# Corundum $\alpha$-$Al_2O_3$ Formation from the Dehydration of Boehmite $\gamma$-AlOOH under Hydrothermal Conditions. II. The Reaction Rates and the Mechanism*

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Aluminum hydroxide are transformed into corundum under hydrothermal conditions near 400°C. In the previous paper,[2] the present authors investigated the factors determining the grain size of the corundum produced from the hydrothermal dehydration of boehmite and proposed a scheme for the reaction mechanism. It seems essential that there be in the reaction a process for forming hydrated polyaluminate ions with a structure related to the lattice of the product phase, corundum in the present case. In the present work, the reaction rates of corundum formation will be measured for the purpose of further discussion of the reaction mechanism.

## Experimental

**Procedure.** — 1.20 or 3.60 g. of boehmite is weighed and laid in a Morey-type reactor, the inner volume being 10 ml., with an appropriate amount

* Subtitled "Investigations into the Processes of Solid Phase Formation." No. 3. The first one is "On the Reaction Mechanism of Boehmite Formation from the Dehydration of Gibbsite,"[1] while the second is Part I of the present main title: "Factors Determining the Grain Size of Corundum and a Proposal for the Formation Mechanism."[2]

1) G. Yamaguchi and H. Yanagida, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 770 (1963).

2) G. Yamaguchi and H. Yanagida, This Bulletin, **36**, 1155 (1963).

of the solvent, 0.1 or 1.0 N aqueous sodium hydroxide. The amount is calculated from Kennedy's table showing the relation among the P. V. T. values of water,[3] in order to produce a hydrothermal pressure of 1000 atm. at the reaction temperature. The reactor is heated up to the reaction temperature within 15 min. in an electric furnace and thereafter kept at that temperature for various periods; then it is quenched to room temperature within 5 min. The residues produced consist of grains of boehmite and/or corundum. The grains are washed with dilute hydrochloric acid and then with pure water, and dried at 110°C.

**The Determination of the Reaction Rates.**—The reaction rates of corundum formation are determined by measuring the ignition loss of the residues. The percentage of boehmite in a residue is calculated from the difference in weight before and after the residue has been heated at 1000°C for 1 hr. in air. In the present work, the ignition loss of boehmite treated at the temperature of 435—445°C under a hydrothermal pressure of 1000 atm. was found to be 16.18%, a value which corresponds to $Al_2O_3$: $1.08H_2O$. Boehmite is usually found in a non-stoichiometric form, $Al_2O_3:(1+x)H_2O$.[4] The present authors will discuss the behavior of the non-stoichiometric water in a later paper.[5]

## Results

The results are shown in Figs. 1 to 5 and are summarized in Table I. The present authors determined the length of the induction period before the onset of the corundum formation by extrapolating the function $f(x,t)\equiv t_x-(t_{2x}-t_x)$ to $x=0$, where $t_x$ indicates the time (hours) required for the formation of corundum by $x$%.

**The Effect of the Initial Amount of Boehmite upon the Reaction Rates of Corundum Formation.**—The reaction rates were first measured under the following conditions: temperature 445°C; the solvent, 0.1 N sodium hydroxide; the pressure, 1000 atm. and the initial amount of boehmite, $B_0$, 1.20 or 3.60 g. without the addition of seed crystals of corundum. Figure 1 shows

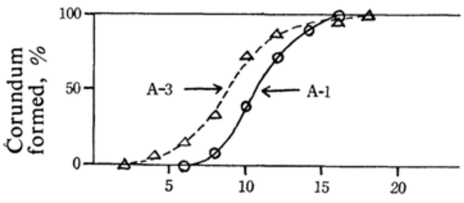


Fig. 1. The reaction rate of corundum formation; 445°C, 1000 atm., 0.1 N NaOH, A-1; $B_0=1.20$ g., A-3; $B_0=3.60$ g., No corundum seed added.

3) G. C. Kennedy, *Am. J. Sci.*, 257, 563 (1953).
4) B. C. Lippens, Ph. D. Thesis of Technische Hochschule, Delft (1961).
5) G. Yamaguchi and H. Yanagida, unpublished.

the results; here A-1 donotes the run of the initial amount of boehmite, $B_0$, 1.20 g., and A-3, that of 3.60 g. We can easily observe that the induction period of A-3 is shorter than that of A-1. The function $f(x, t)$ gives the induction period of the run A-1, 6.6 hr., and that of the run A-3, 2.8 hr. The induction period becomes shorter with the increase the initial amount of boehmite. The curves of the reaction rates after these induction periods are similar, except that a slight retardation of the reaction is noticeable in the curve A-3, especially in the last stage.

**The Effect of the Alkaline Concentration of the Solvent on the Reaction Rates.**—Next the reaction rates were measured under similar conditions to those of A-1 and A-3; that is, the temperature was 445°C, the pressure, 1000 atm., and the initial amount of boehmite, $B_0$, 1.20 or 3.60 g. without the addition of seed crystals of corundum, though in the present runs the alkaline concentration of the solvent was 1.0 N sodium hydroxide. The results are shown in Fig. 2, in which B-1 denotes the run

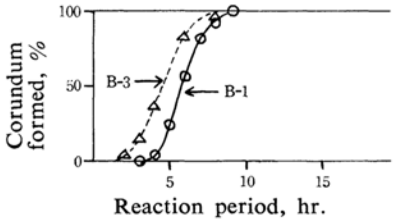


Fig. 2. The reaction rate of corundum formation; 445°C, 1000 atm., 1 N NaOH, B-1; $B_0=1.20$ g., B-3; $B_0=3.60$ g., No corundum seed added.

of the initial amount of boehmite, $B_0$, 1.20 g., and B-3, that of 3.60 g. The induction period of B-3, 1.6 hr., is shorter than that of B-1, 3.6 hr. The induction period also becomes shorter with the increase in the initial amount of boehmite, as is true also in the A runs. The curves after both these induction periods are similar, as was also found in the A runs. Comparing the induction period of A-1 to that of B-1, and the length of A-3 to that of B-3, we find that the induction period becomes shorter with the increase in the alkaline concentration of the solvent.

**The Effect of Seed Crystals of Corundum on the Reaction Rates.**—Third, the reaction rates were measured under conditions similar to those of A-1; that is, the temperature was 445°C; the pressure, 1000 atm.; the initial amount of boehmite, $B_0$, 1.20 g., and the solvent, 0.1 N sodium hydroxide, but here seed crystals of corundum with a surface area of about 1.5 cm$^2$ were added beforehand to the

TABLE I. REACTION RATES OF CORUNDUM FORMATION UNDER SOME HYDROTHERMAL CONDITIONS

| No. of run | | A-1 | A-3 | B-1 | B-3 | AN-1 | AT-1 | ANT-1 |
|---|---|---|---|---|---|---|---|---|
| Temp., °C | | 445 | 445 | 445 | 445 | 445 | 435 | 435 |
| Pressure, atm. | | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 |
| Normality of NaOH | | 0.1 | 0.1 | 1.0 | 1.0 | 0.1 | 0.1 | 0.1 |
| Initial amount of boehmite, g. | | 1.20 | 3.60 | 1.20 | 3.60 | 1.20 | 1.20 | 1.20 |
| Seed crystal of corundum, $cm^2$ | | 0 | 0 | 0 | 0 | 1.5 | 0 | 1.5 |
| Reaction rates % corundum formed | 5 hr. | 0 | 8 | 25 | 69 | 18 | 0 | 0 |
| | 10 hr. | 40 | 72 | 100 | 100 | 84 | 0 | 20 |
| | 15 hr. | 83 | 95 | 100 | 100 | 100 | 0 | 65 |
| | 20 hr. | 100 | 100 | 100 | 100 | 100 | 0 | 100 |
| | 60 hr. | 100 | 100 | 100 | 100 | 100 | 0 | 100 |
| Induction period, hr. | | 6.6 | 2.8 | 3.6 | 1.6 | 3.4 | >60 | 8.1 |
| $t_{70\%}-t_{30\%}$, hr. | | 2.4 | 2.5 | 1.2 | 1.4 | 2.6 | ... | 2.8 |

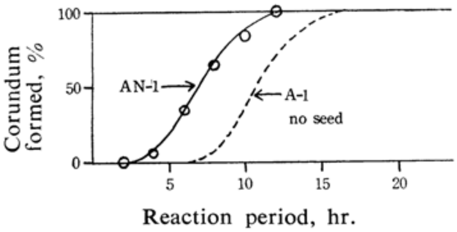


Fig. 3. The reaction rate of corundum formation; 445°C, 1000 atm., 0.1 N NaOH, AN-1: $B_0=1.20$ g,, corundum seed 1.5 $cm^2$ added.

boehmite. The results are shown in Fig. 3, where they are denoted as AN-1; in this figure the run A-1 without any seeds is also shown as a reference. The seed crystals of corundum do shorten the induction period, 6.6 hr. for A-1 to 3.4 hr. for the present AN-1, but it does not have any remarkable effect upon the reaction rate after the induction period. Although the seed crystals grew by about 0.001 g./$cm^2$ hr. throughout the reaction, most of the grains of corundum were formed separately from the seeds.

**The Effect of the Reaction Temperature on the Reaction Rates without Seed Crystals.**—The residue of the run AT-1, obtained from the hydrothermal treatment of boehmite, initially 1.20 g. without any seed crystals of corundum, in 0.1 N sodium hydroxide under 1000 atm. at 435°C for up to 60 hr., was only boehmite grains. No crystals of corundum could be found with microscopic observation. Boehmite had been completely converted into corundum, however, with treatment similar to that of run A-1 at 445°C for less than 20 hr. The temperature difference, 10°C in the present case, had a remarkable effect on the initiation of corundum formation when no seed crystals of corundum had been added beforehand to the boehmite. The curves of the reaction rate of

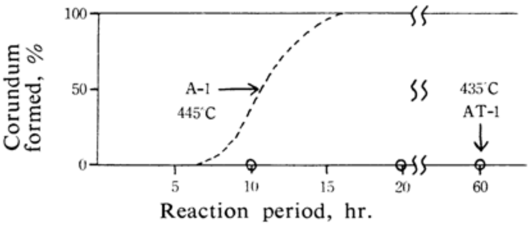


Fig. 4. The reaction rate of corundum formation; 435°C, 1000 atm., 0.1 N NaOH, AT-1: $B_0=1.20$ g., No corundum seed added.

A-1 at 445°C and the present AT-1 at 435°C are shown in Fig. 4.

**The Effect of the Reaction Temperature on the Reaction Rates with the Addition of Seed Crystals of Corundum.**—The residues of the run ANT-1 obtained from the hydrothermal treatment of boehmite, initially 1.20 g. with addition of the seed crystals of corundum with a surface area of about 1.5 $cm^2$, in 0.1 N sodium hydroxide under 1000 atm. at 435°C and for various reaction periods have shown that the reaction of corundum formation takes place under the present conditions. The curve of the reaction rate of the run ANT-1 is shown in Fig. 5, where that of AN-1 at 445°C is also shown as a reference. The induction period of AN-1, 3.4 hr., has been lengthened to 8.1 hr.

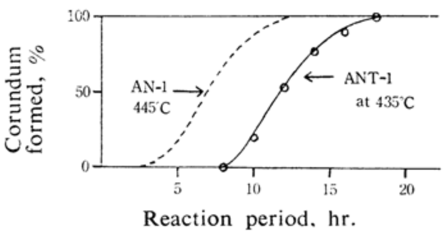


Fig. 5. The reaction rate of corundum formation; 435°C, 1000 atm, 0.1 N NaOH, ANT-1: $B_0=1.20$ g., corundum seed 1.5 $cm^2$ added.

for the present ANT-1 by lowering the temperature by 10°C. The curve of the reaction rate of the run ANT-1 after the induction period is almost the same as that of the run AN-1. The temperature difference of 10°C had a noticeable effect on the initiation of the corundum formation, but it had no remarkable effect on the propagation of the reaction. The effects of the temperature, however, are different depending on whether or not the seed crystals have been added beforehand. At 435°C the initiation of corundum formation can take place in less than 10 hr. when the seed crystals of corundum have been added beforehand, as in the present ANT-1 run, but the reaction does not take place for up to 60 hr. when the seed crystals have not been added, as in the run AT-1.

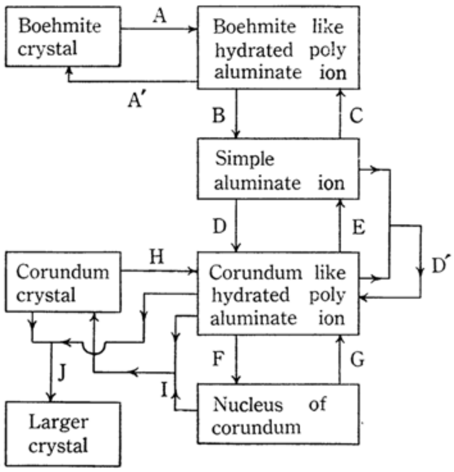


Fig. 6. The reaction scheme for corundum formation under hydrothermal condition.

## Discussion

With the measurements of the reaction rates of corundum formation under some hydrothermal conditions, we have established the following facts; 1) The induction period becomes shorter with an increase in the initial amount of boehmite (A-1 to A-3, B-1 to B-3). 2) The induction period becomes shorter with an increase in the alkaline concentration of the solvent (A-1 to B-1, A-3 to B-3). 3) The curves of the reaction rates after the induction periods are similar, independently of the initial amount of boehmite (A-1 and A-3, B-1 and B-3). 4) The addition of seed crystals of corundum shortens the induction period (A-1 to AN-1). 5) However, the reaction rates after the induction period are inifluenced by the addition of seed crystals (A-1 to AN-1). 6) When no seed crystals of corundum have been added beforehand, the induction period can be very remarkably lengthened by slightly lowering the reaction temperature. As in the present work without corundum seeds at 435°C, no corundum crystals can be formed from boehmite for up to 60 hr. At that temperature corundum phase is more stable than boehmite (A-1 to AT-1). 7) When seed crystals of corundum have been added beforehand, the induction period can be lengthened by lowering the reaction temperature (AN-1 to ANT-1). 8) The reaction rates after the induction periods are only slightly decreased by lowering the reaction temperature (AN-1 to ANT-1). 9) Although the seed crystals grow through the reaction, most of the grains are formed separately from the seed (AN-1 and ANT-1).

The present authors have proposed the reaction scheme for corundum formation which is shown in Fig. 6, where a new process, D′, is added to the previous scheme.[2] The present scheme, with the additional process, D′, can explain the results of the reaction of the corundum formation better than the previous one[2] without the D′. The present results seem to support the mechanism.

Before the initiation of corundum formation, processes A, B, D and F should take place successively. The induction periods of the runs A-1, B-1, A-3, B-3 and AT-1, however, correspond to the time required for the onset of process D. The dissolution equation of aluminas under hydrothermal conditions[6] shows that processes A, A′, B and C have been substantially in equilibrium when the boehmite grain in the reactor is heated up to the reaction temperatures. The grains of boehmite have a large enough specific surface area. Fact 1), therefore, shows that boehmite grains have a slight catalytic behavior in process D. On the basis of the dissolution equation, we can say that fact 2) is not due to the different times required for attaining the equilibrium in processes A, A′, B and C. This may indicate that the concentration of simple aluminate ions in the liquid, not the relative concentration nor the supersaturation ratio, but the absolute one, determines the rate of process D. Fact 4) shows that the corundum grains added beforehand as seed crystals act as an effective catalyst for process D. The seed crystal supplies the corundum-like hydrated poly ions through process H. In the presence of the corundum-like hydrated poly ions in a solution, process D seems to take place easily. Note here that the corundum-like hydrated poly ion is characterized by a structure in which two adjacent aluminum ions are joined through

6) G. Yamaguchi, H. Yanagida and S. Soejima, This Bulletin, 35, 1789 (1962).

three oxygen atoms, as in the lattice of corundum. Interaction between the active sites of the poly ions and the simple aluminate ions may give new poly ions through process D′ more easily than interaction among the simple ions themselves through process D. Fact 6) shows that a high reaction barrier exists against process D. Fact 7), on the other hand, shows that the barrier can be easily passed through another process, D′, when the poly ions are supplied according to process H. Facts 6) and 7), therefore, may mean that the activation energy of process D is considerably higher than those of processes D′, F, or H. In the runs when the seed crystals have been added beforehand, process D′ or F may become the rate-determinant. Process F indicates a nucleation process through the further polymerization of the poly ions; through it, the new crystal of corundum becomes precipitated separately from the seed. Process F, therefore, causes fact 9). After the induction periods, some of the runs show similar curves of the reaction rates, as can be seen in facts 3), 5) and 8), where corundum grain newly produced also becomes a new seed which supplies the poly ions through process H and process D is replaced by process D′. Fact 8) shows that the activation energy of the rate-determinant process after the induction periods is considerably lower than those before the onset of new corundum formation.

**Summary**

The authors have measured the reaction rates of corundum formation from boehmite under some hydrothermal conditions for the purpose of discussing the reaction mechanism. They have proposed that, in such cases as the crystallization of corundum or boehmite, there exists the hydrated poly ion of the structure intimately related to the lattice of the product phase and that the formation process often becomes the rate-determinant if no seed crystals of the product phase have been added beforehand. The seed crystal supplies the poly ions which accelerate the simple ions to transform themselves into the poly ions. The mechanism has been illustrated schematically and discussed in detail.

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