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A HIGH TEMPERATURE STUDY OF CHEMICAL DIFFUSION IN MIXED THORIUM–CERIUM DIOXIDE

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ABSTRACT

High temperature gas–solid reactions in non-stoichiometric actinide and rare earth oxide systems involving oxidation or reduction over a limited range of oxygen-to-metal ratio are usually diffusion controlled in nature, especially when carried out under controlled oxygen potential conditions. Kinetic studies of such reactions can be of use in the elucidation of oxygen chemical diffusion coefficients. This paper presents a mathematical formulation for the treatment of kinetic data of such reactions and evaluation of chemical diffusion coefficients. Details of a high temperature reduction study carried out on thoria–20 mol% ceria solid solution employing a thermogravimetric technique in the temperature range 1000–1200°C are presented and oxygen chemical diffusion coefficients are also evaluated.

INTRODUCTION

In the high temperature oxidation or reduction study of non-stoichiometric binary and ternary oxides, diffusion controlled gas–solid reactions are usually encountered. Reactions of this type in actinide oxides and related systems involving oxidation or reduction over a limited range of oxygen-to-metal ratio under controlled oxygen potential conditions are of interest in understanding the high temperature behaviour of these materials. Rates of these oxidation–reduction reactions are controlled by chemical diffusion of oxygen [1,2] and hence a kinetic study of these reactions offers possibilities for the measurement of oxygen chemical diffusion coefficients. In these types of study a step change is induced in the oxygen partial pressure of the gaseous atmosphere with which the sample is in equilibrium at high temperature. As the surface equilibrates rapidly with the new atmosphere, a chemical potential gradient exists between the sample surface and the bulk providing the necessary driving force for the diffusion. Rates of these reactions can be conveniently followed by thermogravimetry or electrical conductivity measurements and chemical diffusion coefficients can be elucidated. Oxygen chemical diffusion in mixed uranium–plutonium oxide was thus studied by Sari [2], Bayoglu and Lorenzelli [3] and D'Annucci and Sari [4]. The present

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study deals with chemical diffusion in the solid solution $Th_{0.8}Ce_{0.2}O_{2-x}$ ($0 \leqslant x \leqslant 0.02$) in the temperature range 1000–1200°C. A simple mathematical formulation based on a "half-time" concept is also presented for the treatment of reaction kinetic data and elucidation of chemical diffusion coefficients.

THEORETICAL ASPECTS

In the case of a thin specimen having a thickness $2l$, if the region $-l < x < l$ is initially at a concentration C_0 and the surfaces are maintained at a concentration C_1, the solution to Fick's diffusion equation in a one-dimensional treatment can be written as [5]

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left[\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right] \cos\frac{(2n+1)\pi x}{2l} \tag{1}$$

where D is the chemical diffusion coefficient. For a diffusion controlled reaction, if M_t denotes the weight change caused by the diffusing substance in time t and M_∞ the corresponding change at infinite time, the fraction reacted, α can be shown to be

$$\alpha = \frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right] \cdot \tag{2}$$

In the present study, eqn. (2) has been re-written employing a half-time concept. If $t_{1/2}$ denotes the time required for half the reaction to be completed, it can be seen that

$$1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[\frac{-D(2n+1)^2\pi^2 t_{1/2}}{4l^2}\right] = 0.5$$

i.e.

$$\sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[-K(2n+1)^2\right] = 0.5 \tag{3}$$

where

$$K = \frac{\pi^2 D t_{1/2}}{4l^2} \tag{4}$$

Equation (3) was solved for K by computer based calculation to get a value of $K = 0.485414$. Substitution of this value of K in eqn. (4) yields

$$D = \frac{4Kl^2}{\pi^2 t_{1/2}} = 0.1966 \frac{l^2}{t_{1/2}} \tag{5}$$

TABLE 1

Calculated values of α as a function of $t/t_{1/2}$

$t/t_{1/2}$	α	$t/t_{1/2}$	α	$t/t_{1/2}$	α
0.00	0.0000	0.58	0.3811	2.35	0.7409
0.01	0.050	0.60	0.3877	2.40	0.7472
0.02	0.0708	0.62	0.3941	2.45	0.7532
0.03	0.0867	0.64	0.4004	2.50	0.7591
0.04	0.1001	0.66	0.4066	2.55	0.7649
0.05	0.1119	0.68	0.4127	2.60	0.7706
0.06	0.1226	0.70	0.4187	2.65	0.7761
0.07	0.1324	0.72	0.4246	2.70	0.7814
0.08	0.1416	0.74	0.4305	2.75	0.7867
0.09	0.1501	0.76	0.4362	2.80	0.7918
0.10	0.1583	0.78	0.4419	2.85	0.7968
0.11	0.166	0.80	0.4475	2.90	0.8016
0.12	0.1734	0.82	0.4531	2.95	0.8064
0.13	0.1805	0.84	0.4586	3.00	0.8110
0.14	0.1873	0.86	0.464	3.1	0.8200
0.15	0.1938	0.88	0.4692	3.2	0.8285
0.16	0.2002	0.90	0.4746	3.3	0.8366
0.17	0.2064	0.92	0.4798	3.4	0.8444
0.18	0.2123	0.94	0.4849	3.5	0.8518
0.19	0.2182	0.96	0.4900	3.6	0.8588
0.20	0.2238	0.98	0.4950	3.7	0.8655
0.21	0.2294	1.00	0.5000	3.8	0.8719
0.22	0.2347	1.05	0.5122	3.9	0.8779
0.23	0.240	1.10	0.5240	4.0	0.8837
0.24	0.2452	1.15	0.5356	4.2	0.8945
0.25	0.2502	1.20	0.5468	4.4	0.9042
0.26	0.2552	1.25	0.5578	4.6	0.9131
0.27	0.2601	1.30	0.5684	4.8	0.9211
0.28	0.2648	1.35	0.5788	5.0	0.9284
0.29	0.2695	1.40	0.589	5.2	0.9350
0.30	0.2741	1.45	0.5989	5.4	0.9411
0.31	0.2787	1.50	0.6085	5.6	0.9465
0.32	0.2831	1.55	0.6179	5.8	0.9515
0.33	0.2875	1.60	0.6271	6.0	0.956
0.34	0.2918	1.65	0.6360	6.5	0.9654
0.35	0.2961	1.70	0.6448	7.0	0.9729
0.36	0.3003	1.75	0.6533	7.5	0.9787
0.37	0.3044	1.80	0.6616	8.0	0.9833
0.38	0.3085	1.85	0.6698	8.5	0.9869
0.39	0.3125	1.90	0.6777	9.0	0.9897
0.40	0.3165	1.95	0.6854	9.5	0.9919
0.42	0.3244	2.00	0.693	10.0	0.9937
0.44	0.332	2.05	0.7003	11.0	0.9961
0.46	0.3394	2.10	0.7075	12.0	0.9976
0.48	0.3467	2.15	0.7145	13.0	0.9985
0.50	0.3539	2.20	0.7214	14.0	0.9991
0.52	0.3609	2.25	0.7281	16.0	0.9997
0.54	0.3678	2.30	0.7346	19.0	0.9999
0.56	0.3745				

Substitution of D from eqn. (5) into eqn. (2) yields

$$\alpha = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[-(2n+1)^2 K \frac{t}{t_{1/2}} \right] \tag{6}$$

For various values of $t/t_{1/2}$ in eqn. (6), corresponding values of α were generated by calculation. A typical list of the values of α thus calculated as a function of $t/t_{1/2}$ is given in Table 1 which can serve as a reference in these types of studies. The progress of the reaction can be followed by thermogravimetry or electrical conductivity measurements and α measured as a function of time. Agreement between the theoretically calculated and measured values of α as a function of $t/t_{1/2}$ substantiates the diffusion controlled nature of the reaction. Further, from the values of $t_{1/2}$, chemical diffusion coefficients can be evaluated employing eqn. (5).

Two approximate solutions which are generally used [6] in the case of a thin specimen are the parabolic equation given by

$$\alpha^2 = \frac{4Dt}{l^2} \tag{7}$$

valid for $Dt/l^2 < 0.25$ and the logarithmic equation given by

$$\log(1-\alpha) = \log\frac{8}{\pi^2} - \frac{\pi^2 Dt}{9.2 l^2} \tag{8}$$

valid for $Dt/l^2 > 0.15$. Thus, under a "small-time approximation" where eqn. (7) is valid, a plot of α^2 versus t can be made and D can be obtained from the slope. Similarly, under a "large-time approximation" where eqn. (8) is valid, a plot of $\log(1-\alpha)$ versus t can be made and D can be evaluated from the slope.

In the present study the half-time approach presented above has primarily been used to analyse the reaction kinetic data obtained on the reduction of thoria–20 mol% ceria and to calculate the chemical diffusion coefficients. For comparison, the data were also analysed by the earlier methods involving a "parabolic plot" and a "logarithmic plot" described by eqns. (7) and (8) respectively [5].

EXPERIMENTAL

Thoria–20 mol% ceria solid solution was prepared by the method of mechanical mixing. Thorium dioxide and cerium dioxide powders, weighed accurately in the required proportions, were mixed thoroughly, ground well and pelletised. The pellets were preheated at 1000°C for 5 h and finally sintered at 1650°C for 10 h. Formation of a single phase solid solution was confirmed by X-ray diffraction and pellet density was determined to be 91% theoretical by a liquid immersion method. The sample taken for the reduction study was in the form of a thin disc of about 1.4 mm thickness and 10 mm diameter. Thermogravimetric measurements on the sample were carried out employing a Netzsch (model STA 429) thermal analyser. The sample was loaded on a platinum foil supported on the TG alumina holder. The sample was made to rest on its curved surface thus permitting a complete exposure of the sample to the gaseous atmosphere surrounding it. In each of the reduction runs the sample was initially preheated to 1200°C in high-purity argon and up to this temperature it was noted that no significant weight change occurred. Subsequently, the temperature was changed to the required value, lying in the range 1000–1200°C. At each of the chosen temperatures, isothermal reduction runs were carried out under controlled oxygen potential conditions employing an H_2/H_2O technique which involves the use of a moist argon–hydrogen gas mixture with a fixed H_2/H_2O ratio. In the present study the ratio of $H_2O/H_2 \approx 10^{-1}$ was used and the O/M range covered was from 2.00 to 1.98. Details of the use of H_2/H_2O or CO/CO_2 techniques for oxidation–reduction studies over a narrow range of oxygen-to-metal ratio in non-stoichiometric oxides have been dealt with by earlier workers [3,4,7,8].

RESULTS AND DISCUSSION

Progress of the reaction at each temperature is shown in Fig. 1 in terms of α vs. time plots. Figure 2 shows the values of α obtained as a function of $t/t_{1/2}$ at various temperatures. It can be seen that these results at varying temperatures fitted reasonably well with the theoretical plot of α vs. $t/t_{1/2}$ which is shown in the same figure. Oxygen chemical diffusion coefficients

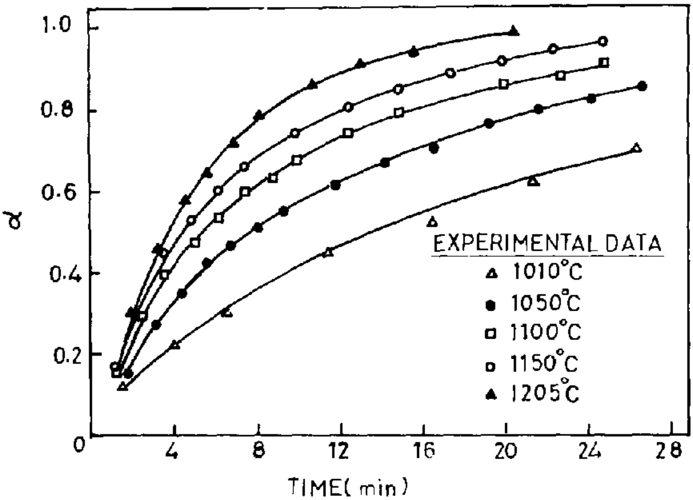

Fig. 1. α versus time plots for the reduction of $(Th_{0.8}Ce_{0.2})$ oxide.

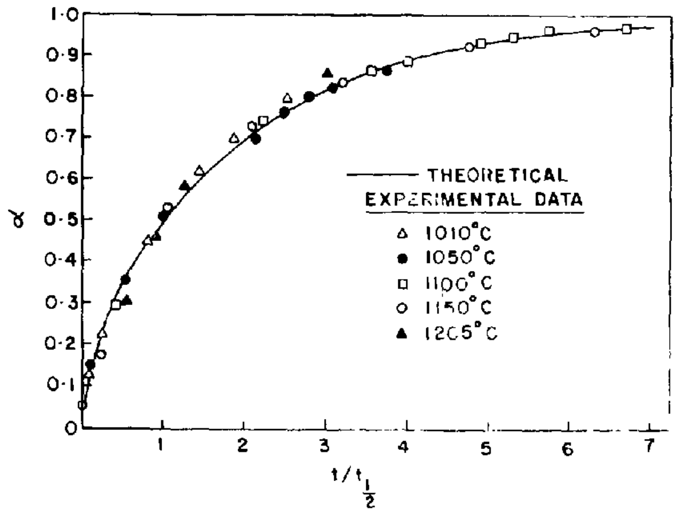

Fig. 2. Comparison of theoretically generated α vs. $t/t_{1/2}$ curve with experimental data on the reduction of mixed $Th_{0.8}Ce_{0.2}O_{2-x}$ $(0 \leqslant x \leqslant 0.02)$.

are also calculated at each temperature employing the present half-time formalism and are shown in Table 2. Figures 3 and 4, respectively, show the parabolic plot and the logarithmic plot obtained by the application of the eqns. (7) and (8) to the present data. Chemical diffusion coefficients calculated from these two plots are also presented in Table 2 and these results are seen to be in close agreement with the values obtained from the present half-time approach. Figure 5 shows an Arrhenius plot of log D as a function of $1/T$ from which the temperature dependence of the oxygen chemical diffusion coefficient can be expressed as

$$D = 1.22 \times 10^{-2} \exp\left[-22.88(\text{kcal mol}^{-1})/RT\right] \ (\text{cm}^2\ \text{s}^{-1})$$

TABLE 2

Chemical diffusion coefficient data for thoria–20% ceria solid solution obtained from the present study

	Temp. (°C)	−log D		
		From the proposed $t_{1/2}$ approach	From the logarithmic plot	From the parabolic plot
1	1010	5.84	5.84	5.89
2	1050	5.67	5.65	5.63
3	1100	5.52	5.51	5.52
4	1150	5.45	5.44	5.40
5	1205	5.34	5.24	5.25

The present half-time approach for the elucidation of chemical diffusion coefficients from a study of oxidation–reduction reactions has several advantages. "Small-time" or "large-time" limitations involved in the earlier approach are avoided and hence the present formalism can be applied throughout the course of the reaction. Temperature dependence of the reaction rate is also conveniently incorporated in the half-time measurement and hence a single plot of α vs. $t/t_{1/2}$ can be used to represent the data from all temperatures. Chemical diffusion coefficients at each temperature can be obtained from the measured $t_{1/2}$ values by making use of eqn. (5).

Ando and Oishi [1] have reviewed the diffusion characteristics of actinide oxides and it may be seen that the chemical diffusion coefficient values

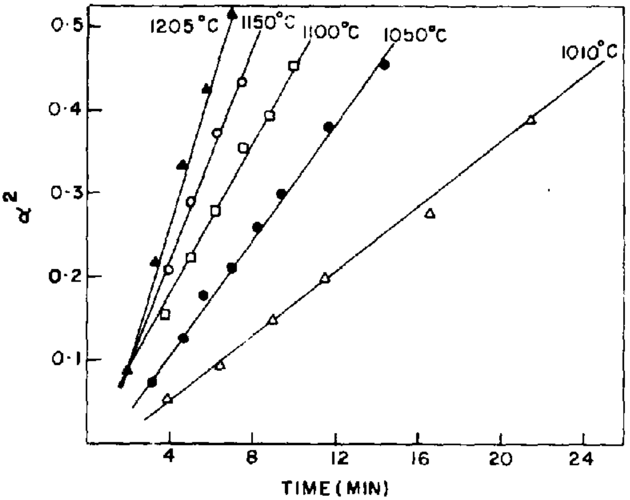

Fig. 3. Parabolic plot of kinetics of reduction of mixed (Th$_{08}$Ce$_{02}$) oxide.

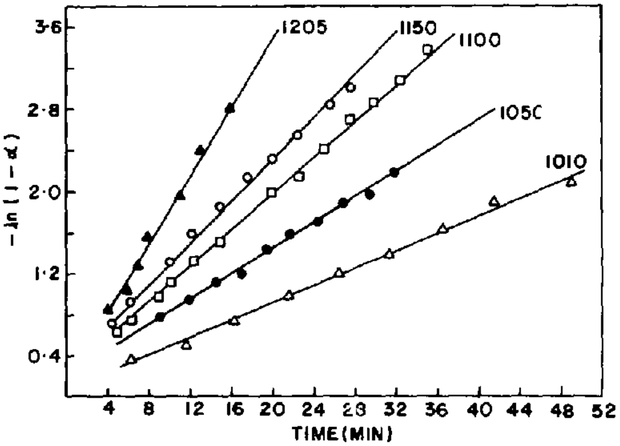

Fig. 4. Logarithmic plot of kinetics of reduction of mixed (Th$_{08}$Ce$_{02}$) oxide.

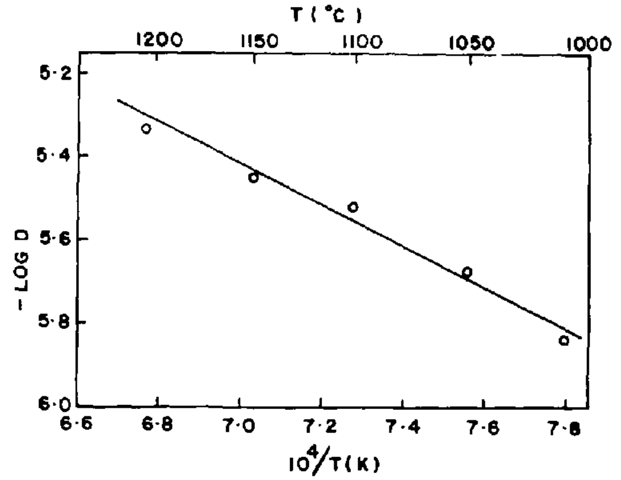

Fig. 5. Chemical diffusion coefficients for $Th_{0.8}Ce_{0.2}O_{2-x}$ solid solution as a function of temperature ($0 \leqslant x \leqslant 0.02$).

obtained in the present study are in the general range expected for the family of actinide oxides. No earlier data on chemical diffusion in the Th–Ce–O system are available. However, a comparison of the present data with the measurements of Bayoglu and Lorenzelli [9] on $U_{0.8}Cd_{0.2}O_{2+x}$ extrapolated to the present temperature range has indicated that chemical diffusion coefficients in the present system are relatively smaller. Further studies on chemical diffusion in non-stoichiometric mixed oxides in the actinide and rare earth oxide systems are under way to enable an understanding of the diffusion-controlled processes in these materials and to facilitate systematic correlations.

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