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KINETICS OF THE HYDROFLUORINATION OF THORIUM DIOXIDE*

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by

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Abstract

Uniformly colored and optically isotropic interference films of thorium tetrafluoride were formed on the polished trigonal faces of single crystals of thorium dioxide by reaction with gaseous hydrogen fluoride. The kinetics were determined spectrophotometrically at six temperatures in the interval 218°C-327°C. The reaction is diffusion controlled with the film thickness proportional to the square-roots of pressure of HF(g) and time corrected for an incubation period. The rate constant is $\beta = \beta_0 \exp(-Q/RT) \text{ A}/(\text{sec-torr})^{1/2}$ in which $\beta_0 = 7.0 \times 10^2$ and $Q = 6,630 \text{ cal/mole}$ with a 75% confidence interval of $\pm 230 \text{ cal/mole}$.

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INTRODUCTION

The hydrofluorination of thoria,

is exothermic with a heat of reaction of 42.7 kcal/mole at 550°C (1).

A previous study of the analogous reaction of HF(g) with urania had shown the feasibility of examining this reaction spectrophotometrically (2).

Cleavage faces of large single crystals of thoria were polished to a fine finish, given further chemical preparation, and under closely controlled conditions reacted with HF(g) to form interference layers. The extent of reaction was determined spectrophotometrically by the measurement of interference wavelength (2). On the flat surfaces of reacted large crystals, it was possible with a metallurgical microscope to examine directly the uniformity of reaction by the uniformity of color of the interference layer. In the temperature interval 218°C-327°C first-, second-, and third-order interference films of fluoride product on thoria were brightly colored and optically isotropic. The interference peaks were sharp so that the second-order wavelengths of maximum interference were measurable to within $\pm 15 \overset{\circ}{\text{A}}$. Both the film and substrate are transparent so that the net discontinuous phase jump is zero. Thus the interference relationships and consequently the optically derived kinetic equations are not complicated by extinction coefficients (3). The interference wavelengths were translated into actual thicknesses by means of the refractive indices of the product layer which had been determined

previously by immersion spectrophotometry (4).

Both the kinetic constants and the incubation periods were obtained as functions of temperature. Metallographic examinations were routinely performed on each specimen in order to judge the quality of the film.

EXPERIMENTAL

The apparatus and reaction procedures have been described previously (2,4). Surface preparation of the reactant $\text{ThO}_2(\text{s})$ has also been reported (4). In addition to the procedure described in ref. 4, some crystals of $\text{ThO}_2(\text{s})$ were given further treatment prior to surface preparation. As received from the Norton Refractories Division (5), the single crystals of thorium were either clear with a slight smoky cast, pale pink, or translucent whitish-pink. The translucence was the result of microscopic internal fracturing along the (111) planes, and although it is not certain, the discoloration appeared to be the result of a carbon impurity. Surfaces for reaction were prepared on the (111) faces of cleaved crystals. The back sides were uncleaved in order to minimize scattered light. An anneal in Ar at approximately 2400°C to remove strain and radiation damage caused some specimens to turn black because of microscopically dispersed opaque precipitates visible at high magnifications with transmitted light in crushed fragments. Because of their small surface area, these inclusions were not seen by light reflected on the surface. Apparently they had no measurable effect upon the hydrofluorination kinetic constants derived from second-order films. Subsequent oxidation at 800°C for 1 hr in flowing O_2 caused these blackened fragments to become clear without discoloration.

Similar oxidation of unannealed crushed pieces had no visible effect upon the discoloration. Reaction specimens were prepared from the unannealed translucent and smoky crystals, a blackened crystal originally almost clear with only a slight smoky cast, a blackened crystal that had been oxidized to clarity in O_2 at $800^\circ C$, and a slightly smoky crystal that was unannealed but oxidized in O_2 . X-ray photographs of pieces from the above five specimens showed them all to consist of a single detectable phase, face-centered cubic and to have the lattice dimension $a_0 = 5.5968 \pm 0.0004 \text{ \AA}$. For comparison, a value of $5.5961 \pm 0.0001 \text{ \AA}$ for 99.99% pure ThO_2 was measured by Lambertson, Mueller and Gunzel (6), and $5.5973 \pm 0.0003 \text{ \AA}$ by Ackermann, et al for 99.9% ThO_2 (7). Substoichiometric $ThO_{1.998}$ was observed by Ackermann with originally stoichiometric thoria heated in vacuo above $2800^\circ K$ (7). Heating caused their crystals to assume a grayish cast which disappeared on heating in air at $1200^\circ K$. The composition of our crystals as received was determined chemically to be $ThO_{2.15} \pm 0.15$. A spectroscopic analysis of the same material as received gave a total cationic impurity of less than 73 ppm.

The interference wavelengths were measured on a Cary 14X spectrophotometer at an angle of incidence of 7° . Each layer was inspected either on a Bausch and Lomb research metallograph or on a Zeiss metallurgical microscope. Representative areas of specimens reacted under varying conditions were routinely photographed on the metallograph with Ektacolor "L" film.

DISCUSSION OF RESULTS

Kinetics - The relationship between film thickness, X , refractive index η , angle of incidence Φ , and interference wavelength λ_k is

$$X = \lambda_k (2K+1-\theta/\pi)/4(\eta^2 - \sin^2\phi)^{1/2} \quad (2)$$

in which θ is the net discontinuous phase jump, and K is an integer equal to zero for first-order films, one for second-order, two for third-order, etc. The refractive index of the film, η , in Eq. 2 is at λ_k . For a transparent all-dielectric interference system at near-normal incidence, $\theta = 0$ (8), and thus for a high-order film, the interference wavelengths divided by $4(\eta^2 - \sin^2\phi)^{1/2}$ are in the inverse ratio of $(2K+1)$. For fluoride films produced on thoria by hydrofluorination, within a small fraction of a percent, the λ_k 's/ $4(\eta^2 - \sin^2\phi)^{1/2}$ are in the ratios of $(2K+1)^{-1}$. Additional confirmation that the film does not absorb is that within the uncertainty of the determinations, the interference wavelengths in acetone are the same as in air. If the film absorbed, λ_k would decrease with immersion according to the magnitude of the extinction coefficient of the film (4). The above two observations are in agreement with the fact that powders of both $\text{ThO}_2(\text{s})$ and $\text{ThF}_4(\text{s})$ are white. Thus, since $\theta=0$, no correction has to be made in the kinetically derived optical equation as was the case with analogous fluoride films on urania (3).

If the hydrofluorination of thoria follows the same kinetics as the analogous reaction with urania, the relation between X , the pressure of gas P , and time t , is $X = \beta(Pt)^{1/2}$ where β is the rate constant. Figure 1 is a plot of X^2 versus t for $P=400$ torr and $K=0$ at 300°C . It is seen that although the line is straight, it does not pass through the origin, but intercepts the abscissa at a positive value, t_0 . With the intercept t_0 subtracted from t , the parabolic relation holds for all K 's as well as $K=0$ according to

$$X = \beta P^{1/2}(t-t_0)^{1/2}. \quad (3)$$

Figure 2 is a plot of X versus $(t-t_0)^{1/2}$ at 300°C and $P=400$ torr which is a straight line passing through the origin and connecting points for $K=0,1,2$ and 3 . Equation 3 is correct within one percent at 300°C for films up to 2μ in thickness. The quantity, t_0 , is taken as the incubation period of the reaction. In the following metallography section are discussed the optical observations which confirm this conclusion.

At each of the six temperatures, t_0 was determined at various wavelengths for $K=0$ and $P(\text{HF})=400$ torr. The kinetic constant, β , was then obtained from data for second-order films. At 327°C , the kinetics were studied also at 200 torr. In Table 1 are listed the values of β and t_0 at each temperature. In Figure 3 are presented the data for $\log \beta$ versus $1/T$. (For comparison, the data for urania are shown by the dashed line.) The reasonably straight line shows the correctness of writing β as $\beta = \beta_0 \exp(-Q/RT)$. A least-squares analysis gave an activation energy of $Q=6,630$ cal/mole with a 75% confidence interval of ± 230 cal/mole. The value of β_0 is $7.0 \times 10^2 \text{ }^\circ\text{A}/(\text{sec-torr})^{1/2}$. For comparison, the analogous values for uranium dioxide were $Q = 6930$ cal/mole and $\beta_0 = 8.2 \times 10^2 \text{ }^\circ\text{A}/(\text{sec-torr})^{1/2}$ (2).

In Figure 4 are plotted the values of $\log t_0$ at 400 torr versus $1/T$. The experimental errors are rather large as shown by the limits. A least-squares analysis of the data on the assumption that $t_0 = t' \exp(-Q/RT)$ gave $Q(t_0) = -19.5$ kcal/mole with a 75% confidence interval of ± 1.7 kcal/mole and $t' = 5.3 \times 10^{-8}$ sec. The plot appears to have curvature, however, so that it may be incorrect to assume that the processes occurring during the incubation period are simply activated and thus may be represented by an Arrhenius equation.

Metallography - First-order interference films of fluoride produced on thoria by Reaction 1 are not uniform in general. The basic color itself does not vary however except in intensity. The surfaces have whitish splotches varying in intensity from white (i.e., no interference) to just a very faint paling of color. Most of the surface is a smooth interference film. These splotches are in the 10-100 μ range and vary in distribution within a given film and between crystals of ThO₂ but are on all first-order films to some degree. As observed metallographically, the thinnest films with $\lambda_k(K=0) \sim 4000\text{\AA}$ appear the worst, blue thicker films are much more uniform, and second-order layers are completely isotropic and uniform for the temperature range 218°C-327°C. Within the uncertainties of measurement, different sample treatments yielded the same kinetics. However, the uncertainties are quite large in first-order films because of the variation in distribution of whitish splotches. Some specimens consistently gave a λ_k lower than the average. The spread in $\lambda_k(K=0)$ is greatest at 218°C and least at 327°C. By reflecting a greater portion of incident light, white areas broadened the peaks which, with the background curves in this study, had the effect of lowering the measured interference wavelength. The values of t_0 in Table 1 and Figure 4 are for those films in which the splotching was at a minimum. By comparison of λ_k with degree of whitish discoloration, the λ_k used in deriving the reported t_0 was estimated to be within a percent or two of the hypothetical λ_k that would be measured with no splotching. The error limits in t_0 reflect the uncertainty of this particular measurement. However the rate-constant, β , was obtained from measurements on uniform second-order films. Since the time to produce a second-order

layer is twenty times as long as t_0 on the average, a 40% variation in t_0 is a 2% error in $(t-t_0)$ for a second-order film and thus results in a 1% uncertainty in β .

The color non-uniformities, or blemishes as they have been called, produced on urania by hydrofluorination which were discussed in reference 2 and in greater detail in (9) are produced also on thoria at higher temperatures. Thus 300°C is the upper useful limit with urania, whereas films produced at 327°C with thoria are completely uniform. There appears to be an approximate 50°C difference in the temperatures at which similar birefringent microstructures form in the two systems.

Scratch and edge experiments were both performed in an attempt to identify the reaction site (see ref. 2). Because ThO_2 is transparent, the micro-fine scratches in these particular specimens could not be photographed with long exposures under dark-field illumination. With less sensitive oblique light, it was seen that a film 2 μ in thickness did not fill the scratches. From this observation alone it appeared that deposition of $\text{ThF}_4(\text{s})$ occurred at the film-substrate interface. However, to the contrary, sharp edges of microcrystals were unmistakably smoothly coated, and from this observation it appeared that deposition of $\text{ThF}_4(\text{s})$ occurred at the gas-film interface. Thus, the same contradiction occurs in the hydrofluorination of thoria as in the analogous reaction of urania.

REFERENCES

1. F. L. Cuthbert, "Thorium Production Technology" (Addison-Wesley, Reading, Mass., 1958) p. 147.
2. W. P. Ellis and B. W. Roberts, J. Chem. Phys. 39, 1176 (1963).
3. W. P. Ellis, J. Chem. Phys. 39, 1172 (1963).
4. W. P. Ellis and R. M. Lindstrom, Optica Acta (in press).
5. Refractories Division, the Norton Company, Worcester 6, Mass.
6. W. A. Lambertson, M. H. Mueller and F. H. Gunzel, Jr., J. Am. Ceram. Soc., 36, 397 (1953).
7. R. J. Ackermann, E. G. Rauh, R. J. Thorn and M. C. Cannon, J. Phy. Chem., 67, 762 (1963).
8. F. A. Jenkins and H. E. White "Fundamentals of Optics" (McGraw-Hill Book Co., Inc., New York 1957) 3rd ed., p. 514.
9. W. P. Ellis and Dana L. Douglass, Technical Document Number LA-3183 (available from Clearing House for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Virginia.)

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Table 1. Summary of Experimental Data

T°C	Rate-Constant, β $\frac{O}{A}/(\text{sec-torr})^{1/2}$	Incubation Period, t_0 min
218 $\pm$ 1	0.771 $\pm$ 0.031	30 $\pm$ 3
240	1.098 $\pm$ 0.016	11 $\pm$ 2
262	1.332 $\pm$ 0.012	3.9 $\pm$ 0.8
286	1.768 $\pm$ 0.035	2.35 $\pm$ 0.4
300	2.07 $\pm$ 0.03	1.2 $\pm$ 0.2
327	2.724 $\pm$ 0.035	0.85 $\pm$ 0.2
327	*2.78 $\pm$ 0.07	*1.7 $\pm$ 0.3

* Note: For all data, P(HF) = 400 torr, except starred values for which P(HF) = 200 torr.

LIST OF ILLUSTRATIONS

Figure 1 - Square of first-order film thickness versus time.

$\text{HF(g)} + \text{ThO}_2(\text{s})$, $P(\text{HF}) = 400$ torr and $300 \pm 1^\circ\text{C}$.

Figure 2 - Film thickness versus square-root of time corrected

for an incubation period. $\text{HF(g)} + \text{ThO}_2(\text{s})$, $P(\text{HF}) =$

400 torr and $300 \pm 1^\circ\text{C}$.

Figure 3 - Logarithmic plot of rate-constant, β , versus $1/T$.

$\text{HF(g)} + \text{ThO}_2(\text{s})$. Dashed line represents kinetic data for

$\text{HF(g)} + \text{UO}_2(\text{s})$.

Figure 4 - Logarithmic plot of the incubation period, t_0 , versus $1/T$.

$\text{HF(g)} + \text{ThO}_2(\text{s})$.

Figure 1 - Square of first-order film thickness versus time. HF(g) + ThO₂(s), P(HF) = 400 torr and 300 ± 1°C.

Figure 2 - Film thickness versus square-root of time corrected for an incubation period. HF(g) + ThO₂(s), P(HF) = 400 torr and 300 ± 1°C.

Figure 3 - Logarithmic plot of rate-constant, β , versus $1/T$. $\text{HF(g)} + \text{ThO}_2\text{(s)}$. Dashed line represents kinetic data for $\text{HF(g)} + \text{UO}_2\text{(s)}$.

Figure 4 - Logarithmic plot of the incubation period, t_0 , versus $1/T$. $\text{HF(g)} + \text{ThO}_2\text{(s)}$.