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THE SURFACE REACTION BETWEEN OXYGEN AND THORIUM

by

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-5- and -6-

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.	7
INTRODUCTION	9
MATERIALS	9
PROCEDURE	10
RESULTS	12
Solubility of Oxygen in Thorium	12
Rates of Reaction	12
DISCUSSION	15
ACKNOWLEDGMENTS.	18
REFERENCES	18

LIST OF TABLES

Table 1. Rate Constants, k , Determined at Various Temperatures	16
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LIST OF FIGURES

Figure 1. Cutaway Section of Reaction-Tube Assembly	11
Figure 2. Oxidation of Thorium at 900 C	14
Figure 3. Thorium-Oxygen Reactions -- Variation of Rate Constant, k , With Temperature.	17

~~CONFIDENTIAL~~

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-7- and -8-

ABSTRACT

The rate of reaction of oxygen with arc-melted and rolled iodide thorium has been found to obey the parabolic rate law in the temperature range of 850 to 1415 C at 1 atmosphere pressure. The rate constant can be expressed as $k = 6 \times 10^7 e^{-63,300/RT} \text{ cm}^2/\text{sec}$. The energy of activation, 63,300 cal/mole, has a probable error of 2,100 cal/mole.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

-9-

INTRODUCTION

The reactions between gases and metals generally have been found to obey either a linear, parabolic, cubic, or logarithmic rate law. The factors controlling the various laws as well as their derivations have been adequately described in the literature⁽¹⁻⁷⁾ and will, therefore, not be repeated here.

Levesque and Cubicciotti⁽⁸⁾ studied the oxidation of thorium at 45 cm pressure in the temperature range of 250 to 700 C. They found the reaction to proceed in accordance with the parabolic rate law between 250 and 350 C and calculated the energy of activation to be 31,000 cal/mole. Between 350 and 450 C, the rates of oxidation were reported to be linear with time. An energy of activation of 22,000 cal/mole was found for this temperature range. Above 450 C, they reported that the temperature of the sample rose considerably above the temperature of the furnace, resulting in nonisothermal conditions.

The present investigation was made to study the reaction between oxygen and thorium for longer times and at higher temperatures and pressures than those studied by Levesque and Cubicciotti.

MATERIALS

The thorium used in this investigation was iodide crystal bar produced by the de Boer process. The crystal bar was arc melted, forged into a 1-in. square rod, and cold finished to a 5/16-in. cylindrical rod. Test specimens, each 1-1/2 in. long, were machined from this rod. The diameters of the specimens were reduced to slightly less than 5/16 in. to remove surface contamination.

The thorium was analyzed by spectrographic, chemical, and vacuum-fusion methods. The principal impurities found were 300 ppm by weight each of carbon and oxygen and 100 ppm each of silicon and molybdenum. All other impurities were present in concentrations of less than 100 ppm.

The oxygen used in this study was prepared from degassed potassium permanganate by the method described by Hoge⁽⁹⁾. The gas was dried by passing through a dry ice-acetone cold trap prior to its reaction with the thorium specimen.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

-10-

PROCEDURE

The experimental apparatus was similar to that described in an earlier report⁽¹⁰⁾ with a few modifications. Since the reaction being studied involved oxygen, it was necessary to use a zirconia tube to separate the thermocouple from the thorium specimen instead of a graphite tube liner. The dead volume of the reaction system was materially reduced by suspending a Vycor tube, sealed at both ends, from a hook in the cap of the reaction tube. A sketch of this arrangement is shown in Figure 1.

A 4-kw tungsten-gap-type Lepel converter was used to heat the specimens. Temperature readings were made with a Pt-Pt + 10% Rh thermocouple calibrated against an optical pyrometer as in previous work⁽¹⁰⁾. The uncorrected thermocouple readings were low and required a correction of about 200 C throughout the temperature range used.

A cylindrical thorium specimen to be used in a reaction-rate study was abraded on 240-, 400-, and 600-grit kerosene-soaked silicon carbide papers. The kerosene minimized oxidation during abrasion and was removed by successively rinsing in naphtha, ether, and cp acetone. The specimen was then suspended in the reaction tube as noted above. After evacuating, the specimen was degassed by heating at 1200 C or higher for at least 15 min to remove hydrogen prior to adding the oxygen. Oxygen was added to the reaction tube to atmospheric pressure in measured amounts from a 50-ml glass buret. The progress of the surface reaction was followed by observing pressure changes in the closed system with a full-length open-end mercury manometer. Further measured amounts of oxygen were added from time to time to maintain the pressure between about 3/4 and 1 atmosphere. The system was evacuated and the specimen was cooled to room temperature in vacuum after the reaction had been followed for the desired time.

The difference between the quantity of oxygen added to the reaction system and that remaining in the gas phase is a measure of the gas absorbed by the specimen at any time. The quantity of gas reacted per unit area was computed by using the original geometrical dimensions of the specimen. The rate constants were calculated by determining the slope of the line resulting when the square of the gas absorbed per unit area was plotted versus time.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

-11-

FIGURE 1. CUTAWAY SECTION OF REACTION-TUBE ASSEMBLY

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~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

-12-

RESULTS

Solubility of Oxygen in Thorium

The solid solubility of oxygen in thorium is low, even at elevated temperatures. Evidence of this can be obtained by observing the angular inclusions of oxide found in the microstructure of thorium. Magnesium-reduced thorium usually contains from 0.10 to 0.15 wt % oxygen and many oxide inclusions are evident. Arc-melted and rolled iodide thorium usually contains less than 0.05 wt % oxygen, and, although fewer in number, discrete oxide inclusions can be noted in its microstructure. Even this lesser amount of oxygen in the arc-melted iodide thorium exceeds the solubility limit of oxygen in thorium at elevated temperatures. This was shown quite clearly by reacting a sample of this thorium with oxygen at 1415 C for 3 hr. The surface oxide layer was removed and the rest of the sample was analyzed for oxygen. A sample of the base material with no oxygen added was also analyzed. Both specimens analyzed 0.028 ± 0.003 wt % oxygen. These results indicate that no oxygen was diffused into the specimen as a result of the reaction at 1415 C, and that the thorium previously had been saturated with oxygen at a temperature higher than 1415 C, probably during reduction or arc melting. This low oxygen solubility made it impossible to obtain diffusion data.

Rates of Reaction

The rate of surface reaction of oxygen with thorium was studied in the temperature range of 850 to 1415 C at atmospheric pressure. It was observed that, as the oxygen first contacts the thorium, an exothermic reaction occurs, increasing the temperature of the specimen instantaneously by as much as several hundred degrees Celsius. A similar observation was made by Levesque and Cubicciotti⁽⁸⁾ for temperatures above 450 C. With the use of induction heating and the continuous control of power available, this effect could be counteracted by reducing rapidly the heat input from the converter. At higher temperatures, where the rate of reaction is quite rapid, the temperature could be effectively controlled by this technique. However, at lower temperatures, where the rate of reaction is normally quite slow, the amount of oxygen reacted during even a brief nonisothermal period is relatively large compared to the amount of gas reacted isothermally thereafter. This was especially significant at temperatures below about 1055 C where as much gas might be absorbed

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

-13-

in the first fraction of a minute with the specimen at the elevated temperature as would be absorbed by the specimen at the desired temperature in several hours.

A plot of the rate of reaction of oxygen with thorium at 900 C is shown in Figure 2 to illustrate the typical case described above. The squares of the amounts of oxygen absorbed per unit area (ml/cm^2)², plotted against time in minutes, are shown by the open circles. The gas is absorbed very rapidly at the start of the reaction, the line rising almost vertically from the origin during the first minute or two of reaction. The data do not appear to fit the parabolic law, as indicated by the straight section of the plot, until 15 to 30 min of the reaction time has elapsed.

It appears that the rapid initial absorption of gas at the elevated temperature causes an oxide film of significant thickness to form on the surface of the thorium specimen. However, during this nonisothermal period as the specimen is rapidly increasing in temperature and later cooling to the operating temperature, the film is cracked in certain areas giving little or no protection against further oxidation. This cracking appears to be caused by the different coefficients of expansion of the oxide and the metal. As the heat input is adjusted, the reaction becomes isothermal and the cracking of the oxide film ceases. The film then becomes protective, causing the reaction to be diffusion controlled and establishing a parabolic rate.

One method of correcting for the rapid initial oxidation observed is to subtract the amount of oxygen absorbed during the initial brief period of rapid nonisothermal reaction. This correction was used by Mallett, et al.⁽¹¹⁾, in treating experimental data obtained when nitrogen was reacted with beta zirconium. Morton and Baldwin⁽¹²⁾ used a somewhat similar correction for their data on the scaling of titanium in air. The equation describing the reaction in the present investigation is

$$(w - w_0)^2 = k(t - t_0) \quad (1)$$

instead of the familiar parabolic equation

$$w^2 = kt, \quad (2)$$

where

w is the quantity of oxygen absorbed in time, t,
w₀ is the quantity of oxygen absorbed in time, t₀, and
k is the parabolic rate constant.

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-14-

FIGURE 2. OXIDATION OF THORIUM AT 900 C

CONFIDENTIAL

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-15-

In all cases where the correction was applied in the work, t_0 is equal to 5 min or less. A plot of the oxygen absorbed versus time, which corrects the experimental data for the oxidation at 900 C, is shown by the open squares in Figure 2. The corrected data follow the parabolic rate law and the slope of a log-log plot of these data is 0.53, very close to the theoretical slope of 0.50.

The slopes obtained from log-log plots of the corrected data for the gas absorbed in milliliters per square centimeter versus time for the 14 experimental runs in the temperature range of 850 to 1415 C are listed in Table 1. The slopes vary from 0.42 to 0.58, showing that the corrected experimental data follow the parabolic rate law reasonably well. The values of the rate constants, k , calculated for the reactions are also listed in Table 1. Figure 3 shows a plot of these parabolic rate-law constants versus $1/T$. The position of the best straight line through the experimental points was calculated using the method of least squares. The energy of activation of the reaction was calculated using the Arrhenius-type equation $k = Ae^{-Q/RT}$. The energy of activation is $63,300 \pm 2,100$ cal/mole. The rate constant, k , in square centimeters per second can be expressed as:

$$k = 6 \times 10^7 e^{-63,300/RT} \quad (5)$$

DISCUSSION

One aspect of the oxidation of thorium at high temperatures is the relatively high activation energy for the reaction compared with those found in the oxidation of other metals. Levesque and Cubicciotti⁽⁸⁾ reported an energy of activation of 31,000 cal/mole for the parabolic oxidation of thorium between 250 and 350 C, but our results indicate an activation energy of 63,300 cal/mole for the temperature range 850 to 1415 C. Energy of activation values for other parabolic oxidation reactions range from 18,000 to 55,000 cal/mole.⁽¹³⁾ However, Cubicciotti⁽¹⁴⁾ reported a value of 62,000 cal/mole for the high-temperature parabolic oxidation of beryllium. Since the rate-determining step in the oxidation reaction is the diffusion of some species through the growing oxide film, the observed activation energy is that of diffusion through the oxide.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

-16-

TABLE 1. RATE CONSTANTS, k , DETERMINED
AT VARIOUS TEMPERATURES

Run	Temperature, C	$k \times 10^3$ cm^2/sec	t_0 , min	Slope of log- log plot*
1	850	0.038	2	0.55
2	900	0.160	1	0.53
3	955	0.222	5	0.58
4	1005	0.780	5	0.58
5	1055	2.78	1	0.51
6	1110	3.10	0	0.42
7	1110	2.62	0	0.42
8	1160	28.1	0	0.52
9	1210	25.8	0	0.52
10	1210	59.9	0	0.56
11	1260	63.7	0	0.50
12	1310	59.3	0	0.48
13	1310	104.	0	0.44
14	1415	748.	0	0.55

* Slope of experimental data corrected to t_0 , w_0 .

Slope of 0.50 indicates a parabolic rate law is being obeyed.

~~CONFIDENTIAL~~

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-17-

FIGURE 3. THORIUM-OXYGEN REACTIONS — VARIATION OF RATE CONSTANT, k , WITH TEMPERATURE

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-18-

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-19- and -20-

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