*Corundum α-Al_2O_3 Formation from the Dehydration of Boehmite γ-AlOOH under Hydrothermal Conditions. I. Factors Determining the Grain Size of Corundum and a Proposal for the Formation Mechanism**

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The fact that aluminum hydroxides are transformed into corundum through dehydration in a relativery low temperature range near 400°C under hydrothermal conditions has been noted by Laubengayer and Weisz,[2] Ervin and Osborn[3] and Kennedy,[4] while the temperature of transformation by calcination in air is usually above 1000°C. Using this reaction, the present authors obtained grains consisting of separated single crystals of corundum of a uniform size and habit of hexagonal plate or column ;[5] the grains showed excellent qualities as abrasive material.[6] It is worth clarifying the mechanism of this reaction as an approach to the investigation of the processes of solid phase formation. The solubilities of corundum and boehmite under the condition of corundum formation from boehmite have been discussed in a previous paper.[7] In the present paper, the grain size of corundum crystals obtained under various hydrothermal conditions with such varying factors as reaction temperature, hydrothermal pressure and quantity of the seed crystals of corundum, has been measured to provide other information for a discussion of the formation mechanism.

Experimental

Procedure.—Aluminum hydroxide, boehmite or gibbsite is weighed and laid in a Bridgeman-sealed Morey-type reactor with an aqueous solution of alkali. The reactor is then heated to an appointed temperature within 15 min. in an electric furnace and kept at the temperature for enough hours to convert the boehmite completely into corundum. The hydrothermal pressure is calculated from the relation among the pressure, volume and temperature of the water after the table of Kennedy.[8] The reactor is quenched to room temperature, also within 15min. and the corundum residue is washed out with pure water into a glass beaker.

Grain Size Determination. — The grain size of corundum is measured by the sedimentation method using Shimadzu's sedimentograph. Glycerol diluted with pure water is used as a sedimentation medium. The viscosity of the medium is calculated from the relation among the viscosity, density and temperature of glycerin diluted with water.[9]

Results

1) The Effect of Reaction Temperature.— The grain size of corundum crystals obtained when the pressure was 1000 atm., the solvent was a 0.1 N sodium hydroxide solution, and the temperature was 460 to 550°C was measured. The results are shown in Fig. 1, while the appearance of the corundum crystal is shown in Fig. 2. The shape of the corundum crystal is scarecely at all similar to that of boehmite,

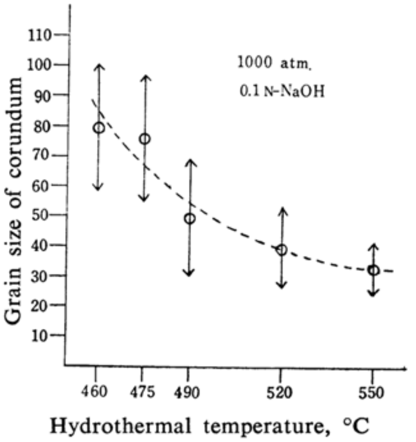

Fig. 1. Relation between grain size of corundum and hydrothermal temperature.

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* This paper is subtitled "Investigations into the Processes of Solid Phase Formation" No. 2. The first paper was "On the Reaction Mechanism of Boehmite Formation from the Dehydration of Gibbsite"[1].

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

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

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

4) G. C. Kennedy, *Am. J. Sci.*, **257**, 563 (1959).

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

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

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

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

9) "Kagaku-Benran" Ed. by the Chemical Society of Japan, Maruzen Co., Ltd., Tokyo 1958.

Fig. 2. Corundum obtained at 490°C under 1000 atm.

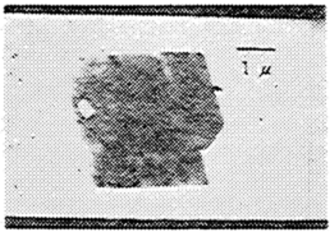

Fig. 3. Boehmite as starting material.

the starting material, as Fig. 3 shows. This suggests that the reaction of corundum formation under the conditions of the present section is due to a dissolution-precipitation process. The activation energy of the nucleation process of corundum should be larger than that of crystal growth judging from the fact that the grain size of corundum is decreased with the rise of temperature.

2) The Effect of Hydrothermal Pressure.—The grain size of corundum obtained when the temperature was 500°C, the solvent was a 0.1 N sodium carbonate solution, and the hydrothermal pressure was 250 to 1500 atm. was also measured. The results are shown in Fig. 4. The appearance of the crystals of corundum are shown in Figs. 5 and 6. The figures show that corundum obtained under lower hydrothermal pressure has a less perfect shape than that obtained under higher pressure. The former seems to be composed of aggregates of small crystals. This phenomenon is closely related to that of boehmite formation from gibbsite under various hydrothermal pressure.[1] In that case, boehmite was formed in its own rhombic tabular shape, as is shown in Fig. 3, when the nucleus of boehmite was formed and grew practically in a free hydrothermal solvent, while boehmite was formed as an aggregate of fine crystals with the original shape of gibbsite when the processes took place within the original grain. In the present case of corundum formation from boehmite, the nucleus formation and the crystal growth of corundum seem to occur practically in a free hydrothermal solvent not enclosed within boehmite grain when the hydrothermal pressure is higher, and so when the solvent is rich and dence, whreas the processes seems to occur within the grain when the pressure is lower, and so when the solvent is poor in outer free space.

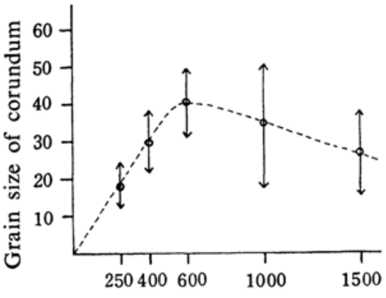

Fig. 4. Relation between grain size of corundum and hydrothermal pressure.

Fig. 5. Corundum obtained at 500°C under 250 atm.

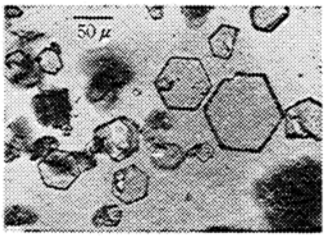

Fig. 6. Corundum obtained at 500°C under 1000 atm.

3) The Effect of the Addition of Seed Crystals of Corundum.—Corundum was formed from boehmite hydrothermally above 440°C when no seed crystal of corundum was added.[2,5,7] The equilibrium point between boehmite and corundum, however, should be 370°C under 1000 atm.[10-12] An equilibrium relation between two species must be discussed for the condition when the two co-exist, if the reaction of the formation of the more stable phase is of great activation energy of nucleation.[11] By the addition of seed crystals of corundum, the induction period before the initiation of corundum formation can be considerably

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10) H. Yanagida "Research on the Synthesis of Minerals," Master Degree Thesis, The University of Tokyo (1960).

11) H. Yanagida, "Hydrothermal Reactions of Aluminas," Ph. D. Thesis, The University of Tokyo (1963).

12) G. Yamaguchi and H. Yanagida, to be published later in This Bulletin.

TABLE I. EFFECT OF ADDITION OF SEED CRYSTAL OF CORUNDUM UPON THE GRAIN SIZE OF NEWLY FORMED CORUNDUM IN 0.01 N NaOH SOLUTION UNDER 1000 ATM. AT 450°C

Addition of seed crystals of corundum			Newly formed corundum
μ	g.	Surface area cm^2	μ
—	—	—	55.0 ± 16.0
2.1	0.5	2.5×10^3	2.8 ± 1.1
2.1	1.0	5.0×10^3	1.8 ± 1.2
47.0	0.5	100	29.2 ± 7.5
500	0.1	2.0	34.2 ± 10.4

shortened,[11,12] as Table I shows, the grain size of the newly-formed corundum is decreased. The results was obtained when the temperature was 450°C, the solvent was a 0.01 N sodium hydroxide solution, and the pressure was 1000 atm. with the addition of various quantities, of seed crystals of corundum. The larger the surface area of the seed crystals of corundum, the finer the size of the newly-formed corundum. It is supposed, therefore, that the crystal as seed promotes the nucleus formation. Since the effect was also observed when the seed crystal was far separated from boehmite grain in the reactor, the nucleation process must also take place in outer free space, not enclosed within the original boehmite grain, when some seed crystals are present. The seed crystal grew a little and the boehmite grain was converted into corundum even when boehmite existed metastably without any addition of corundum seed crystals. Moreover, the corundum crystal newly obtained from boehmite behaves as new seed. Just after the initiation of corundum formation when no seed crystals of corundum were added, as has been in preseding sections, therefore, the corundum behaved as seed and the nucleation process and the growth took place in the free space instead.

Summary of the Results and Some Suggestions.—The results may be summarized as follows; (1) The corundum crystal in most cases is in the shape of hexagonal plate (the habit modification is discussed in another paper)[13] except when the hydrothermal pressure is lower and the solvent is poor. (2) The grain size of corundum decreases with the rise of the reaction temperature. (3) By the addition of seed crystals of corundum, the grain size of newly-formed corundum can be decreased. These findings suggest that; (a) the reaction of corundum formation is closely related to that of boehmite formation from gibbsite; (b) according to the first finding, the reaction is carried out through a hydrothermal dissolution-precipitation process; (c) the nucleation process is of a higher activation energy than the growth; (d) the nucleus is formed both within the original boehmite grain and in the free space of a solution (the latter contribution becomes larger if the solvent is rich enough or if some corundum seed crystals have formerly been added); (e) after the initiation of corundum formation, the newly-formed corundum acts as new seed, and (f) the process of crystal growth takes place practically always in the free space of a solution, not within the original boehmite grain; the growth within it is noticeable when the outer solvent is poor, as when hydrothermal pressure is low.

Conclusion

A Proposal for the Mechanism of Corundum Formation under Hydrothermal Conditions.— Considering these results, the present authors propose the reaction schema shown in Fig. 7 for the formation mechanism of corundum under hydrothermal conditions. This schema is closely related to that of boehmite formation from the dehydration of gibbsite.[1] In that schema, gibbsite and boehmite were in the positions of boehmite and corundum respectively in the present schema. The most important hypothesis of these proposals is the existence of certain hydrated polyions whose structure is like the corresponding crystal lattice. Process A in Fig. 7 involves the dissolution of boehmite to boehmite-like hydrated polyions and process A′, the precipitation of boehmite.

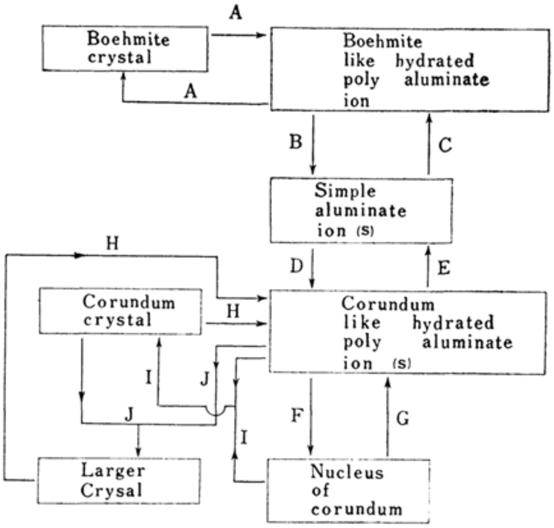

Fig. 7. Reaction schema for corundum formation.

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[13] G. Yamaguchi, H. Yanagida and S. Ono, *J. Ceram. Assoc. Japan*, 71, 182 (1963).

Process A′ is more complex in fact and is carried out through a cycle similar to that of the F, G, H and I processes; it is, however, written here in a simplified way. Process B indicates the dissociation of boehmite-like hydrated polyions into such simpler ones as $Al(OH)_4^-$ or $Al(H_2O)_2(OH)_4^-$, and C, the process of their association. The dissolution equation of aluminas in the previous paper⁷⁾ shows that an equilibrium among A, B, C and D has already been attained when the reaction temperature reaches above 400°C. Process D indicates the association of the simpler aluminate ions into corundum-like hydrated poly-aluminate ions, and E, the process of the dissociation. Process D, the present authors propose, is of high activation energy and it becomes the rate-determining one when the poly ions are not present at all. The seed crystals of corundum, whether added formerly or newly formed, supply the polyions according to Process H. The corundum-like hydrated poly aluminate ions are characterized by the structure of the two nearest aluminum ions being jointed through three oxygen atoms as in corundum lattice, while that of the boehmite-like one is of the nearest two aluminum ions being jointed through one or two oxygen atoms as in boehmite lattice. Process F indicates the nucleus formation of corundum crystal through the polymerization of the corundum-like polyions and G, the process of its depolymerization. Further polymerization results in the precipitation of corundum crystals according to Process I. The corundum crystals grows through Process J and at the same time supplies the polyions through the Process H.

Explanation of the Results According to the Reaction Schema.—The results in the present work can be explained with this reaction schema as follows. Finding (1) in the summary of the results in the preceding section is due to the reaction schema of a dissolution-precipitation process; Finding (2) is interpreted as meaning that the activation energy of the nucleation of corundum, Processes D and F, especially D at the early stage of the reaction, when any corundum seed crystals are not added, is larger than that of crystal growth J, and Finding (3) is due to the fact that the addition of corundum seed crystals makes it possible to initiate Process F and to promote Process D through Process H, and (e), therefore, is due to the fact that newly-formed corundum supplies the polyions through the Process H.

A reaction mechanism of corundum formation under hydrothermal condition has been discussed on the basis of the findings that the grain size of corundum varies with the hydrothermal conditions of temperature, pressure, and the addition of corundum seed crystals. The present authors have proposed a reaction schema by adapting the conception of hydrated poly aluminate ions with crystal lattice structure as proposed in the previous paper.¹⁾ The reaction schema will be discussed also in a later paper¹²⁾ in connection with the results concerned with the reaction velocity of corundum formation under various hydrothermal conditions.

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