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The Reduction of Thoria with Graphite

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The reduction of thoria with excess graphite was studied with a thermobalance in vacuum between 1620 and 1920 K. From $ThO_2:C = 1:50$ the rate of reaction was independent of the ratio of the reactants; the endproduct was always ThC_2. The logarithmic weight loss was directly proportional to the time, and the *Arrhenius* plot showed a break at 1710 K: below this temperature the activation energy was found to be 440 kJ, above 260 kJ. The temperature corresponding to the break coincides with the transition temperature of monoclinic to body-centered tetragonal ThC_2.

(Keywords: Graphite; Kinetics; Reduction; Thoria; Thoriumcarbide)

Die Reduktion von Thoriumoxid mit Graphit

Die Reduktion von Thoriumoxid mit Graphit im Überschuß wurde mittels einer Thermowaage zwischen 1620 und 1920 K im Vakuum untersucht. Ab $ThO_2:C = 1:50$ war die Reaktionsgeschwindigkeit vom Mischungsverhältnis unabhängig; das Endprodukt war immer ThC_2. Der logarithmische Gewichtsverlust war direkt proportional der Zeit, und die *Arrhenius*gerade zeigte einen Knickpunkt bei 1710 K: unterhalb dieser Temperatur ergab sich eine Aktivierungsenergie von 440 kJ, oberhalb eine solche von 260 kJ. Die Temperatur des Knickpunkts entspricht der Umwandlungstemperatur von monoklinem in tetragonal raumzentriertes ThC_2.

Introduction

During a previous study of the reactions between refractory oxides and graphite[1] a few preliminary tests were performed with thoria by following the change in CO pressure with time. Since the experiments were insufficient for a kinetic analysis of the reaction, it was decided to carry out a more extensive investigation.

The thermodynamics of the reaction between ThO_2 and graphite have been studied manometrically by *Prescott* and *Hincke*[2] between

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2 000 and 2 500 K, by *Hollahan* and *Gregory*[3] with a torsion effusion method between 1 560 and 1 680 K, and again manometrically by *Heiss* and *Djemal*[4] between 2 156 and 2 410 K and by *Djemal* and *Dodé*[5] between 1963 and 2 043 K. The temperature of the beginning of the reaction between thoria and graphite has been stated to be < 1 600 K[6], 1 650 K[7], 1 700 K[1], 1 870 K[8], > 1 920 K[9], and 1 910 K[10], resp. The reaction product using an excess of graphite has been found to be ThC_2[2–4,6]. Although thorium dicarbide is of interest as fuel for graphite-base high-temperature gas-cooled nuclear reactors and the reaction between thoria and graphite has been employed to produce spherical ThC_2 particles[11], the only kinetic study of the reaction appears to have been made by *Imai* and coworkers[6].

In the present investigation mixtures of thoria powder and small round spheres, resp., with graphite powder were heated using a thermobalance and the rates of reaction were measured isothermally at various temperatures by following the weight-change as a function of time.

Experimental Procedure

The materials used in the investigation were spectrographically pure graphite powder (United Carbon Products Co., Mich., USA) with a particle size of 44 μm, 99.9% ThO_2 microspheres (NUCHEM, Hanau, BRD), 99.9% ThO_2 powder (Heavy Minerals Co., USA), and 99.9% pure thoria crucibles (ZIRCOA, USA).

The thoria crucibles were comminuted and, as was the case with the ThO_2 powder, only particles of sizes < 56 μm were used. The ThO_2 microspheres were black and of uniform size with the following average dimensions and properties:

diameter 0,503 mm, volume 0.0666 mm^3, surface area 0.795 mm^2, weight 0.6525 mg, density 9.79 g cm^{-3}; 87.86 wt% Th, 60 ppm C, 0.5 ppm U.

To minimize oxygen adsorption the graphite powder was heated in high vacuum at 1 500 K until the weight became constant, and after cooling was stored in argon atmosphere. Mixtures of the following molar ratios ThO_2:C were prepared: A = 1:5, B = 1:15, C = 1:50, D = 1:150. Mixtures A, B, and C were prepared in amounts of about 1 g, and between 80 and 110 mg of mixture, evenly spread in a graphite crucible, were used in one experiment. Because of the high and very voluminous graphite content mixture D was separately prepared for each experiment. The depth of the powder in the graphite crucible was about 0.5 to 1.0 mm for A and B, 1.0—1.5 mm for C, and ~ 2,4 mm for D.

The experiments were carried out with a thermobalance (Mettler Thermoanalyzer TA—1) in connection with a resistance furnace (Mettler SHT-furnace) for temperatures up to 2 700 K. This furnace consisted of a watercooled steel shell with a vertical slotted hexagonally shaped tungsten heating element (110 mm long, 23 mm inner diameter, 0.2 mm wall thickness) which was concentrically surrounded by several tungsten radiation shields. The crucible holder in the center of the furnace consisted of two flat tungsten squares (6 mm × 6 mm) side by side, separated about 0.5 mm and welded to the top of a tungsten tube (3 mm diameter, 100 mm long, the upper 10 mm slotted) which fitted onto a four-bore alumina tube (2.8 mm diameter, 160 mm long). Two thin

W-26% Re wires were spot-welded to the tungsten squares at the outer edges and passed into two holes near the junction of the tungsten tube and the alumina tube. A third hole contained a tungsten wire welded to the tungsten tube so that each tungsten square had attached to its outer edge a W/W-26% Re thermocouple. The bottom end of the alumina tube ended in a plug which fitted directly onto the arm of a semimicro balance (sensitivity ± 0.03 mg) and which also transmitted the emf of the thermocouples. The encased semimicro balance and the furnace were screwed together to give a high-vacuum tight seal. Since both the heating element and the crucible holder were made of tungsten, measurements could be performed only in vacuum or in inert gas atmosphere. The sample could be observed through a movable quartz window in the upper part of the furnace so that for each observation a fresh part of the window was exposed and the measurement was not influenced by evaporated material deposited on the window.

Temperature calibration was carried out by visual observation of the melting points of pure metals through the eye piece of a micropyrometer (Au 1337 K, Mn 1 520 K, Ni 1 728 K, Fe 1 811 K, Pt 2 045 K). Thin wires or ribbons were twisted into spirals and placed into tungsten crucibles (4.5 mm outer diameter, 0.5 mm wallthickness) so that contact with the crucible was minimized and most of the spiral was standing free. The metals were heated first rapidly to about 100 K below the melting point and then slowly (2 K min^{-1}) until melting commenced and the power to the furnace was turned off. Melting could be thus clearly observed and the temperature of the furnace determined with great accuracy. The melting points of Au, Mn, Ni, and Fe were also checked with a Pt/10% Rh-Pt thermocouple.

The crucibles machined from spectroscopically pure graphite rods had an inner diameter of 10 mm and an inner height of 2.5 mm. They were placed on the crucible holder with a tungsten disc (2.5 mm thick) in between to prevent direct contact between graphite and the thermocouple. Prior to use the graphite crucibles were heated in high vacuum at 2 100 K until their weight was constant. Measurements were carried out under a vacuum of 10^{-2} to 10^{-3} Pa. Before opening the furnace the entire system was filled with argon to minimize the amount of oxygen which would enter the system during manipulation. The argon was purified by passing through a column (1 000 mm long, 40 mm diameter) filled with activated copper (BTS-catalyst) which was heated to 430 K. It was then cooled and dried with magnesium perchlorate.

Results and Discussion

In a preliminary experiment a sample of mixture A with ThO_2-powder was heated with a heating rate of 1 K min^{-1} up to 2 220 K. The reaction commenced with a measureable rate at 1 620 K and was completed at 2 020 K. The weight loss was 17.43 wt % and corresponded to the equation

$$ThO_2 + 5C \rightarrow ThC_x + 2CO + (3-x)C$$

Since the theoretical weight loss based on the loss of two moles CO is calculated to be 17.39 wt%, oxygen was quantitatively removed.

In the following experiments for the determination of the reaction rate constant k and the activation energy the ThO_2-powder—graphite

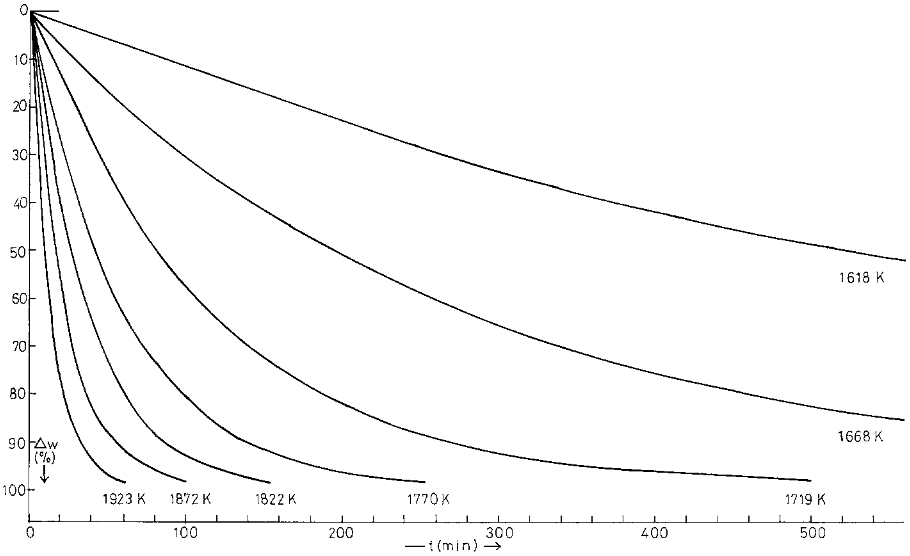

Fig. 1. Relative weight loss as a function of time for mixture A ($ThO_2 + 5C$)

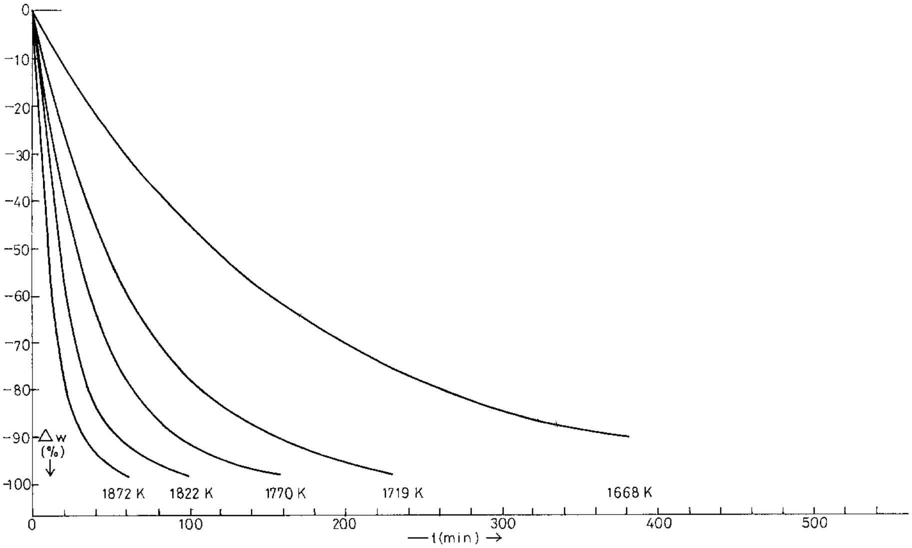

Fig. 2. Relative weight loss as a function of time for mixture B ($ThO_2 + 15C$)

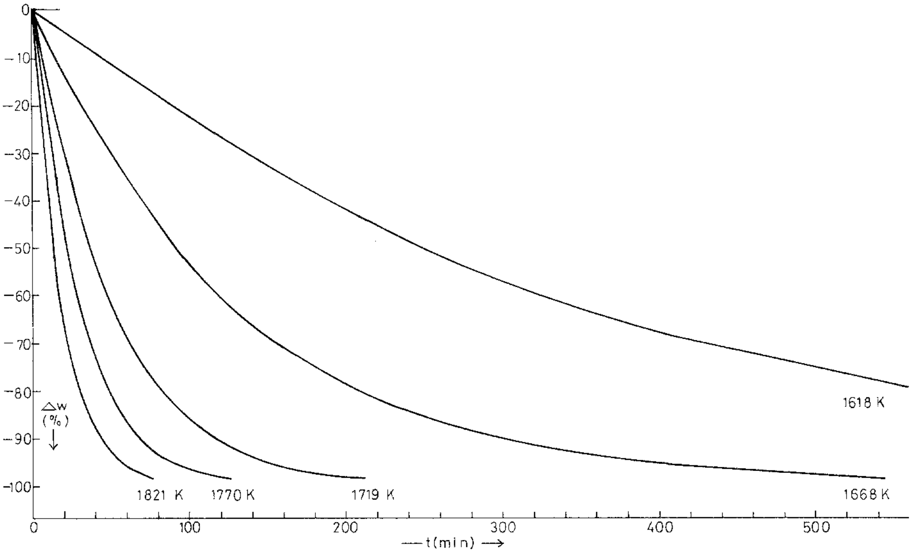

Fig. 3. Relative weight loss as a function of time for mixture C ($ThO_2 + 50C$)

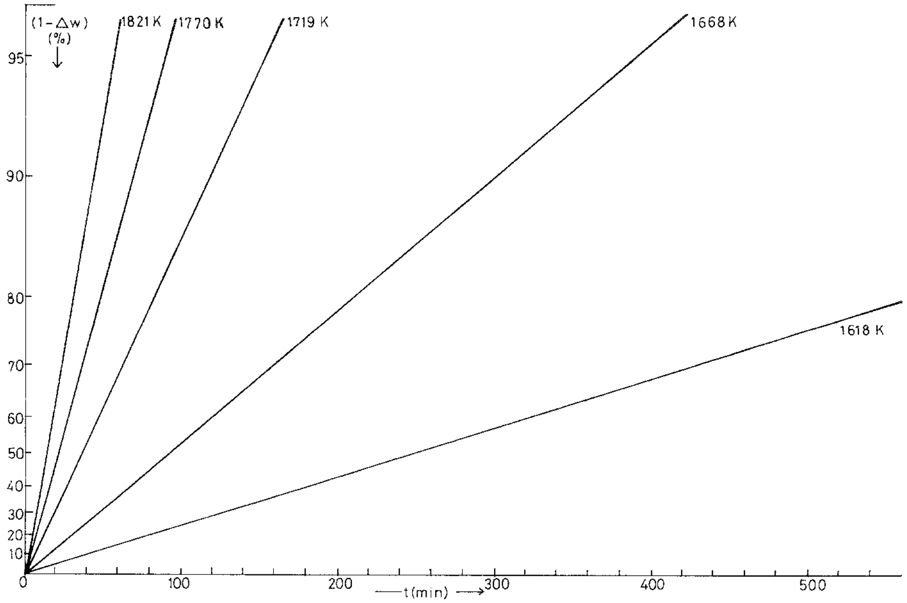

Fig. 4. Logarithm of relative weight loss as a function of time for mixture C ($ThO_2 + 50C$)

Table 1. *Reaction rate constants k for the reaction between thoria and graphite*

Composition	T (K)	t_H (min)	k (min^{-1})
A (1 mM ThO_2 : 5 mM C)	1618	523	0.00132
	1668	196	0.00353
	1719	81.0	0.00853
	1770	42.0	0.0165
	1821	25.7	0.0269
	1872	16	0.0433
	1923	10.5	0.0660
B (1 mM ThO_2 : 15 mM C)	1668	116	0.00599
	1719	46.0	0.0151
	1770	27.4	0.0253
	1821	16.5	0.0420
	1872	10.3	0.0673
C (1 mM ThO_2 : 50 mM C)	1618	244	0.00284
	1668	90.7	0.00764
	1719	35.4	0.0196
	1770	21.0	0.0330
	1821	12.8	0.0541
C (compacted and crushed)	1618	54.8	0.01265
	1668	22.0	0.03150
	1719	12.6	0.0550
	1770	8.1	0.0955
C (crucible comminuted; particle size < 56 μm)	1623	350	0.00198
	1673	135	0.00513
	1723	67.7	0.01023
	1773	33.5	0.02068
	1823	23.6	0.02936
	1873	15.0	0.04620
D (1 mM ThO_2 : 150 mM C)	1668	89.4	0.00775
	1719	31.9	0.02179
	1770	18.9	0.03666

mixtures were heated at a rate of 100 K min^{-1} to the reaction temperatures which for mixture A were selected to be every 50 K between 1 620 and 1 920 K. At higher temperatures the reaction proceeded so rapidly that in spite of a heating rate of 100 K min^{-1} the weight loss during the time necessary to reach the desired temperature introduced too high an uncertainty. For a similar reason mixture B could be studied only at temperatures up to 1 870 K, and mixtures C and D only up to 1 820 K, since the rate of reaction increased with higher graphite content from mixture A to C.

The results for mixtures A, B and C are shown in Figs. 1 to 3 where the relative weight loss, ΔW, recorded continuously by the balance (in weight percent of the amount of CO given off relative to the total loss of CO) is plotted versus the time. The weight loss curves approach exponentially 100% and follow a first order rate law with a maximum deviation from the calculated curve even at 90% of less than ± 3%. The curves for mixture D are practically identical with those for mixture C and are therefore not shown. If the logrithm of the relative weight loss is plotted as a function of time one obtains straight lines as shown for mixture C in Fig. 4. From the slope of $-\ln(1-\Delta W)$ vs. t the reaction rate constants k have been calculated and are listed in Table 1. Also tabulated is t_H, the time in minutes for the reaction to be 50% completed. In Fig. 5 the logarithms of k are plotted as a function of the reciprocal absolute temperature. For all four mixtures A, B, C, and D the points for each mixture fall on two straight lines intersecting at about 1 710 K the lines of the different mixtures all having about the same slope. Below 1 710 K an activation energy of 440 kJ, above 1 710 K

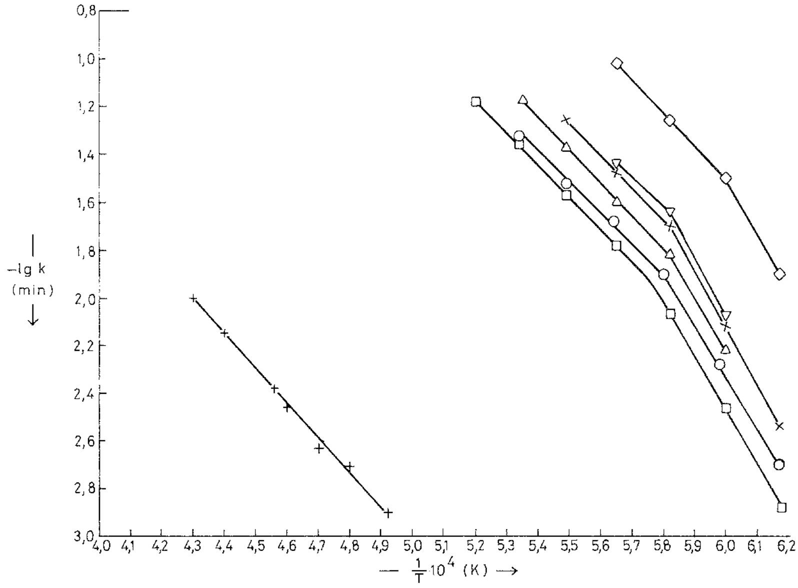

Fig. 5. Logarithm of the reaction rate constant as a function of reciprocal temperature (□: mixture A; △: mixture B; × : mixture C; ◇: mixture C (compacted and crushed); + : mixture C (microspheres); o: mixture C (comminuted crucibles); ▽: mixture D)

an activation energy of 260 kJ was calculated from the slopes. The reaction product of mixture A (originally a layer 10 mm in diameter, 1 mm high) was a gray-yellow rather hard sintered platelet (6 mm diameter, < 1 mm thick) containing about 4.5 wt% C. The rest according to X-ray analysis was ThC_2. The same result was obtained whether the mixture was heated above (at 1 920 K) or below (at 1 620 K) the intersection. On air the reaction product decomposed rather rapidly to a more voluminous yellow-gray powder. Some decrease in volume was also observed with mixture B but not with C and D on account of the large excess of graphite. Further experiments were made at 1 773 K with mixture C to study the influence of the amount of the mixture and of the surface contact on the rate of reaction (Table 2). Mixture C was chosen because the ratio ThO_2 to C of 1:50 with a particle ratio of ~ 1:260 and a surface ratio of ~ 1:200 guaranteed that each ThO_2 particle was covered by and imbedded in graphite particles, and because a further increase of the ratio (mixture D) did not change the rate of reaction. The reaction rate constant k was essentially independent of the sample size between 36 and 120 mg but different depths of the mixtures in crucibles of the same diameter can cause a slight scatter of the values of k.

Table 2. *Reaction rate at 1 773 K as a function of the sample size and of the surface contact*

Sample size (in mg)	$-\log k$	Remarks
121.05	1.50	mixed, evenly spread
115.85	1.51	mixed, evenly spread
79.30	1.44	mixed, evenly spread
37.71	1.45	mixed, evenly spread
38.23	1.41	mixed, evenly spread
115.74	1.51	mixed, heaped
39.36	1.46	mixed, heaped
36.34	1.51	mixed, heaped
77.70	1.38	compacted (low pressure), crushed, spread
36.66	1.44	compacted (low pressure), crushed, spread
37.90	1.23	compacted ($\sim 3 \cdot 10^8$ Pa), crushed, spread
41.42	1.21	compacted ($\sim 7 \cdot 10^8$ Pa), crushed, spread
25.65	1.70	compacted ($\sim 3 \cdot 10^8$ Pa), not crushed
31.97	1.91	compacted ($\sim 7 \cdot 10^8$ Pa), not crushed

The contact between the ThO_2-powder and graphite was increased by compacting mixture C in a piston with cylinder to a pill 5 mm in diameter and 1.5 mm high. At a pressure low enough just to compact the pill k is not materially changed (Table 2). If the pressure is high and the pill is subsequently crushed the rate of reaction is significantly increased. On the other hand, if pills compacted under high pressure are not crushed the rate is markedly reduced. The reaction of pills compacted under a pressure of $\sim 7 \times 10^8$ Pa was studied also as a function of temperature.

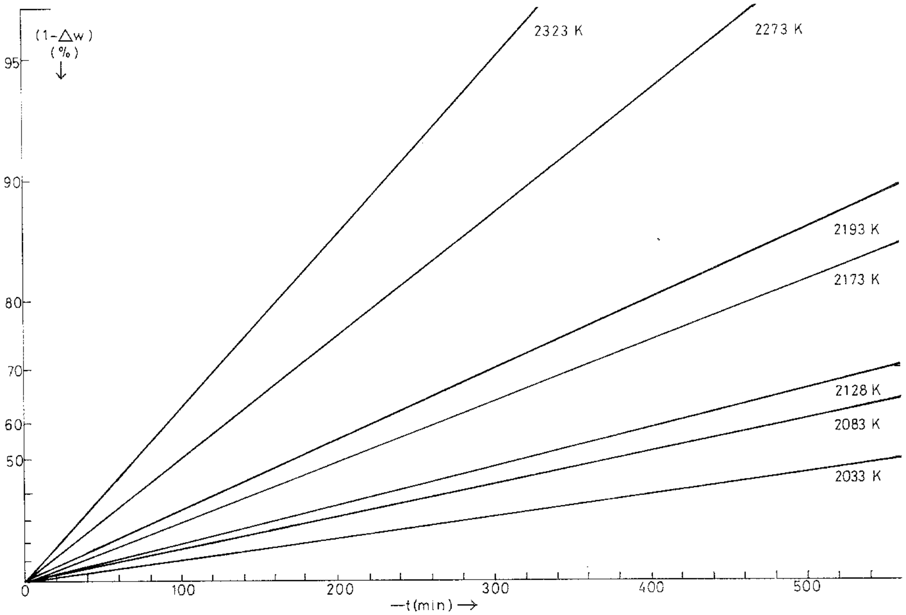

Fig. 6. Logarithm of relative weight loss as a function of time for mixture C (microspheres)

The rate of reaction increased noticeably (Fig. 5) but the slopes of the two intersecting lines remained unchanged although the temperature of intersection seemed to have shifted to a somewhat lower temperature (1 670 K).

In a further experiment mixture C was prepared with powder from comminuted ThO_2 crucibles of the same particle size ($< 56\,\mu m$) as the ThO_2 powder. The rate of reaction was slightly reduced (Fig. 5) because of the smoother surface, the more compact form of the particles and the smaller contact area but both the slopes of the two intersecting lines and the temperature of intersection remained unchanged.

In an attempt to define more precisely the contact area between ThO_2 and graphite a thin-walled ThO_2-ring (cut from a crucible) was imbedded in graphite and heated at 1 773 K. The reaction was exceedingly slow and did not go to completion since hollow spaces formed between the ring and the graphite powder and the ring in the course of the reaction slowly sank to the bottom of the crucible. Experiments with ThO_2 microspheres of well-defined dimensions were more successful. Although the rate of reaction was considerably slower since the diameter of the microspheres was about ten times larger than that of the ThO_2-powder, reproducible results were obtained between 2 033 and 2 323 K (Fig. 6). The slope of the $\log k$ vs. $1/T$ curve was identical with the slopes obtained with the ThO_2-powders above the temperature of intersection (Fig. 5). Activation energy and reaction mechanism were therefore the same.

In compacted powder mixtures of metal oxides and graphite the reaction occurs via the intermediate reaction products CO and CO_2, i.e.

$$MO_x + x\mathrm{CO} = x\mathrm{CO}_2 + M \tag{1}$$

$$\mathrm{CO}_2 + \mathrm{C} = 2\,\mathrm{CO} \tag{2}$$

and in many systems so far studied the overall rate of reduction is controlled primarily by the rate of oxidation of graphite in the CO/CO_2 mixture that exists within the interparticle pores. When a carbide is formed the rate of reaction might be controlled by other mechanisms. If the rate is controlled by mass transfer (diffusion) in the reaction-product layer then the following equation should apply for spherical particles[12, 13]:

$$1 - 2\,\Delta W/3 - (1 - \Delta W)^{2/3} = (k/r_0^2)\,t \tag{3}$$

with r_0 the initial radius of the reactant particles. The reduction of uranium dioxide with graphite[14] and of ilmenite with graphite[15] both in argon, and of thoria with graphite[6] in vacuum followed Eq. (3).

If the rate is controlled by a slow chemical reaction at the receding interface then[12]

$$1 - (1 - \Delta W)^{1/3} = (k/r_0)\,t \tag{4}$$

The results of the present investigation followed neither Eq. (3) nor Eq. (4). A plot of $[1 - 2\,\Delta W/3 - (1 - \Delta W)^{2/3}]$ and of $[1 - (1 - \Delta W)^{1/3}]$, resp., vs. t did not give straight lines.

The reaction between thoria and graphite under the experimental conditions of the present investigation can best be expressed by the equation for product growth controlled by product nucleation at each active site[16]

$$-\ln(1-\Delta W) = kt \qquad (5)$$

i.e. for the case of a uniform internal reaction like that of complete gas diffusion in a porous pellet[17]. Such a linear dependence of $-\ln(1-\Delta W)$ on time was observed by *Turkdogan* and *Vinters*[18, 19] in the reduction of Fe_2O_3 by hydrogen or by CO/CO_2-mixtures. As the rate controlling step they suggested the reaction of H_2 (or CO) with oxygen on the surface of a thin layer of iron on the pore walls of wustite. In analogy the rate of reaction between thoria could be controlled by the reaction of CO with oxygen at the surface of the ThC_2 layer.

From the average dimensions of the ThO_2 microspheres a surface area of 12.18 $cm^2 g^{-1}$ is obtained. The surface area of the ThO_2-powder assuming spherical shape is 122.7 $cm^2 g^{-1}$ for a diameter of 50 μm, and 306.5 $cm^2 g^{-1}$ for a diameter of 20 μm. Since the particles in the ThO_2 powder have irregular shapes and therefore definitely a larger surface area, the increase of the rate of reaction by a factor of 250 when going from the microspheres to the ThO_2-powder can be explained by the larger surface contact area of the latter. Compacting the ThO_2-powder—graphite mixture under pressure (7×10^8 Pa) will further increase the contact area and therefore further increase the rate of reaction by a factor of 2.8.

The product of the reaction as identified by X-ray analysis was ThC_2, and the quantitative removal of oxygen was taken as proof that the carbide did not contain oxygen. *Potter*[20] in his study of the Th—O—C observed a solubility of oxygen in ThC in the presence of ThC_2 and ThO_2 up to $ThC_{0.8}O_{0.2}$ but apparently no solubility of oxygen in ThC_2. *Heiss* and *Djemal*[4] observed complete reduction to ThC_2 only with molar ratios $C:ThO_2 \geq 4:1$. To explain deviations from calorimetric data they proposed as the end product of the reaction $ThC_{1.96}O_{0.04}$.

According to *Benz* and *Stone*[21] the carbon-saturated ThC_2 phase boundary is constant with the value of 1.94 ± 0.03 between 1 463 and 2 273 K. ThC_2 is monoclinic from room temperature to 1 713 K, body-centered tetragonal between 1 713 K and 1 768 K, and face-centered cubic from 1 768 K up to the melting point (2 883 K). The temperature of intersection of the two straight lines $\log k$ vs. $1/T$ (Fig. 5) was found to be 1 710 K, and corresponds to the $\alpha \rightleftharpoons \beta$ transition of ThC_2. Obviously the structure of the ThC_2 layer has a pronounced influence on the reaction mechanism with the activation energy much larger in the monoclinic stability range than in the b c tetragonal and/or f c c range. The $\beta \rightleftharpoons \gamma$ transition temperature is too close to the $\alpha \rightleftharpoons \beta$

transition to obtain an activation energy in the β-ThC_2 stability range but it is reasonable to assume that it will not differ very much from the activation energy in the γ-range.

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