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Note

Studies on kinetics of oxidation of uranium–plutonium mixed oxides under controlled oxygen potential

S. SAMPATH, R. G. HADAP, R. K. SWAMY AND D. M. CHACKRABURTTY
Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)
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Oxidation kinetics of UO_2 have been studied by thermogravimetry[1] and parabolic rate behaviour has been observed showing bulk diffusion mechanism. In the UO_2–PuO_2 system, kinetics of oxidation of mixed oxide pellets have been studied exhaustively in air with reference to volatile fission products removal from the fuel prior to aqueous reprocessing[2]. No data is available on kinetics of oxidation under controlled oxygen potential. The present study is on the kinetics of oxidation of $(U,Pu)O_{2-x}$ pellets to $(U,Pu)O_{2.00}$ in the temperature range 400–1000°C in moist argon/hydrogen.

EXPERIMENTAL

In our experiments, the kinetics have been followed by nearly isothermal oxidation. The samples used in our studies were 30% PuO_2–UO_2 and 75% PuO_2–UO_2 sintered pellets of 4 mm diameter and 6–8 mm length. The pellets were introduced in platinum crucibles into a Mettler thermoanalyser. The sample chamber was evacuated to 10^{-1} mm and filled with moist argon–hydrogen gas mixture containing 8% hydrogen. The gas mixture was saturated with water vapour by passing through a water trap kept at 20°C. The gas flow over the sample was kept constant throughout the experiment at 100 ml min^{-1}. The sample was rapidly heated (25°C min^{-1}) to the predetermined temperature which was then held constant. The mass gain as a function of time was recorded. The final composition of the sample was determined by equilibration in moist argon/hydrogen at 800°C[3]. Isothermals were run at various temperatures in the range 400–1000°C.

RESULTS AND DISCUSSION

Figures 1 and 2 show plots of fraction oxidised (α = wt. gain at time t/total wt. gain) vs. time for oxidation of 30 and 75% PuO_2–UO_2, respectively, at various isothermal temperatures. The observed parabolic rate behaviour may be interpreted

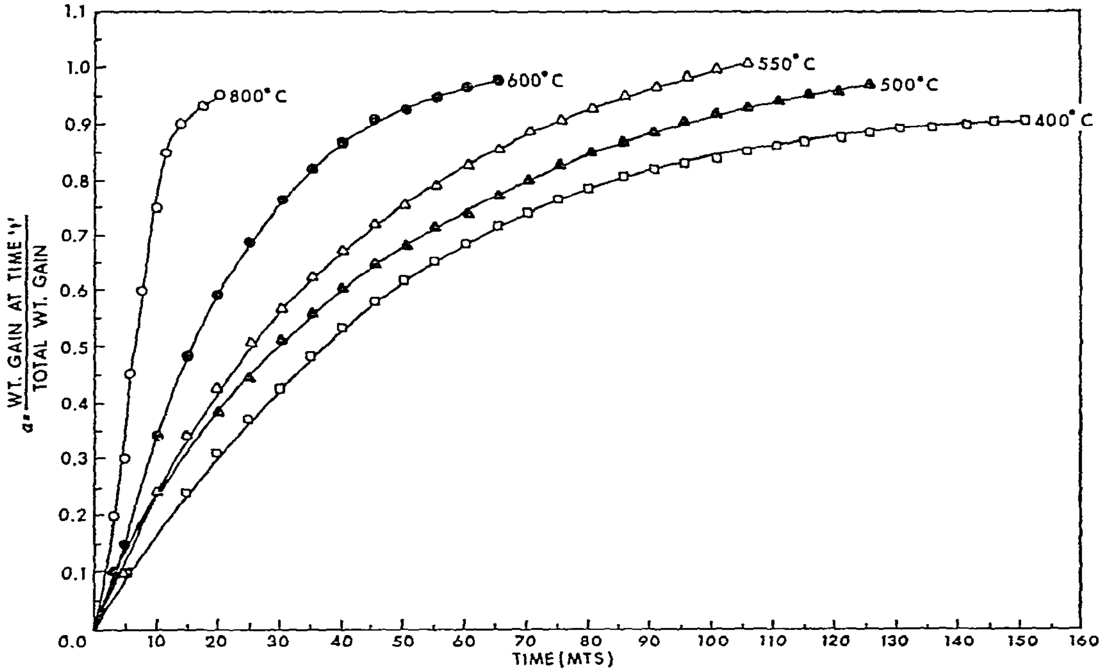

Fig. 1. Plot of α vs. time for 30% PuO_2–UO_2.

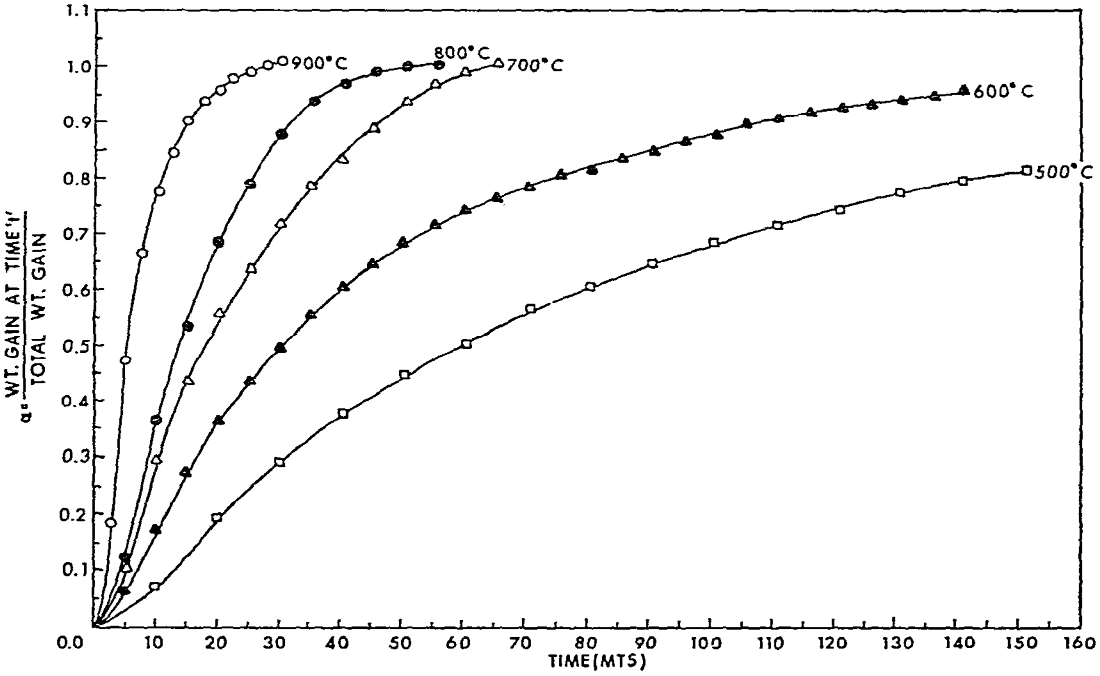

Fig. 2. Plot of α vs. time for 75% PuO_2–UO_2.

in terms of diffusion-controlled oxidation. Various models have been proposed[4, 5] for following the kinetics of solid state reactions by thermogravimetry. Table 1 gives the range of linearity in α obtained from our data for various functions of α vs. time. No linearity was observed on models based on the rate determining step being

TABLE 1

RANGE OF LINEARITY OBSERVED FOR VARIOUS MODELS[a]

Temp. (°C)		*Range of linearity*			
		$D_2(\alpha)$	*$D_3(\alpha)$*	*$A_2(\alpha)$*	*$A_3(\alpha)$*
30% PuO_2–UO_2	400	0.24–0.82	0.31–0.86	0.82–0.90	0.82–0.90
	500	0.14–0.94	0.44–0.90	0.70–0.95	0.50–0.95
	550	0.24–0.88	0.34–0.85	0.43–0.92	0.50–0.96
	600	0.34–0.80	0.48–0.96	0.76–0.96	0.68–0.97
	800	0.45–0.90	0.50–0.85	0.40–0.95	0.50–0.90
75% PuO_2–UO_2	500	0.20–0.81	0.20–0.81	0.56–0.81	0.56–0.81
	550	0.17–0.99	0.27–0.85	0.72–0.89	0.72–0.93
	600	0.40–0.95	0.27–0.91	0.68–0.91	0.64–0.95
	700	0.43–0.99	0.63–0.89	0.43–0.96	0.43–0.96
	800	0.36–0.93	0.53–0.99	0.36–0.99	0.53–0.99
	1000	0.43–0.88	0.58–0.99	0.27–0.82	0.82–0.99

[a] The equations followed are

(1) $D_2(\alpha)$: $(1 - \alpha)\ln(1 - \alpha) + \alpha = (k/r^2)t$

(2) $D_3(\alpha)$: $[1 - (1 - \alpha)^{1/3}]^2 = (k/r^2)t$

(3) $A_2(\alpha)$: $2\sqrt{-\ln(1 - \alpha)} = kt$

(4) $A_3(\alpha)$: $3\sqrt{-\ln(1 - \alpha)} = kt$.

TABLE 2

DATA FOR 30 AND 75% PuO_2–UO_2 FROM PLOTS OF $D_2(\alpha)$ VS. TIME

Temp. (°C)	*k*	*$1/T \times 10^4$*	*$-\log k$*
30% PuO_2–UO_2			
800	0.0513	9.318	1.29
600	0.0178	11.453	1.7496
550	0.0105	12.148	1.9788
500	0.0074	12.934	2.1308
400	0.0068	14.855	2.1675
Slope = 0.26; E =;12 ± 2 kcal			
75% PuO_2–UO_2			
1000	0.0497	7.856	1.3098
800	0.0285	9.318	1.5452
700	0.0195	10.276	1.7100
550	0.0077	12.148	2.1135
500	0.0038	12.934	2.4202
Slope = 0.16; E =;7.4 ± 2 kcal			

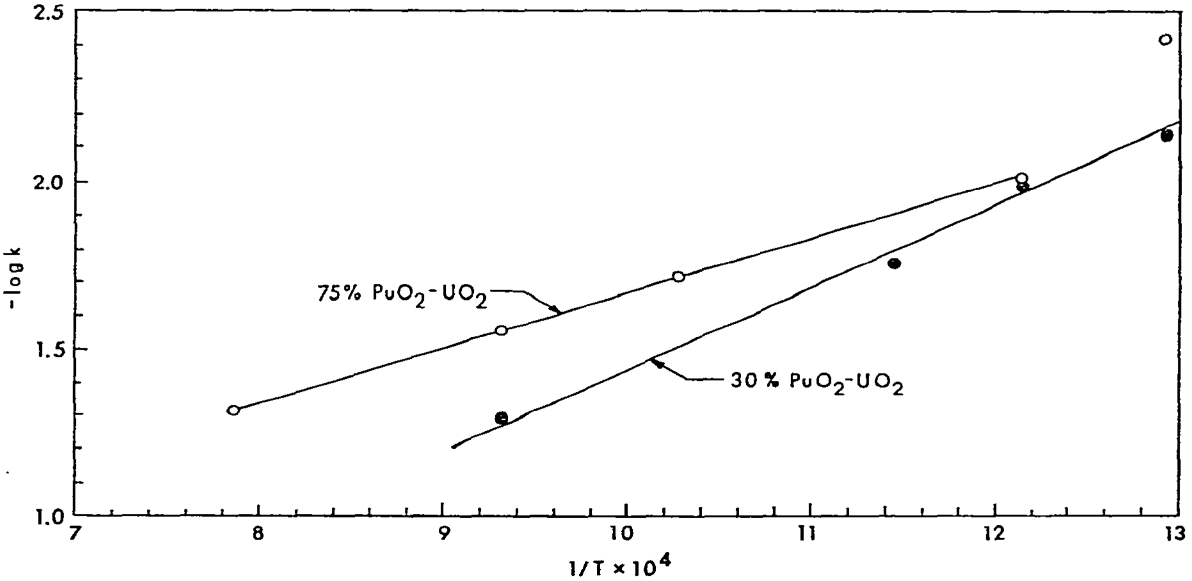

Fig. 3. Plot of − log k vs. $1/T$.

controlled by phase boundary reactions. Observed linearity in α can be satisfactorily explained by both two and three-dimensional diffusion-controlled models, as per equations given in Table 1, with functions like $D_2(\alpha)$ and $D_3(\alpha)$. The difference between plots of $D_2(\alpha)$ and $D_3(\alpha)$ is negligible. Because in our experiments pellets were heated in long narrow crucibles (6 mm diameter, 1.5 cm length) open at the top, thus imposing a constraint, the two-dimensional model has been preferred over the three-dimensional model. Table 2 gives rate constant and activation energy data obtained from plots $D_2(\alpha)$ vs. T, for 30 and 75% PuO_2–UO_2. Figure 3 shows Arrhenious plots for the two compositions. The data fit is poor at low temperatures (around 400 °C); probably other factors like chemisorption control the kinetics at low temperatures in addition to diffusion. The activation energies obtained from these plots are 12 ± 2 kcal mole^{-1} and 7 ± 2 kcal mole^{-1} for 30 and 75% PuO_2–UO_2, respectively.

At present there is no data on activation energy for diffusion under chemical potential for mixed oxides. The activation energy for UO_2 oxidation obtained from steam oxidation kinetics[1] has been reported to be around 56 kcal mole^{-1}. This apparently involves anion interstitial migration. Our activation energy data for mixed oxides compare favourably with the reported activation energy data for anion vacancy migration in uranium oxide[6] and plutonium oxide[7].

Our results show that oxidation of mixed uranium–plutonium oxides in the region MO_{2-x}–$MO_{2.00}$ is diffusion-controlled, probably associated with anion vacancy migration. The relatively higher activation energy obtained for oxidation of 30% PuO_2–UO_2 could be due to some contribution from interstitial migration in addition to vacancy migration.

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