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Reaction kinetics and mechanism of α-Al_2O_3 formation

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The calcination of alumina hydrate (aluminium hydroxide) can be described by a brutto reaction, where a solid material is thermically decomposed evaluating gases. During this process several structure transformations and crystal growths in solid phases take place.

In this complicated process the formation of α-Al_2O_3 phase has been investigated to such extent to receive information on the regularity of the changes taken place in the order of magnitude of 100 to 1000 Å. By means of miromorphological analysis the growth rate of crystallites has been determined as the function o fdifferent crystallographic directions and that of technological parameters, and the same conclusions have been driven for the mechanism of the process.

On the basis of investigations some general conclusions are given for the crystallization process of inorganic materials in solid state, within this the role of temperature and time, as well as the possibility of their mutual replaceability is determined during the crystallization of corundum. The concluded results afford the possibility to fix in advance the parameters of calcination of an alumina with the requested morphology or conversely, subsequently the circumstances of the heat treatment can be determined of an unknown alumina probe. A relation has been established between the morphology of alumina and the numerical values of the methods generally applied for qualification cangle of repose, packing density, specific surface, etc.). The effect of the various mineralizators on the rate of crystallization and on the morphology of the crystallites has also been investigated.

Metallurgical-grade alumina consists predominantly — or, if its minor contaminants are disregarded, totally — of the alpha modification of alumina, termed corundum in mineralogy. In the present paper, leaving aside for the moment the complex processes occuring at aluminium hydroxide dehydratation, I wish to present some observations concerning the final stage of product alumina formation, viz. the solid-phase growth of corundum crystallites. Since crystal growth proceeding during heat treatment at temperatures below the melting point is a frequent phenomenon in chemical technology and metallurgy, it may be hoped that our conclusions, if applied with due circumspection, might contribute to the interpretation of the behaviour of other substances. On the other hand, our objective was to elucidate the relationships between the properties of alumina, and thereby to establish the technologically optimum grade of product alumina.

The properties of product alumina will decisively be affected — in addition to the

calcination parameters — by the properties of the starting material. Let us therefore shortly survey the main characteristics of aluminium hydroxide particles.

Aluminium hydroxide precipitated from aluminate liquor consists of the gamma modification. Its structure is identical with that of gibbsite occuring in nature. It crystallizes in monoclinic (sometimes in the triclinic) system with a pseudo-hexagonal symmetry. The particles having an average diameter of 60 to 80 μm are usually aggregates of small (~ 10 μm diam.) crystals (Fig. 1). More rarely, particles consisting of larger (~ 30 μm diam.) crystallites also occur (Fig. 2).

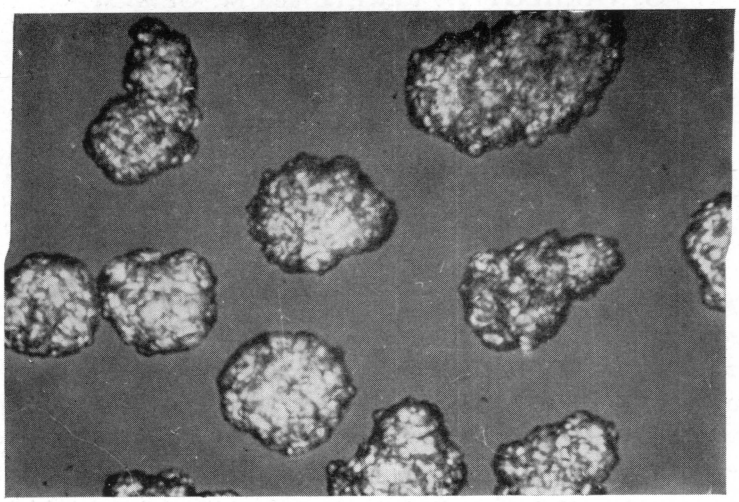

Fig. 1. — Samples of $Al(OH)_3$. Crossed nicols and gyps-slide.
Magnification (M): 69 x (207 x)

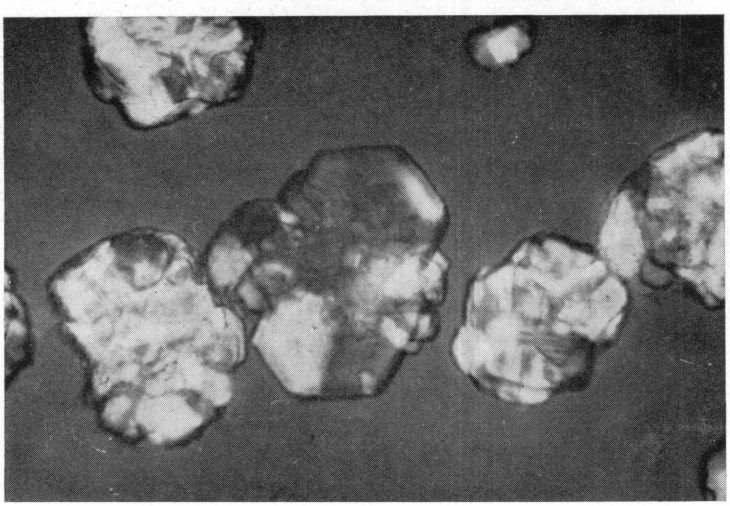

Fig. 2. — Sample of $Al(OH)_3$. Crossed nicols and gyps-slide.
M: 145 x (435 x)

Micrographs taken in polarized light show that the orientation of the individual crystallites within the particle differs. The short prismatic crystal shape characteristic for gibbsite, showing in the top view the hexagonal end face and in the side view the quadrangular prism face, can clearly be observed on these particles.

To investigate the effect of heat treatment, alumina samples subjected to heating for various periods at various temperatures were studied with the electron microscope, allowing to follow changes in the range below the μm order of magnitude (Figs 3 and 4).

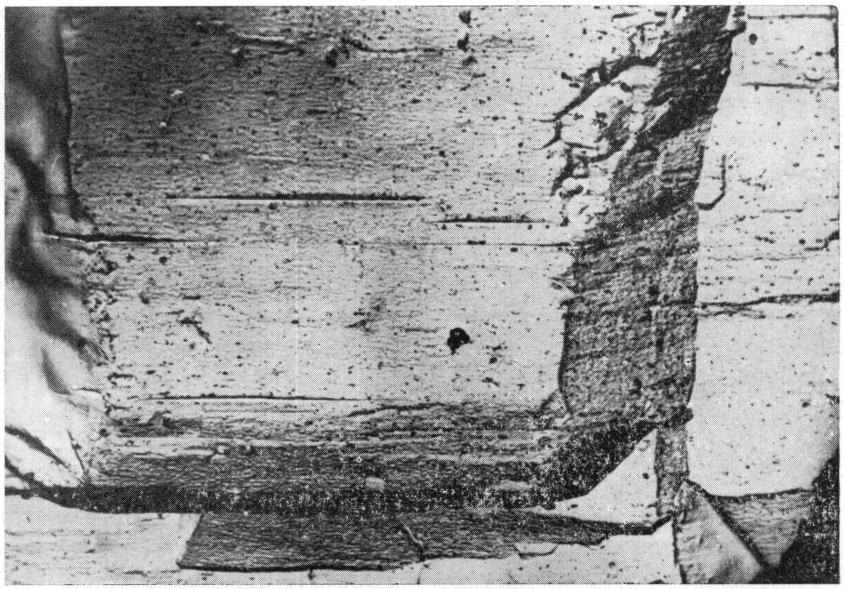

Fig. 3. — Electronmicrograph of alumina heated at 1000 °C for 1.5 hours.
Prismatic face. M: 6000 x

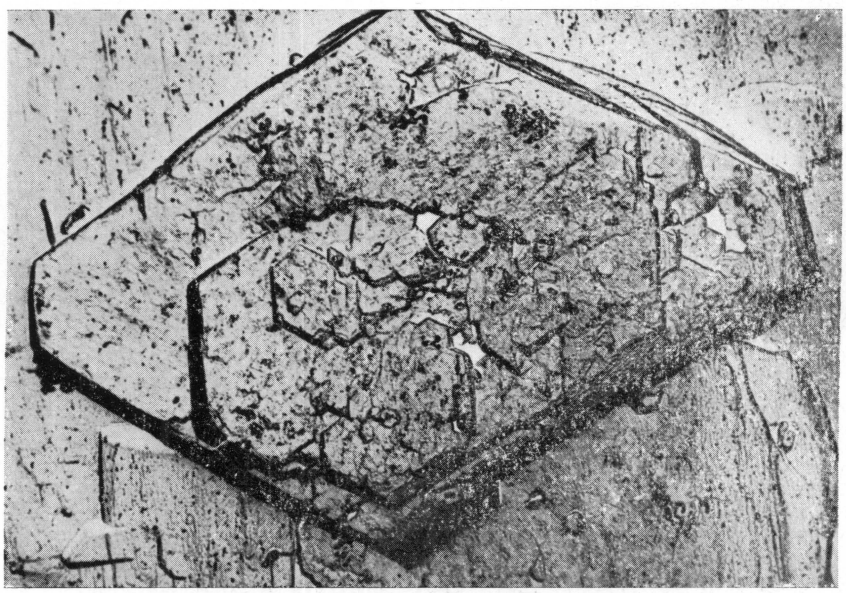

Fig. 4. — Electronmicrograph of alumina heated at 1000 °C for 1.5 hours.
Basal face. M: 6000 x

Signs of changes may be suspected already after heat treatment at 800 °C. With absolute certainty, however, changes can only be detected after treatment at 1000 °C. These changes consist in crystal growth of the alpha phase and a simultaneous roughening of the originally smooth crystallite surface. The extent of roughening and striatedness successively increases with increasing heat treatment temperature and period; however, in spite of the changes, the crystalline form of the original gibbsite is retained. The obtained product can therefore be considered a pseudomorph of the initial gibbsite. The growth of the corundum crystal proceeds in almost parallel planes on the prism faces of the pseudomorph (Fig. 5), corresponding to the gibbsite lattice (in the direction [hkio]). The thickness of these layers corresponds to the thickness of a single corundum crystallite. Initially the thickness of the corundum crystallites is the order of 10^{-2} μm, their length 10^{-1} μm. With

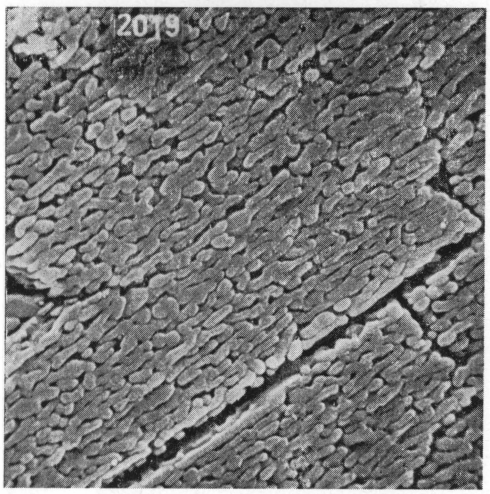

Fig. 5. — Electronmicrograph of alumina heated at 1200 °C for 4 hours.
Prismatic face. M: 10 000 x

Fig. 6. — Electronmicrograph of alumina heated at 1400 °C for 4 hours.
Basal face. M: 3000 x

Fig. 7. — Electronmicrograph of alumina heated at 1200 °C for 4 hours
Basal face. M: 10 000 x

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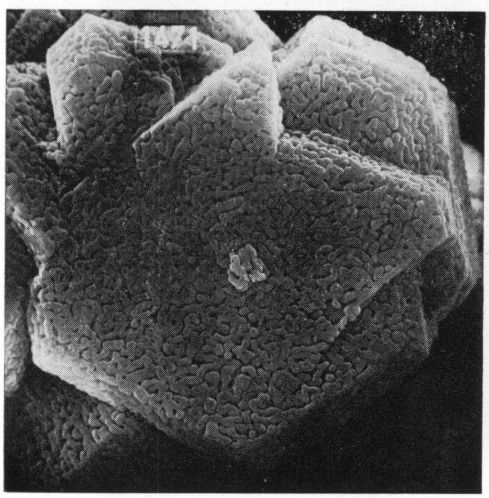
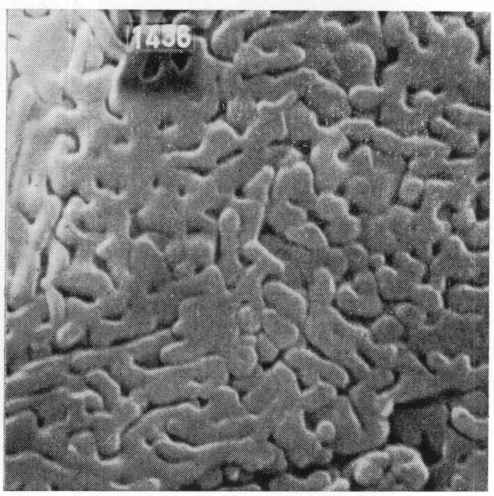
6	7





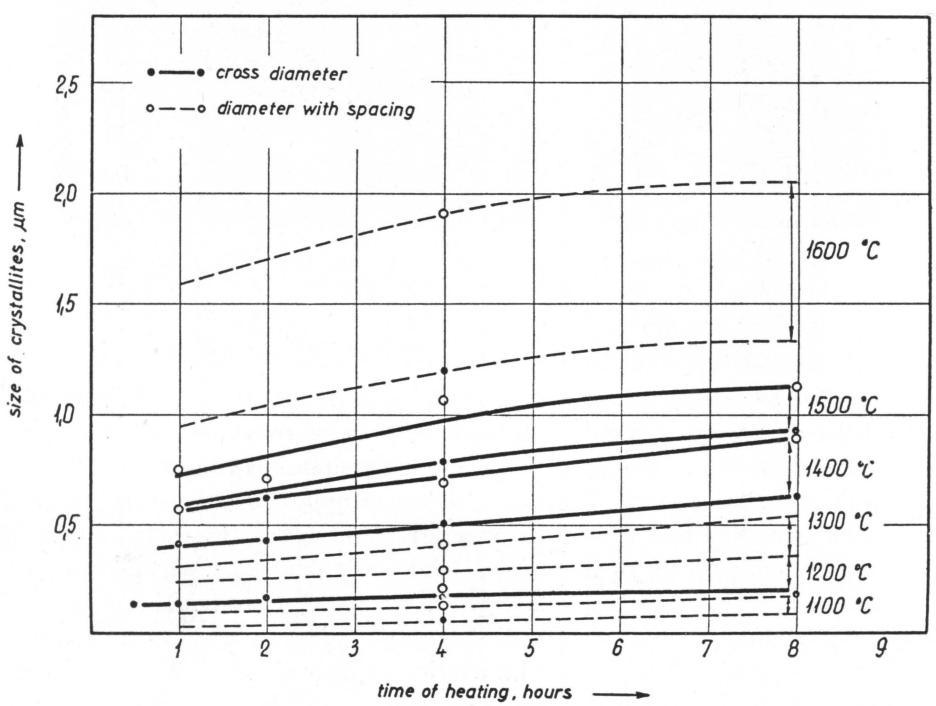


Fig. 8. — Growth of corundum crystallites in function of time

increasing intensity of the heat treatment, the crystallites grow to particles with thickness of the order of μm and lengths of some μm. In view of the lattice constants of the alpha phase (size of the elementary cell $a = 4.76$ Å, $c = 13.00$ Å), our electron micrographs represent the growth of the crystallites from thicknesses corresponding to some ten elementary cells to thicknesses corresponding to some hundred elementary cells. Similar changes can be observed (Fig. 6) on the basal faces of the pseudomorph, allowing to study the feature of the corundum crystallites in a projection perpendicular to the above-discussed direction (Fig. 7). The thickness of the crystallites is similar to that measured on the prism faces as the length of the crystallite will appear now as diameters of bodies branched without any particular orientation or preferred direction. In contrast to the crack-like gaps on the prism faces, isometric or close to isometric channel ends perpendicular to the basal face are observable. Hence, alumina particles should not be considered a system of rod-shaped crystallites, but rather a system of platelets with edge lengths close to 10,000 Å, arranged as the basal face of the pseudomorph and stacked one upon the other

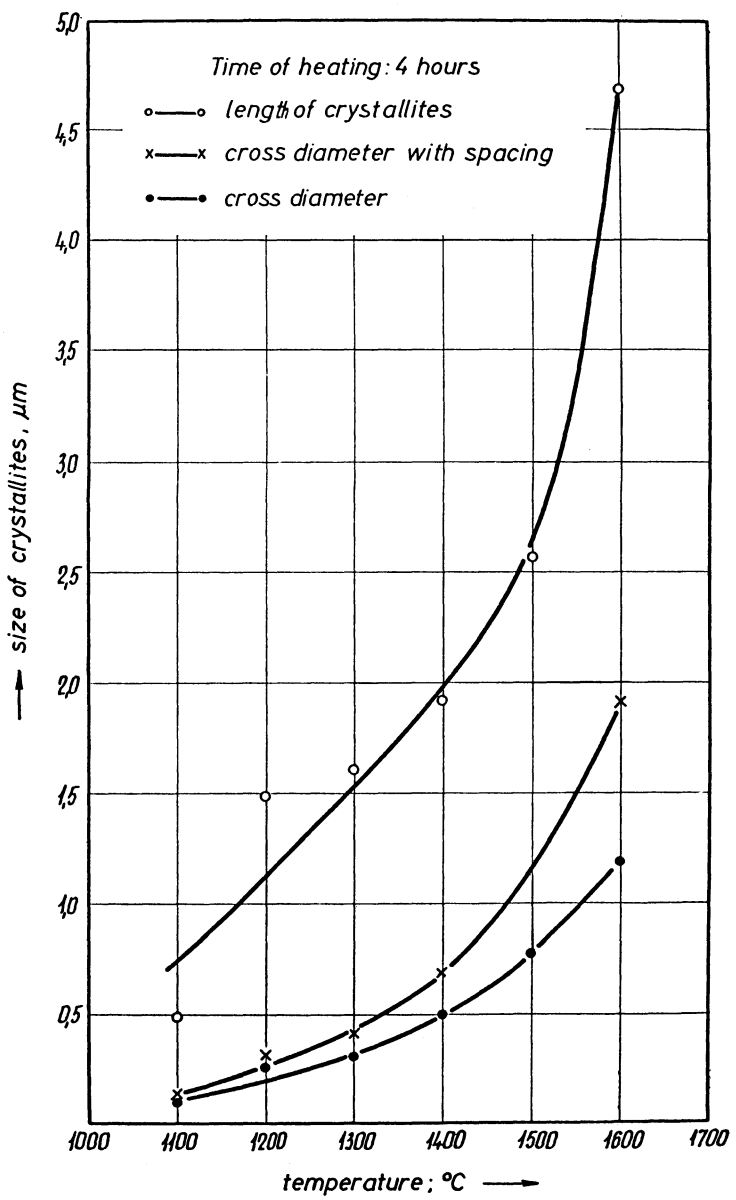


Fig. 9. — Growth of corundum crystallites in function of temperature

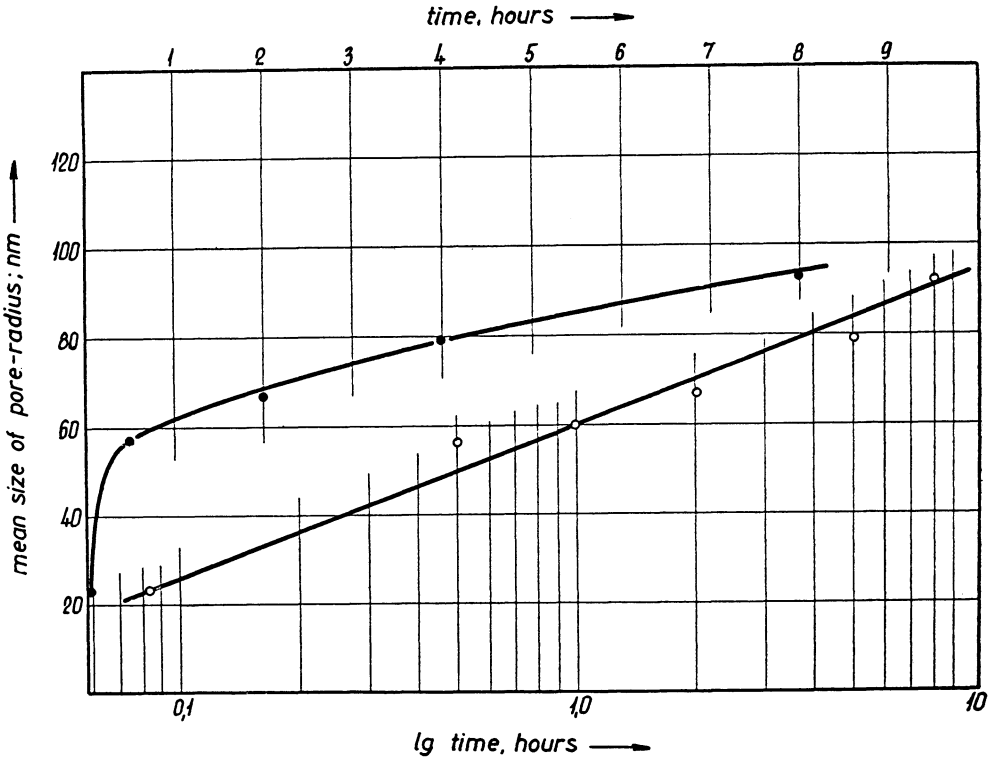


Fig. 10. — The change of mean pore radius in dependence of heating time

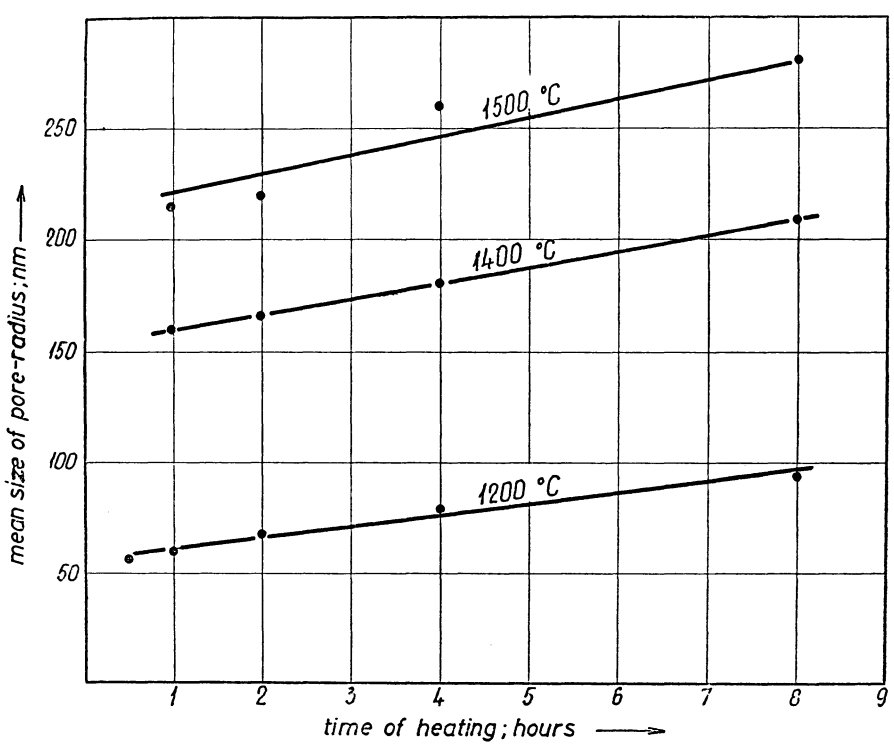


Fig. 11. — Change of mean pore radius in dependence of heating time at different temperatures

like a pile. On the other hand, the platelets are intended by holes and branches to such a great extent and rounded off at their edges that they may be considered as composed of cylinders with diameters of 0.1-1 μm.

The discussed growth process of corundum crystallites is numerically reflected in Figure 8. If the initial stage of crystal growth is disregraded, the increase in crystal thickness *vs.* time can be well approached by a linear relationship.

Temperature increase has a substantially greater effect on the growth of corundum crystals. Thickness and length changes of corundum crystallites *vs.* temperature are presented in Figure 9. If it is assumed that the shape and size of the pseudomorphs remains unchanged to the end of calcination, the figures also indicate that the growth of the corundum crystallites can proceed only at the expense of crystallites smaller than the average. Thus, while the size of the crystallites arranged more or less in planes within the crystalline form of the pseudomorph, as well as the size of the gaps between the crystallites increases, the number of the planes correspondingly decreases.

Essentially identical relationships are found if the gaps between the individual crystallites, *i.e.* the pores are considered in the heat-treated alumina samples instead of the growth of crystallites. The changes in the pore radius occuring with the highest frequency *vs.* heating time can be described by a logarithmic relationship (Fig. 10). If, however, the initial stage of the process is disregarded, the changes can be described with satisfactory accuracy by a linear relationship. Figure 11 shows the change of the most frequent pore radius *vs.* heating time at different temperatures. The clearest picture of changes in pore size is obtained by the differentiation of the pore size distribution curves. The obtained frequency curves are shown in Figure 12 indicating that with increasing heating time, simultaneously with the growth of pore sizes, the size distribution range also becomes broader.

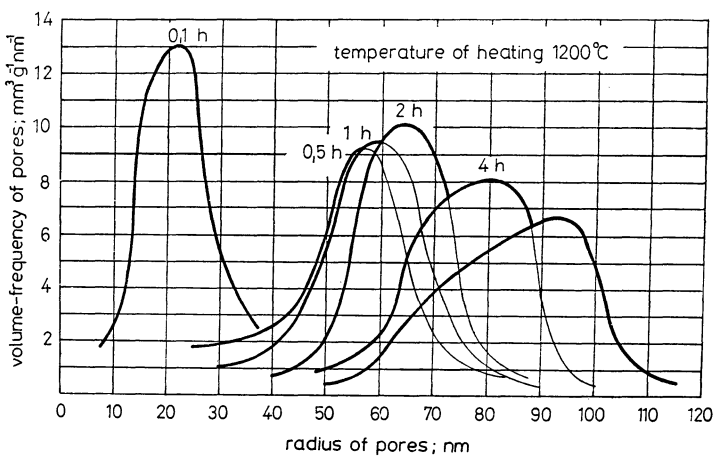


Fig. 12. — Pore size frequency curves of samples heated for different periods of time

The same is valid for the change of frequency curves with temperature, with the difference that with increasing temperature the total volume of the pores decreases (Fig. 13). This implies, in other words, that — in contrast to our model — the pseudomorph particles do shrink at high temperatures. The decrease of total pore volume, at a simultaneous increase of the most frequent pore radius is presented in Figure 14.

Based on the above-discussed findings, the growth mechanism of corundum crystallites can be described as follows: The very small particles which — as a first approach — may be considered spherical and are in contact with each other begin to grow according

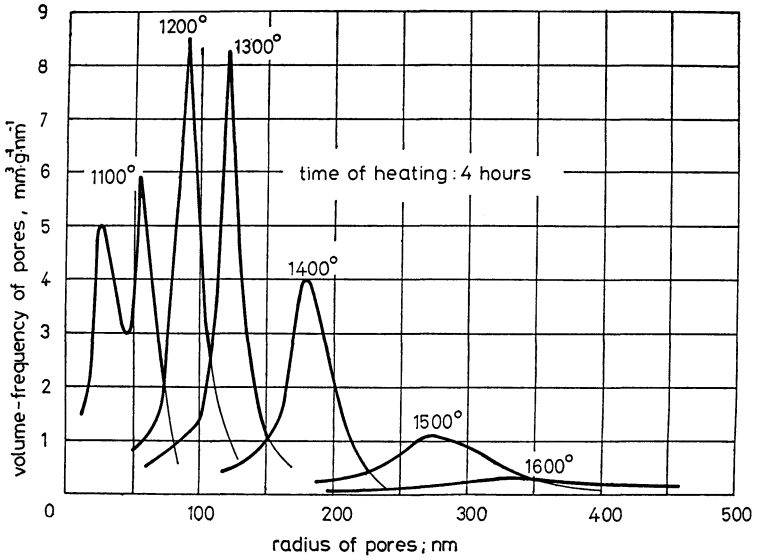


Fig. 13. — Pore-size frequency curves of samples heated at different temperatures

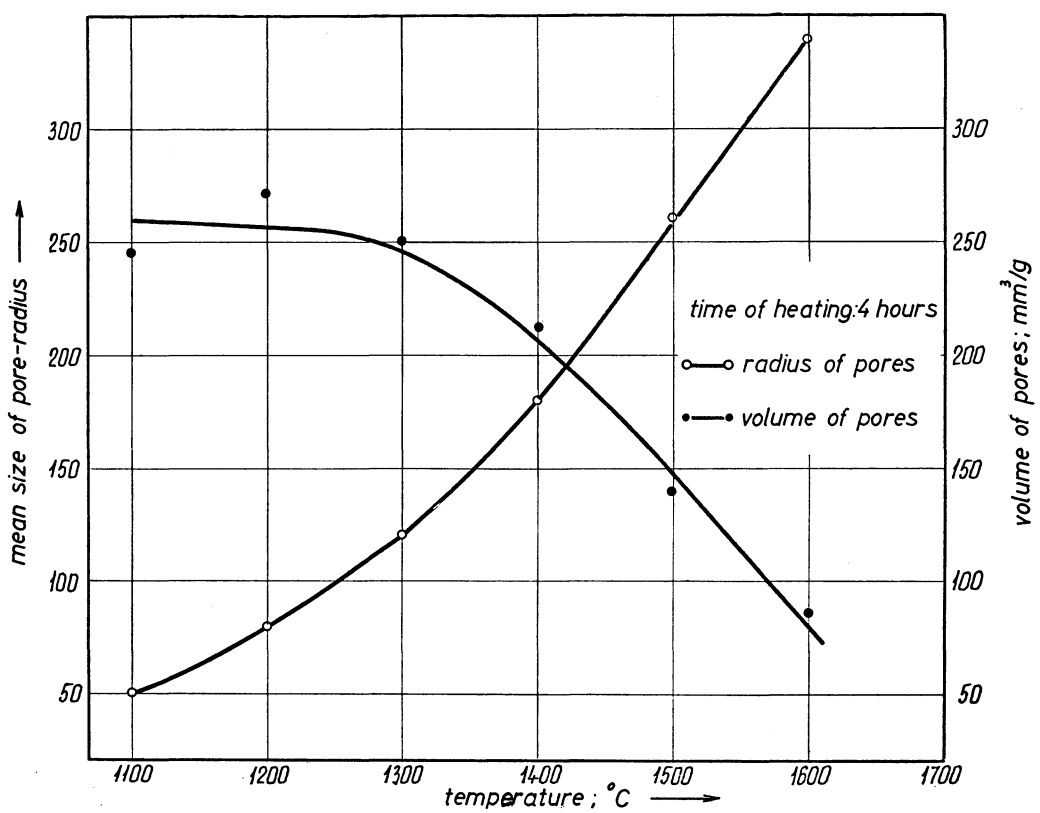


Fig. 14. — Changes of mean pore-radius and pore-volume in dependence of heating temperature

to the neck forming mechanism known from the sintering process in powder metallurgy. Between two contacting spheres differing in size, a neck is first formed. This neck — by a multiple transport mechanism — disappears in the direction of the smaller sphere, the driving force being created by the surface tension on the particle boundary. As a result, a body conical at one end will be formed. At lower temperatures and particularly in the case of very small particles, growth proceeds ultimately as the result of surface diffusion (Fig. 15). With larger particles and higher temperatures, volume diffusion comes to the fore, as indicated by increased shrinkage, accelerated crystal growth and the appearance of crystal edges and faces (Figs 16 and 17). In our case, volume diffusion becomes predominant at 1500 to 1600 °C.

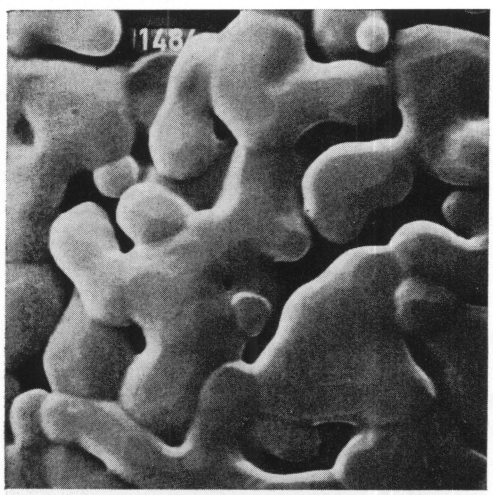


Fig. 15. — Electronmicrograph of alumina heated at 1600 °C for 4 hours
M: 10 000 x

Fig. 16. — Electronmicrograph of alumina heated at 1600 °C for 4 hours
M: 10 000 x

Fig. 17. — Growth in corundum crystallites in function of temperature

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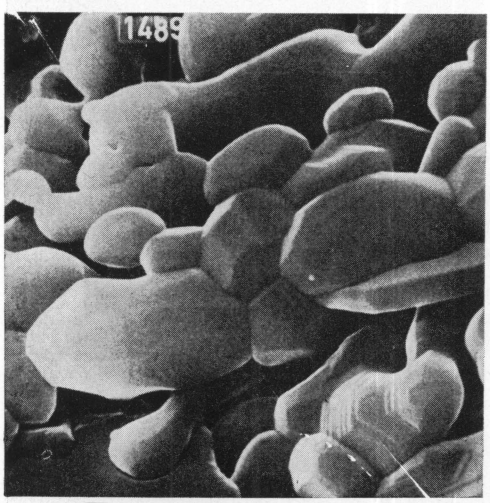
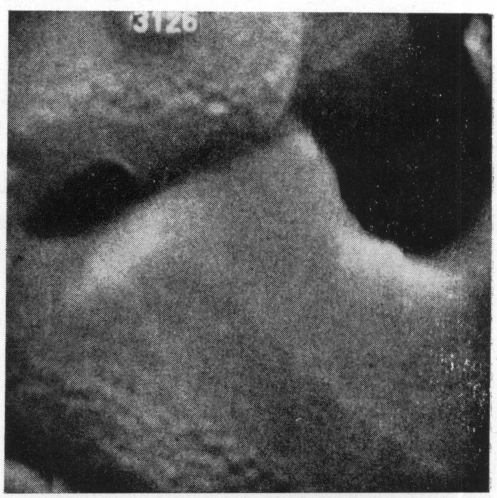
16	17





Finally I wish to summarize our findings in some practical conclusions, allowing to fix the calcining parameters to obtain product alumina having the desired morphological properties, or conversely, to determine the applied calcining conditions for an unknown alumina sample.

The size of corundum crystallites formed at different temperatures can be calculated by the formula

$$D = 1070 \exp\left(-\frac{12\,780}{T}\right)$$

where D is the thickness of the crystallites in μm and T is the temperature of heating in K.

Assuming that — with the exception of the initial stage — ignition time has the same effect on crystal growth at all temperatures, crystallite size can be calculated using the empirical formula

$$d = 0.03\ t - 0.12 + 1070 \exp\left(-\frac{12\,780}{T}\right)$$

where t is the heating time in hours.

Mineralizers substantially change not only the shape but also the size of the crystallites. Their effect is significant in ranges where their vapour tension is sufficient to bring about crystal growth by a gas phase transport reaction of intermediate compounds. Within this temperature range, the size of the formed crystallites will then be practically independent of temperature and heating time. Electron micrographs of typical alumina samples calcined in the presence of AlF_3 and HBO_3 resp., are shown in Figs 18, 19 and 20. On the Figure 21 crystallites of ß-Al_2O_3 phase formed in presence of AlF_3 addition can be seen.

Fig. 18. — Electronmicrograph of alumina calcined in factory with addition of AlF_3. M: 750 x

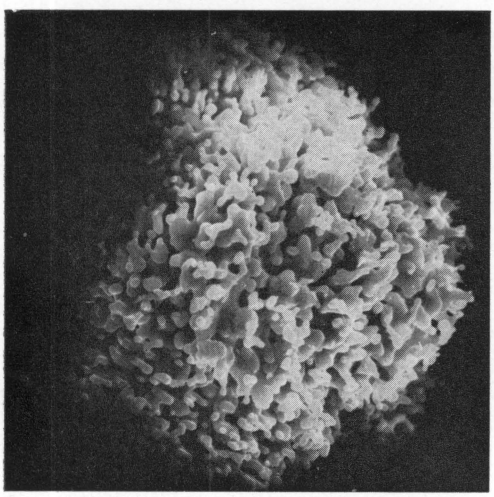
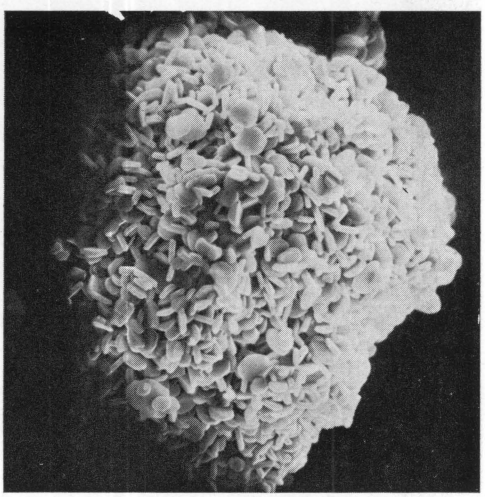


Fig. 19. — Electronmicrograph of alumina calcined at 1100 °C with addition of AlF_3. M: 3000 x



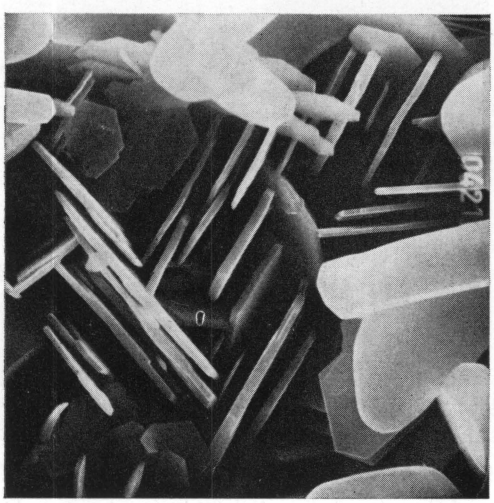


Fig. 20. — Electronmicrograph of alumina calcined at 1300 °C with addition of H_3BO_3. M: 1000 x

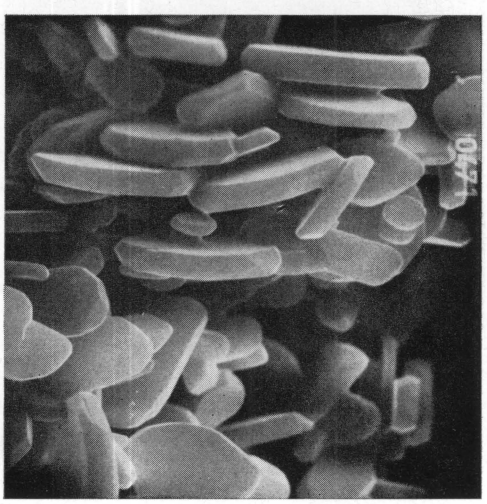


Fig. 21. — β-Al_2O_3 crystallites, formed in heating alumina at 1100 °C with addition of AlF_3. M: 6000 x

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