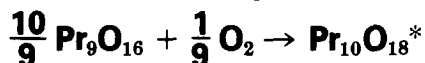


A Kinetic Study of the Oxidation of ζ Phase Praseodymium Oxide:



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Kinetic and thermodynamic studies of the oxidation of ζ ($n = 9$ in $\text{Pr}_n\text{O}_{2n-2}$) to epsilon ($n = 10$) phase have been carried out using a thermogravimetric technique. The experiments covered a temperature range of 464 to 503°C and oxygen pressure varied from 0.01 to 50 Torr. The existence of a reproducible hysteresis loop which depends on the temperature and pressure is shown. Measurements of the oxidation rate under isothermal conditions were fitted to different rate equations and have been found to be well represented by the equation $f = 1 - (1 - kt)^3$. This fact indicated that the process of oxidation was predominantly controlled by the chemical reaction at the interface. The activation energy for the reaction has been calculated to be 15.9 kcal/mole.

Introduction

The praseodymium oxides form a fluorite-related homologous series ($\text{Pr}_n\text{O}_{2n-2}$; $n = 4, 7, 9, 10, 11, 12, \infty$) of phases with well-defined stoichiometries and ordered structures and two nonstoichiometric phases, i.e., $\text{PrO}_{1.5+x}$ and PrO_{2-x} , of wide composition range (1-5). The homologous series is further divided into odd and even series depending upon whether n is odd or even (1). Thermodynamic studies of phase transformations between these intermediate phases have shown that reproducible hysteresis loops are found when the phase reaction cycle is completed between any

two phases (3-12). The causes of chemical hysteresis are no doubt varied and are not well understood. In order to model theoretically the nature and the mechanism of hysteresis, it is necessary to have a detailed knowledge of the structure, thermodynamic and kinetic relationships of the phase reaction.

In a calorimetric study (13, 14), the two-phase regions have been interpreted as intrinsic hysteresis regions and are discussed in terms of the regular solution model. Coherent intergrowth of many ordered phases between the ordered praseodymium ι and the disordered praseodymium α phase is considered responsible for the observed asymmetric hysteresis.

In previous kinetic studies (12, 15), it was found that a phenomenological treatment of a phase reaction based on the known hysteresis loop is capable of correlating the experimental data for the praseodymium $\iota \rightarrow \zeta$ and the $\iota \rightarrow \alpha$ systems.

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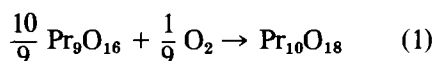
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The kinetics of the $\text{TbO}_{1.5}$ – $\text{TbO}_{1.714}$ system (16) is explained satisfactorily by using a moving boundary model. This model consists of two different parts, phase boundary reaction and diffusion terms. It was found from this analysis that the oxidation rate between $\text{TbO}_{1.5+x}$ and $\text{TbO}_{1.714}$ is determined by competition between a phase boundary and a diffusion process, and the diffusion process becomes rate determining as the temperature increases.

In the present kinetic study, the oxidation reactions between the praseodymium ζ ($n = 9$) and ϵ ($n = 10$) phases are carried out. This extends the kinetic studies to an odd–even phase reaction without reconstruction. The earlier studies mentioned above are odd–odd for ι – ζ odd–disorder for ι – α , and even–odd with reconstruction for the ϕ – ι reaction. We can expect that the influence of diffusion is eliminated in the reaction to be studied due to the equilibria between the two phases at lower temperature.

Experiments

Kinetic and thermodynamic measurements of the phase reaction



have been carried out on a uniform powder sample using an Ainsworth thermobalance. This sample was prepared from precipitated oxalate which was decomposed by heating at 1000°C for 48 hr. The details of the experimental procedure were given in a previous paper (12).

The experimental error in the weight measurement from the irreproducibility of each run and the correction for the TMF effect was estimated to be ± 0.2 mg corresponding to a compositional error of about ± 0.001 in the oxygen/metal ratio.

In the thermodynamic (hysteresis) study, oxygen was admitted and the weight

change observed until equilibrium was attained. The process required a rather short time (ca. 30 min.) in the single-phase regions, but a relatively long time (about 1 day) in the two-phase regions.

In the kinetics runs, the sample was kept at an appropriate pressure at each temperature (ca. 0.10 Torr at 464°C, 0.70 Torr at 503°C, etc.) for more than two days to insure complete reduction to the ζ phase starting composition. It should be noted that reproducible kinetics data could not be obtained when the annealing time was less than 1 day. The kinetics data were collected by a PDP-8 computer as previously described (12), and the final values of the weight were taken 0.5–4 hr later when the reaction was complete.

Results and Discussion

The Hysteresis Study

An isothermal hysteresis study has been carried out between ζ and ϵ phases at different fixed temperatures by changing the pressure. The results are shown in Fig. 1. The compositions of the praseodymium oxides were not determined absolutely, rather the O/Pr ratio at pressures of 0.1–0.5 Torr at each temperature was set as 1.7778 on the basis of previous experience.

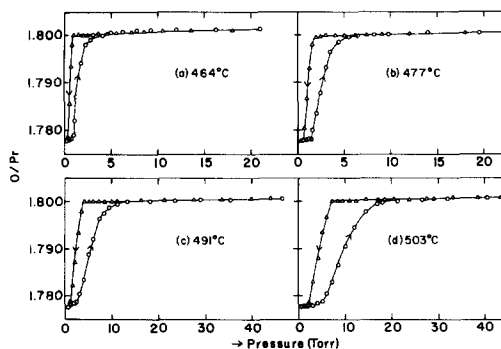


FIG. 1. Isothermal hysteresis loops between ζ and ϵ phases.

The features of the hysteresis curves are similar to those obtained in the $\text{TbO}_{1.5+x} \rightarrow \text{TbO}_{1.714}$ system (16). The complete loops are not symmetrical but have marked curvature in the oxidation branches. This suggests distinct pseudophase behavior along an oxidation branch. The loops shift to higher pressures with an increased width as the temperature is increased.

The Kinetic Study

A kinetic run at 491°C and 18 Torr is shown as a typical example in Fig. 2. Here the weight fraction, f , is plotted against time. The kinetics of reaction in solids may consist of several simple physical and chemical "elementary" processes involving, for example, movement of a particle of matter, changes in structure, physical state, or chemical composition. The experimental kinetic data must be fitted to a particular kinetic model which reflects the elementary processes associated with this phase reaction in praseodymium oxide.

In attempts to fit the measured kinetic curve, several theoretical models have been utilized. According to the moving boundary mechanism (17, 18), the reaction takes place on the moving boundary between the product and the reactant. The reaction interface which is a proportionately smaller replica of the initial exterior

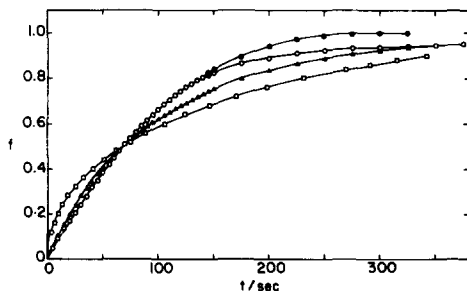


FIG. 2. A typical kinetic run at 491°C and 18.0 Torr and the fitting of various models. The fraction of reaction (f) is plotted against time: \circ , observed; \bullet , $f = 1 - (1 - kt)^2$; ∇ , $kt = \frac{1}{2} - \frac{1}{2}(1 - f)^{2/3} - \frac{1}{3}f$; \square , $[\beta(1 - f)/\beta - f] = \exp[-k(P - P_n)t]$.

surface (so-called contracting geometry) shrinks toward the center of the crystal. For a spherically symmetric system the model has been solved only when the steady-state approximation has been used (18). In this case, the expression for f is represented by

$$Kt = R[1 - (1 - f)^{1/3}] + \frac{1}{2} - \frac{1}{2}(1 - f)^{2/3} - \frac{1}{3}f, \quad (2)$$

where $R = k_d/k_p r_0$ and $K = k_d(C^* - C_{eq})/(C_0 r_0^2)$. Here C_0 represents the concentration of the reactant, r_0 is the particle radius and C^* , C_{eq} are concentrations of the diffusing species in the product layer, and k_d , k_p are the diffusion constant and the reaction constant, respectively.

When movement of the reaction boundary is controlled by the diffusion of absorbed species (in this case oxygen), Eq. (2) reduces to

$$Kt = \frac{1}{2} - \frac{1}{2}(1 - f)^{2/3} - \frac{1}{3}f. \quad (3)$$

A plot of Eq. (3) is compared with the experimental results in Fig. 2. The theoretical curve is chosen to fit the experimental plot at $f = 0.5$. Theory and experiment do not agree.

When R in Eq. (2) is very large the reaction rate governs the movement of the phase boundary, and the so-called phase boundary reaction controlled mechanism is obtained. From Eq. (2) we then have

$$f = 1 - (1 - kt)^2, \quad (4)$$

where $k = K/R = k_p(C^* - C_{eq})/C_0 r_0$. Since $f = 1$ at $kt = 1$, this model cannot represent a kinetic curve near $f = 1$ satisfactorily. It is seen to fit the experimental data satisfactorily below $f \approx 0.9$ as shown in Fig. 2.

In order to check further the applicability of this model, Eq. (4) was applied to two other experimental curves from other temperatures and pressures. The results are shown in Figs. 3 and 4. It is clear that

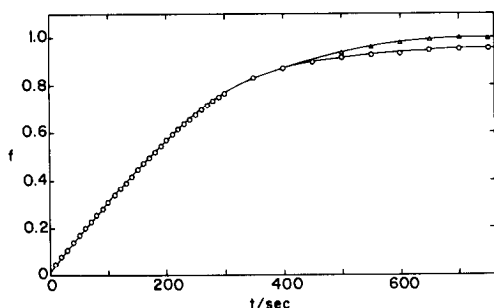


FIG. 3. Experimental data and the theoretical phase boundary model at 464°C and 7.80 Torr.

agreement between theory and experiment is excellent except in the final stages of the reaction. The reasons for the deviation could include the following: (1) the existence of an ϵ pseudophase analogous to the $\text{TbO}_{1.5+x} \rightarrow \text{TbO}_{1.714}$ system (16) as suggested by the shape of the oxidation branches of the hysteresis loops. (2) The assumption of the contracting reaction geometry is no longer valid in the final stages. This point will be amplified below with discussion of kinetics in a two-phase hysteresis region. (3) Equation (4) fails as f approaches 1; i.e., $f > 1$ at $t > 1/k$.

In a previous paper (12), a new model was developed in which the oxidation reaction was assumed to pass through the oxidation branch of the hysteresis loop. The rate equation was

$$\frac{\beta(1-f)}{\beta-f} = \exp[-K(P - P_n)t], \quad (5)$$

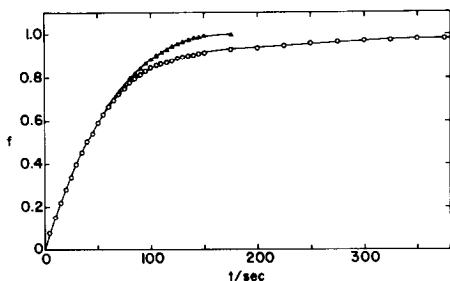


FIG. 4. Experimental data (Δ) and the theoretical phase-boundary-model (\circ) fit at 503°C and 28.0 Torr.

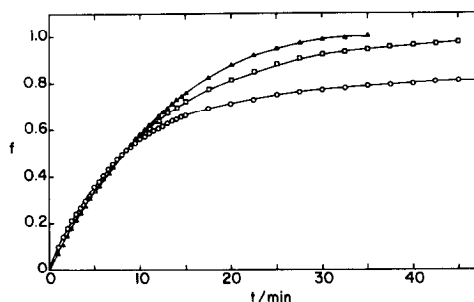


FIG. 5. A typical kinetic run terminating in the two-phase hysteresis region at 503°C and 9.10 Torr: \circ , observed; Δ , $f = 1 - (1 - kt)^3$; \square , $f = 1 - e^{-kt}$.

where $\beta = (P - P_0)/(P_n - P_0)$, P_0 and P_n are the initial and final pressures of the oxidation branch of the hysteresis loop, respectively. As can be seen from Fig. 2, this phenomenological model cannot explain these experimental data. The phenomenological model apparently has restricted applicability for reactions in systems showing hysteresis.

A kinetic reaction where the final product is still in the hysteresis region was studied. A typical experimental curve at 503°C is shown in Fig. 5. The phase-boundary-controlled model is no longer applicable to the experimental results. The best fit is obtained by the following theoretical equation in the initial and intermediate regions

$$f = 1 - \exp(-kt). \quad (6)$$

This equation has been used to interpret grain boundary nucleation and growth (19) or first-order reaction (20) suggesting that the mode of nucleation and growth changes gradually in the hysteresis region. This is reflected in the change in slope in Fig. 6d. Above the break the phase-boundary-controlled mechanism is followed.

The deviation between theory and experiment becomes pronounced in the final stages as shown in Fig. 5. In fact, more than 10 hr are needed to complete the reaction. There are two phases (ζ and ϵ) coexisting in this part of the hysteresis region. The slow-

TABLE I

T (°C)	
464	$U_{0.5} = 0.000785 (P - 1.02)$
477	$U_{0.5} = 0.000935 (P - 2.03)$
491	$U_{0.5} = 0.00114 (P - 5.26)$
503	$U_{0.5} = 0.00143 (P - 10.7)$

ness of the reaction may be due in part to the reverse reaction from ϵ to ζ . When the final product is two-phase the reaction is very slow and a full day is required to be sure equilibrium is reached.

The kinetic runs were made as a function of pressure at various temperatures. The pressure dependence of $U_{0.5}$ ($= 1/t_{0.5}$, the time for the reaction to be one-half com-

pleted) is shown in Fig. 6a–d, and also summarized in Table I. As is apparent in this figure, $U_{0.5}$ is linearly dependent on the pressure. This linear behavior has been a common experience in the phase reactions observed in the rare earth oxide system.

From the linear relationship between $U_{0.5}$ and pressure we can assume that the concentration of absorbed species (i.e., O atoms) at the interface is proportional to the ambient oxygen pressure, P_{O_2} , that is

$$C^* = \alpha P_{O_2}^{\text{ambient}}, \quad C_{\text{eq}} = \alpha P_{O_2}^{\text{eq}} \quad (7)$$

From Eq. (4),

$$\frac{\alpha k_p (P_{O_2}^{\text{ambient}} - P_{O_2}^{\text{eq}})}{C_0 r_0} t = 1 - (1 - f)^{1/3}. \quad (8)$$

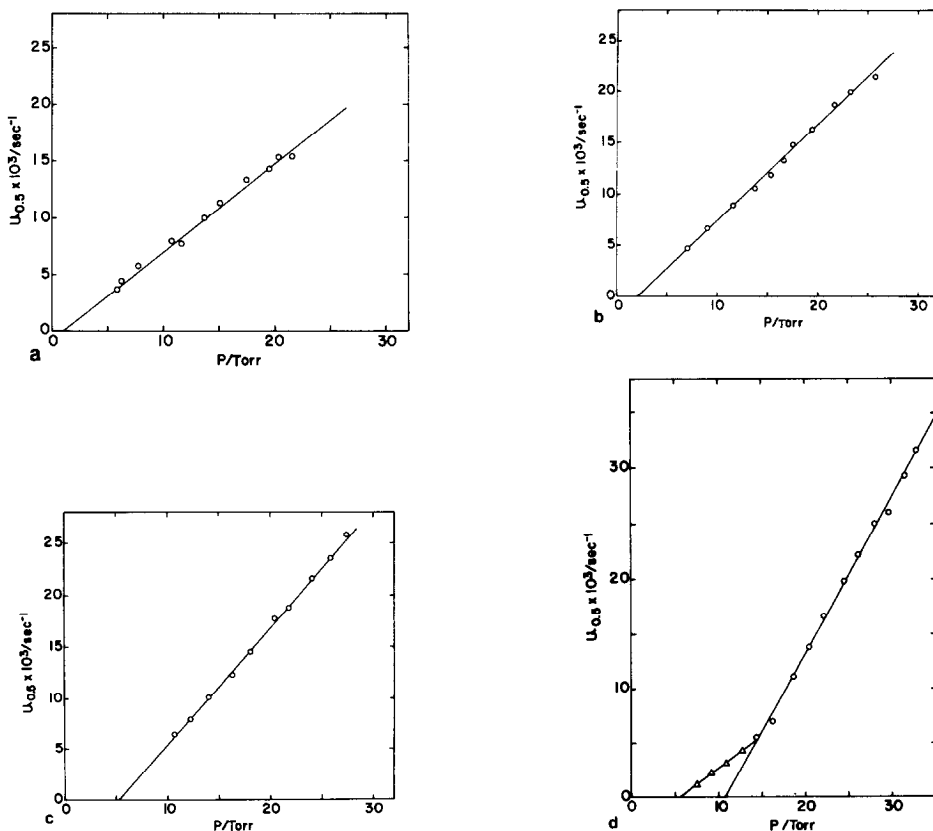


FIG. 6. $U_{0.5}$, the reciprocal of the time required for 50% reaction, against pressure. (a) 464°C; (b) 477°C; (c) 491°C; (d) 503°C.

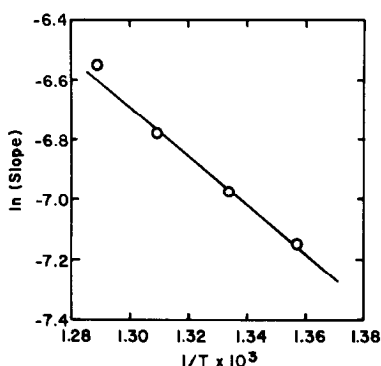


Fig. 7. A plot of $\ln(\text{Slope})$ vs $1/T$.

At $f = 0.5$,

$$U_{0.5} = \frac{1}{t_{0.5}} = \frac{\alpha k_p}{0.2063 C_0 r_0} (P_{O_2}^{\text{ambient}} - P_{O_2}^{\text{eq}}), \quad (9)$$

thus, the linear relationship between U and P is demonstrated. Pressures at which the straight lines intersect the abscissa in Fig. 6 show the equilibrium oxygen pressure corresponding to the phase-boundary-controlled reaction.

From the slopes of the straight lines in Fig. 6, we can determine k_p as a function of temperature. An Arrhenius plot of the slopes is shown in Fig. 7, from which an activation energy of 15.9 ± 0.5 kcal/mole is obtained. This value is comparable to that obtained from the oxidation of $\text{TbO}_{1.5+x}$ to $\text{TbO}_{1.714}$ (16). These lower values seem to be associated with the hysteresis effect.

Oxidation kinetics in solid-gas reactions are generally controlled by either a diffusion or a phase boundary reaction process. At lower temperatures ($\leq 500^\circ\text{C}$) the phase boundary reaction dominates the reaction speed as in the case of the ζ - ϵ reaction. On the other hand, at higher temperatures ($\sim 800^\circ\text{C}$) the contribution from the diffusion process can no longer be neglected as has been shown in the oxidation of $\text{TbO}_{1.5+x}$ to $\text{TbO}_{1.714}$ (16). This indicates that the activation energy of the diffusion process

should be lower than that of phase boundary reaction process.

Conclusion

The predominate kinetic behavior in this odd-even reaction suggests a phase boundary controlled mechanism when the final product is single phased. Although marked intrinsic hysteresis is observed, the pressure dependence of the phase reaction is attributed to the activity of oxygen at the phase boundary being determined by the ambient oxygen pressure. It will be important to clarify the nature of the phase boundary reaction at the atomic level by such means as high-resolution electron microscopy. In the meantime the macroscopic behavior and subtle differences among the several connected reactions in the praseodymium oxide-oxygen system are being studied.

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