO_{2+x} in air with [Pu]/[U + Pu] = 0.75, 0.3 and 0.05, and the curve-fits obtained are shown in Fig. 2. The curves represent $-\log[p(x)]$ values as a function of T for activation energies of 19, 19 and 17 kcal mole^{-1}. The shaded points on the curves show $\log[f(\alpha)]$ values as a function of T obtained from experimental $\alpha-T$ data for the three compositions.

Table 1 gives complete data on composition, initial O/M of the sample, initial weight, rate of heating, activation energy and log A values obtained. All log A values, except that of $Pu_{0.3}U_{0.7}O_{2-x}$ oxidation, are similar.

The quasi-isothermal method has been considered to give more accurate kinetic data since the reactions take place under conditions close to equilibrium [6]. Figure 3 shows the quasi-isothermal oxidation of $U_{0.25}Pu_{0.75}O_{2.00}$ in air. The plots show variations of temperature, weight and dw/dt vs. time.

TABLE 3

Activation energy data on $U_{1-y}Pu_yO_{2+x}$

Diam. of cylindrical pellets (mm)	y	Method	Temp. range (K)	Activation energy (kcal mole^{-1})	Ref.
4	0.75	Non-isothermal TG	500–1000	19	Present work
		Quasi-isothermal TG	500– 800	15	Present work
4	0.3	Non-isothermal TG	500–1000	19	Present work
5	0.2	Isothermal TG	1173–1823	17	3
4	0.05	Non-isothermal TG	500–1000	17	Present work

The two limits of dw/dt chosen were 0.03 mg min^{-1} and 0.05 mg min^{-1} and the rate of heating employed was 4°C min^{-1}. The average activation energy was obtained from the expression

$$\ln C = \frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where C is a constant depending on the limits of dw/dt used, and T_1 and T_2 are the absolute temperatures at the two succeeding steps. The average activation energy obtained was 15 ± 2 kcal mole^{-1} as compared to 19 ± 2 kcal mole^{-1} obtained by the non-isothermal method. This method, however, was not attempted for the other two compositions since the dw/dt limits had to be controlled manually in our experiments and it was difficult to avoid overshooting of temperature.

Tables 2 and 3 give activation energy data obtained by us as well as the data of others for the various compositions for MO_{2-x} and MO_{2+x}, respectively. The following conclusions can be arrived at:

(1) the activation energy for the oxidation of MO_{2-x} or MO_{2+x} is not significantly dependent on plutonium content;

(2) the activation energy for the oxidation of MO_{2-x}, which involves filling up of oxygen vacancies, is in the range 7–11 kcal mole^{-1} whereas the activation energy for the oxidation of MO_{2+x}, which involves oxygen interstitials, is in the range 15–19 kcal mole^{-1};

(3) the data obtained by us on the oxidation of $MO_{2\pm x}$ is comparable with the oxygen chemical diffusion data on $MO_{2\pm x}$ already reported in the literature. Thus, Bayoglu and Lorenzelli [2] report activation energy of 12 kcal mole^{-1} for oxygen chemical diffusion in $(U_{0.8}Pu_{0.2})O_{2-x}$. Sari [3] reports the relationship of oxygen chemical diffusion with temperature for $(U_{0.8}Pu_{0.2})O_{2+x}$ as

$$\log D = -\frac{3780}{T} - 2.18$$

which gives an activation energy of 17 kcal mole^{-1} for oxygen chemical diffusion;

(4) these conclusions indicate that the oxidation of MO_{2-x} to $MO_{2.0}$ and $MO_{2.00}$ to MO_{2+x} is controlled by oxygen chemical diffusion;

(5) the results show that conventional non-isothermal methods of thermogravimetry can be used with advantage to obtain reliable data on oxygen chemical diffusion.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. P.R. Natarajan, Head, Radiochemistry Division, for his keen interest in the work, and Shri N.K. Kulkarni for valuable assistance during the progress of the work.

REFERENCES

1 A.S. Bayoglu and R. Lorenzelli, J. Nucl. Mater., 82 (1979) 403.
2 A.S. Bayoglu and R. Lorenzelli, J. Nucl. Mater., 79 (1979) 437.
3 C. Sari, J. Nucl. Mater., 78 (1978) 425.
4 S. Sampath, R.G. Hadap, R.K. Swamy and D.M. Chackraburtty, Thermochim. Acta, 32 (1979) 326.
5 J. Sestak, V. Satava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 335.
6 O. Toff Sorensen, Thermochim. Acta, 50 (1981) 163.
7 S. Sampath, K.L. Chawla and D.M. Chackraburtty, B.A.R.C.-810, Bhabha Atomic Research Centre, Trombay, India, 1975.
8 V. Satava and F. Skvara, J. Am. Ceram. Soc., 52 (1969) 591.