On the Solubility and the Velocity of Dissolution of Corundum under Hydrothermal Conditions[*]

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The fact that the dehydration of boehmite under hydrothermal conditions gives corundum directly has been noted by Laubengayer and Weisz1), Ervin and Osborn2) and Kennedy3). Using this reaction, the present authors obtained grains consisting of separated single crystals of corundum of a uniform size and habits4). The grains showed excellent qualities as abrasives for germanium, silicon and glass materials5). The uniformity in the grain size and habits may be attributed to a proper reaction mechanism under hydrothermal conditions. The mechanism, however, has not been clarified yet. In order to obtain some basic and important data for a discussion of the mechanism, the present authors have measured the solubilitiy of corundum under hydrothermal conditions.

The solubilities of aluminum hydroxides and aluminas as measured by Russell, Edwards and Taylor6) have been widely accepted. It is, however, almost impossible to extrapolate these values to the temperature at which boehmite may be transformed into corundum. Yalman, Shaw and Corwin have presented

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[*] This investigation was reported on at the 15th Annual Meeting of the Chemical Society of Japan, No. 3314 (Kyoto, April, 1962).

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1) A. W. Laubengayer and R. S. Weisz, *J. Am. Chem. Soc.*, **65**, 247 (1943).

2) G. Ervin, Jr. and E. F. Osborn, *J. Geol.*, **59**, 391 (1951).

3) G. C. Kennedy, *Am. J. Sci.*, **257**, 563 (1953).

4) G. Yamaguchi and H. Yanagida, 13th Annual Meeting of the Chemical Society of Japan, No. 5A27 (Tokyo, April, 1960).

5) G. Yamaguchi, H. Yanagida, Y. Suwa and S. Soejima, Congress on Artificial Minerals, No. 2-2 (Osaka, November, 1961).

6) A. S. Russell, J. D. Edwards and C. S. Taylor, *Transaction AIME J. Metals*, 1123 (1955).

some data about the solubility of corundum[7], but they are insufficient to discuss the transformation of boehmite into corundum without the seed crystal, which has been observed practically only above 440°C[4]. The data above 420°C have not been included in their paper[7]. In the present work, the solubility of corundum has been measured up to 500°C under different conditions of hydrothermal pressure, alkaline solution and reaction period.

Experiments

Procedure.—Fused corundum grains of a uniform size, over 99 per cent pure and weighing 0.40 mg. on the average, were weighed and laid in a Morey-type reactor with an aqueous solution of sodium hydroxide or sodium carbonate. They were heated from room temperature to an appointed temperature within 15 min. and then kept at that temperature for some hours in an electric furnace. The hydrothermal pressure at that temperature was calculated from Kennedy's table showing the relations among pressure, density and temperature of water[8]. They were also quenched to room temperature within 15 min. The quenched contents, the solution and the residue were washed out completely with distilled water into a glass beaker. The residue was then washed with hot hydrochloric acid, and the gelatinous precipitate of aluminum hydroxide was eliminated by decantation, leaving only the corundum residue in the beaker.

Analysis.—Aluminum dissolved in a solution is usually analyzed by the EDTA titration method, with an indicator such as chromazurol S[9]. This method, however, cannot applied when an aluminum hydroxide is precipitated. A hydrothermal solution may become supersaturated through cooling it to room temperature, and aluminum hydroxide may be newly precipitated. In this case, the solubility obtained by the titration method may show a lower value. Actually, the gelatinous precipitate was observed in some runs in the present work. The true corundum residue was separated from the gelatinous precipitate by the above-mentioned procedure, and the difference in the weight of corundum between that placed in the reactor and that which remained after hydrothermal treatment was considered to indicate the dissolved alumina in the solution.

Results and Discussion

Effects of the Sample Quantity on the Solubility and Velocity of Dissolution.—0.5 or 1.0 g. of the corundum grain was treated with 3 normal sodium carbonate aqueous solutions at 450°C under a 1000 atmospheric pressure; the results of this experiment are shown in Table I and Fig. 1. It can be seen there that the time derivative of dissolved corundum has a term proportional to the surface area of the sample. This may mean that the rate-determinant process of the dissolution is an elementary process occurring on or near the surface of the grain and that the diffusion velocity in space is sufficiently large. After being supersaturated, the dissolved alumina recrystallizes into corundum and the concentration of dissolved alumina approaches 0.024 g. per 1 cc. of the solution regardless of the sample quantity. This value corresponds to a 0.47 g. equiv. of dissolved alumina per 1 g. equiv. of sodium carbonate in the solution and can be considered as an equilibrium solubility. Here, the 1 g. equiv. of corundum 1/6 Al_2O_3, is 17 g. and that of sodium carbonate 1/2 Na_2CO_3, is 53 g.

TABLE I. SOLUBILITY OF CORUNDUM IN SODIUM CARBONATE AQUEOUS SOLUTION

(Corundum grain; 0.40 mg. per each grain, 33 cm^2/g.; Hydrothermal condition; 450°C, 1000 atm., 3 N Na_2CO_3 5 cc.)

Initial corundum grain wt.	Reaction period	Dissolved corundum wt.		$\frac{\text{g. eq.}}{\text{g. eq. of } Na_2CO_3}$
g.	hr.	g.	g./cc.	
1.000	0.5	0.065	0.013	0.25
1.000	1.0	0.131	0.026	0.51
1.000	1.5	0.132	0.026	0.52
1.000	2.0	0.177	0.035	0.69
1.000	4.0	0.155	0.031	0.61
1.000	5.0	0.145	0.029	0.57
1.000	9.0	0.126	0.025	0.49
1.000	12.0	0.121	0.024	0.47
1.000	26.0	0.120	0.024	0.47
0.500	1.5	0.085	0.017	0.33
0.500	2.0	0.090	0.018	0.35
0.500	3.0	0.152	0.030	0.60
0.500	4.0	0.205	0.041	0.80
0.500	8.0	0.139	0.028	0.54
0.500	10.0	0.130	0.026	0.51
0.500	40.0	0.123	0.025	0.48

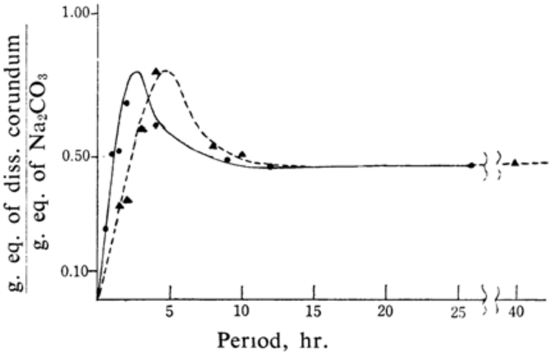

Fig. 1. Dissolution curve of corundum in sodium carbonate aqueous solution at 450°C (1000 atm.).
● —— 1.000 g. ▲ ---- 0.500 g.

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[7] R. G. Yalman, E. R. Shaw and J. F. Corwin, *J. Phys. Chem.*, **64**, 300 (1960).

[8] G. C. Kennedy, *Am. J. Sci.*, **248**, 540 (1950).

[9] M. Z. Theis, *Anal. Chem.*, **144**, 106 (1955).

TABLE II. SOLUBILITY OF CORUNDUM IN SODIUM HYDROXIDE AQUEOUS SOLUTION AT 400°C

Initial corundum wt. g.	Reaction period hr.	g. eq. of NaOH	Liquid volume cc.	Press. atm.	Dissolved corundum g.	$\frac{\text{g. eq.}}{\text{g. eq. of NaOH}}$
1.000	2.0	0.005	4.9	500	0.171	2.01
1.000	6.0	0.005	4.9	500	0.218	2.57
1.000	41.0	0.005	4.9	500	0.218	2.57
1.000	2.0	0.005	5.9	1000	0.172	2.02
1.000	4.0	0.005	5.9	1000	0.202	2.38
1.000	18.0	0.005	5.9	1000	0.230	2.70
1.000	42.0	0.005	5.9	1000	0.223	2.62
1.000	2.0	0.005	6.4	1500	0.173	2.03
1.000	3.0	0.005	6.4	1500	0.219	2.58
1.000	3.0	0.010	5.9	1000	0.376	2.21
1.000	8.0	0.010	5.9	1000	0.424	2.49
1.000	12.0	0.010	5.9	1000	0.420	2.47
1.000	17.5	0.010	5.9	1000	0.435	2.56
1.000	0.8	0.010	6.4	1500	0.187	1.10
1.000	2.0	0.010	6.4	1500	0.281	1.61
1.000	4.0	0.010	6.4	1500	0.343	2.02
1.000	8.0	0.010	6.4	1500	0.434	2.55
1.000	18.0	0.010	6.4	1500	0.444	2.61

TABLE III. SOLUBILITY OF CORUNDUM IN SODIUM HYDROXIDE AQUEOUS SOLUTION AT 450°C

Initial corundum wt. g.	Reaction period hr.	g. eq. of NaOH	Liquid volume cc.	Press. atm.	Dissolved corundum g.	$\frac{\text{g. equiv.}}{\text{g. eq. of NaOH}}$
1.000	0.5	0.005	3.4	500	0.185	2.18
1.000	1.0	0.005	3.4	500	0.161	1.98
1.000	2.0	0.005	3.4	500	0.221	2.60
1.000	12.0	0.005	3.4	500	0.232	2.73
1.000	1.0	0.005	5.2	1000	0.191	2.25
1.000	2.4	0.005	5.2	1000	0.221	2.60
1.000	3.0	0.005	5.2	1000	0.228	2.69
1.000	12.0	0.005	5.2	1000	0.237	2.79
1.000	1.0	0.005	5.9	1500	0.192	2.26
1.000	8.0	0.005	5.9	1500	0.227	2.68
1.000	1.0	0.010	5.2	1000	0.377	2.22
1.000	1.6	0.010	5.2	1000	0.431	2.54
1.000	4.0	0.010	5.2	1000	0.439	2.56
1.000	12.0	0.010	5.2	1000	0.445	2.62
1.000	20.0	0.010	5.2	1000	0.457	2.69
1.000	2.0	0.010	5.9	1500	0.383	2.25
1.000	2.0	0.010	5.9	1500	0.411	2.42
1.000	8.0	0.010	5.9	1500	0.442	2.60
5.000	18.0	0.020	2.0	100	0.948	2.28
5.000	20.0	0.020	2.0	100	0.910	2.68

Effects of Pressure, Alkaline Concentration and Temperature on the Solubility and Velocity of Dissolution.—The solubility of corundum at 400°C and at 450°C were measured under atmospheric pressures of 100, 500, 1000 and 1500 with 0.005, 0.010 and 0.020 g. equiv. of sodium hydroxide in an aqueous solution for various reaction periods. Table II and Fig. 2 show the results at 400°C, and Table III and Fig. 3 those at 450°C. The supersaturation which was found in the sodium carbonate solution could not be observed here in this sodium hydroxide solution. The total gram equivalent of alumina in a saturated solution may be expressed in terms of temperature, total gram equivalent of sodium hydroxide in the solution, and hydrothermal pressure as follows:

$$x_\infty^{\text{cor}}=f(T)\cdot g(x_{\text{OH}})\cdot h(P_{\text{H}_2\text{O}}) \qquad (1)$$

where, x_∞^{cor} is the total gram equivalent of dissolved alumina in the saturated solution, $f(T)$, the temperature term, $g(x_{\text{OH}})$, a function of

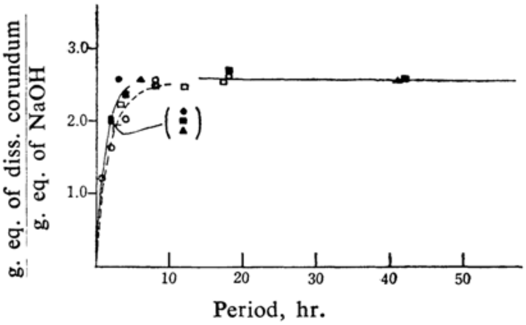

Fig. 2. Dissolution curve of corundum in sodium hydroxide aqueous solution at 400°C.

	P_{H_2O} atm. 500	1000	1500	
x_{OH} 0.005	▲	■	●	——
x_{OH} 0.010		□	○	----

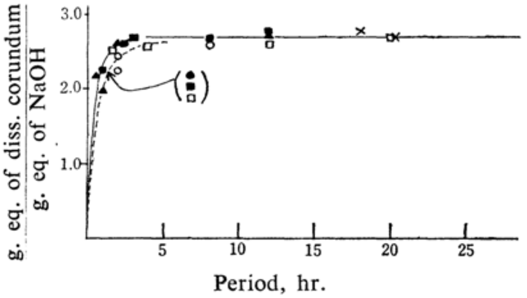

Fig. 3. Dissolution curve of corundum in sodium hydroxide aqueous solution at 450°C.

	P_{H_2O} atm. 100	500	1000	1500	
x_{OH} 0.005		▲	■	●	——
x_{OH} 0.010			□	○	----
x_{OH} 0.020	×				

the total gram equivalent of sodium hydroxide in the solution, and $h(P_{H_2O})$, the pressure factor. In the present work, x_∞^{cor} appeared nearly proportional to x_{OH} independently of pressure. This means that

$$g(x_{OH}) \simeq x_{OH} \quad (2)$$

$$h(P_{H_2O}) \simeq 1 \quad (3)$$

Substituting 2 and 3 into 1, the present authors obtained the temperature term as:

$$f(T) = \begin{cases} 2.58_8 \pm 0.02 & \text{at } 400^\circ\text{C} \quad (4) \\ 2.70_0 \pm 0.05 & \text{at } 450^\circ\text{C} \quad (5) \end{cases}$$

From the fact that the velocity of dissolution appeared proportional to the total gram equivalent of sodium hydroxide in the solution independently of the hydrothermal pressure, it can be considered that the rate-determinant process of dissolution is an elementary process occurring on or near the sample surface and that the diffusion velocity in space is sufficiently large, as the sodium carbonate solution.

$$\frac{\mathrm{d}(x_{cor}/x_{OH})}{\mathrm{d}t} = kS(x_\infty^{cor}/x_{OH} - x_{cor}/x_{OH}) \quad (6)$$

may be proposed as a general equation of dissolution in the present case; here k is a velocity constant dependent on the temperature, S, the total surface area of corundum grains at t, and x_{cor} the total gram equivalent of dissolved alumina in the solution, also at t. In Eq. 6, $\mathrm{d}(x_{cor}/x_{OH})/\mathrm{d}t$ indicates the relative velocity of dissolution and $(x_\infty^{cor}/x_{OH} - x_\infty^{cor}/x_{OH})$, a driving force to a saturated solution instead of a term of the concentration gradient. Two variables, S and x_{cor}, are included in 6. The total surface area of the initial corundum grains before hydrothermal treatment is expressed as

$$S_0 = N_0\theta_0\left(\frac{17}{4}a_0\right)^{2/3} \quad (7)$$

where S_0 indicates the initial surface area in cm^2, N_0, the numbers of corundum grains, θ_0, a factor depending on the shape, and a_0, the gram equivalent of corundum per each initial grain. It is assumed that N_0 and θ_0 are invariants throughout the hydrothermal dissolution treatment. Therefore, it may be also expressed as

$$S = N_0\theta_0\left(\frac{17}{4}a\right)^{2/3} \quad (8)$$

where S is the total surface area of corundum grains during dissolution at t and a, the gram equivalent of corundum per each grain during dissolution, also at t. A_0, the total gram equivalent of the initial corundum grains, can be expressed as:

$$A_0 = N_0 a_0 \quad (9)$$

and A, that of the corundum residue during dissolution at t, as:

$$A = N_0 a \quad (10)$$

From the mass balance in the corundum,

$$A_0 \equiv A + x_{cor} \quad (11)$$

Substituting 7, 8, 9, 10 and 11 into 6, an equation including only one variable, x_{cor}/x_{OH}, is obtained:

$$\frac{\mathrm{d}(x_{cor}/x_{OH})}{\mathrm{d}t} = kS_0\left(\frac{A_0}{x_{OH}}\right)^{-2/3}\left(\frac{A_0}{x_{OH}} - \frac{x_{cor}}{x_{OH}}\right)^{2/3} \times\left(\frac{x_\infty^{cor}}{x_{OH}} - \frac{x_{cor}}{x_{OH}}\right) \quad (12)$$

This can be solved as follows;

$$\frac{2}{3}\ln\left\{\frac{\left(\frac{A_0}{x_{\mathrm{OH}}}\right)^{1/3}-\left(\frac{A_0}{x_{\mathrm{OH}}}-\frac{x_\infty^{\mathrm{cor}}}{x_{\mathrm{OH}}}\right)^{1/3}}{\left(\frac{A_0}{x_{\mathrm{OH}}}-\frac{x_{\mathrm{cor}}}{x_{\mathrm{OH}}}\right)^{1/3}-\left(\frac{A_0}{x_{\mathrm{OH}}}-\frac{x_\infty^{\mathrm{cor}}}{x_{\mathrm{OH}}}\right)^{1/3}}\right\}$$
$$+\frac{1}{3}\ln\left\{\frac{\left(\frac{x_\infty^{\mathrm{cor}}}{x_{\mathrm{OH}}}\right)-\left(\frac{x_{\mathrm{cor}}}{x_{\mathrm{OH}}}\right)}{\left(\frac{x_\infty^{\mathrm{cor}}}{x_{\mathrm{OH}}}\right)}\right\}$$
$$+\sqrt{3}\left\{\left(\frac{A_0}{x_{\mathrm{OH}}}\right)-\left(\frac{x_\infty^{\mathrm{cor}}}{x_{\mathrm{OH}}}\right)\right\}^{1/3}$$
$$\times\left\{\tan^{-1}\frac{\left(\frac{A_0}{x_{\mathrm{OH}}}-\frac{x_{\mathrm{cor}}}{x_{\mathrm{OH}}}\right)^{1/3}+\frac{1}{2}\left(\frac{A_0}{x_{\mathrm{OH}}}-\frac{x_\infty^{\mathrm{cor}}}{x_{\mathrm{OH}}}\right)^{1/3}}{\frac{\sqrt{3}}{2}}\right.$$
$$\left.-\tan^{-1}\frac{\left(\frac{A_0}{x_{\mathrm{OH}}}\right)^{1/3}+\frac{1}{2}\left(\frac{A_0}{x_{\mathrm{OH}}}-\frac{x_\infty^{\mathrm{cor}}}{x_{\mathrm{OH}}}\right)^{1/3}}{\frac{\sqrt{3}}{2}}\right\}$$
$$=k(T)S_0\left(\frac{A_0}{x_{\mathrm{OH}}}\right)^{-2/3}\left(\frac{A_0}{x_{\mathrm{OH}}}-\frac{x_\infty^{\mathrm{cor}}}{x_{\mathrm{OH}}}\right)^{2/3}t \qquad (13)$$

The velocity constant, $k(T)S_0$, can be calculated according to 13 by comparison with the experimental results as follows;

$$k(T)S_0=\begin{cases}0.80/\mathrm{hr.} & \text{at } 400^\circ\mathrm{C} \quad (14)\\ 1.90/\mathrm{hr.} & \text{at } 450^\circ\mathrm{C} \quad (15)\end{cases}$$

The surface area of the initial corundum grains is estimated to be 33 cm²/g. assuming the shape of corundum grain to be a tetragonal prism 1 : 1 : 2 in edge length. Putting this value into S_0 of 14 and 15, the present authors calculated the general velocity constant, not including the S_0 term, to be:

$$k(T)=\begin{cases}0.024/\mathrm{cm}^2\,\mathrm{hr.} & \text{at } 400^\circ\mathrm{C} \quad (16)\\ 0.056/\mathrm{cm}^2\,\mathrm{hr.} & \text{at } 450^\circ\mathrm{C} \quad (17)\end{cases}$$

From the velocity constant ratio, 0.056/0.024, with the temperature difference between 400°C and 450°C, the activation energy for the rate-determinant process is considered to be of the order of 3.8 kcal.

Effect of Temperature on the Equilibrium Solubility.—From 2 and 3, the equilibrium solubility can be considered in the term of $f(T)$ independently of pressure. The $f(T)$ term was obtained at 350°C and at 500°C in addition as at 400°C and 450°C. The $f(T)$ value at 350°C was measured for more than 70 hr. under an atmospheric pressure at 500 and that at 500°C for more than 12 hr. under an atmospheric pressure of from 500 to 1500. These are summarized in Table IV and are illustrated in Fig. 4.

TABLE IV. TEMPERATURE DEPENDENCE OF THE SOLUBILITY OF CORUNDUM

Temp. °C	g. eq. of diss. corundum / g. eq. of NaOH
350	2.46 ± 0.09
400	$2.58_8 \pm 0.02$
450	$2.70_0 \pm 0.05$
500	2.85 ± 0.10

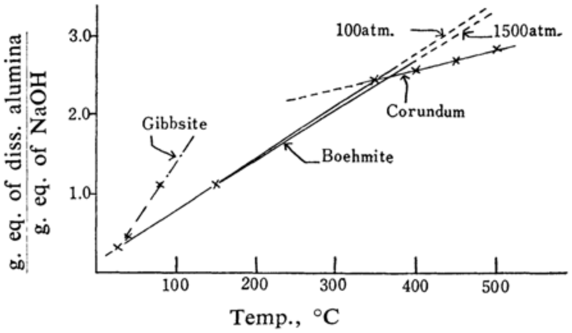

Fig. 4. Solubility curves of aluminas in sodium hydroxide aqueous solution ($Na_2O \lessdot 100$ g./l.).

Russell et al.⁶⁾ showed boehmite to be dissolved by 5.6% as alumina in 90 g. of sodium oxide per 1 l. aqueous solution at 150°C. This corresponds to a 1.14 g. equivalent of boehmite to be dissolved in a 1 g. equiv. of a sodium hydroxide aqueous solution. Here, the 1 g. equiv. of boehmite, 1/3 AlOOH, is 20 g. Russell et al. proposed that the equilibrium point between boehmite and gibbsite should be 27°C with extrapolation of the solubility. Near this temperature of 30°C, gibbsite is dissolved by 1.82% as alumina in 96.8 g. of sodium oxide per 1 l. of an aqueous solution¹⁰⁾. This corresponds to a 0.34 g. equiv. of gibbsite to be dissolved in a 1 g. equivalent of a sodium hydroxide aqueous solution. Here, the 1 g. equiv. of gibbsite, 1/3 $Al(OH)_3$, is 26 g. In these alkaline concentrations lower than 100 g. of sodium oxide per 1 l., the ratio of the gram equivalent of dissolved alumina to that of sodium hydroxide in the solution may be considered to be invariant with the concentrations at the same temperature¹¹⁾. The solubility of gibbsite at 40°C is 0.45, and that at 80°C is 1.11 in the ratio.

The equilibrium point between boehmite and corundum varies with the pressure³⁾; 355°C under 100 atm., 360°C under 500 atm., 365°C under 1000 atm. and 370°C under 1500 atm. The solubility curves of boehmite and corundum may intersect each other at these points. This indicates that the supersaturation

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10) "Kagaku-Binran," Ed. by the Chemical Society of Japan, Maruzen Co., Tokyo (1958), p. 610.

11) J. Shimozato, Ph. D. Thesis, Tokyo Univ. (1961).

factor seems to be about 0.12 at the temperature where boehmite can be transformed into corundum without seed.

The curves illustrated in Fig. 4 give the basic information for a discussion about the transformation mechanism and for the growth of a single crystal of corundum under hydrothermal conditions. The present authors will discuss the mechanism in a later paper.

Summary

The solubility of corundum was measured under hydrothermal conditions. The equilibrium solubility seems independent of the pressure. The temperature term, $f(T)$, the ratio of the gram equivalent of dissolved corundum to that of sodium hydroxide in the solution, was as follows:

$$f(T)=\begin{cases} 2.46\pm0.09 & \text{at } 350^\circ\text{C} \\ 2.58_8\pm0.02 & \text{at } 400^\circ\text{C} \\ 2.70_0\pm0.05 & \text{at } 450^\circ\text{C} \\ 2.85\pm0.10 & \text{at } 500^\circ\text{C} \end{cases}$$

The velocity of dissolution was proportional to the surface area of the corundum crystal and the total gram equivalent of sodium hydroxide in the solution. This is shown as

$$\frac{\mathrm{d}(x_{\mathrm{cor}}/x_{\mathrm{OH}})}{\mathrm{d}t}=kS(x_{\infty}^{\mathrm{cor}}/x_{\mathrm{OH}}-x_{\mathrm{cor}}/x_{\mathrm{OH}})$$

The velocity constant was as follows:

$$k(T)=\begin{cases} 0.024/\mathrm{cm}^2\ \mathrm{hr.} & \text{at } 400^\circ\text{C} \\ 0.056/\mathrm{cm}^2\ \mathrm{hr.} & \text{at } 450^\circ\text{C} \end{cases}$$

The nucleation of corundum may be initiated at the supersaturation ratio of 0.12 without seed.

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