

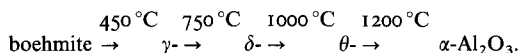
The development of porous microstructures during the dehydration of boehmite

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SUMMARY. Electron-microscope observations have been used to follow the low-temperature dehydration of boehmite, and show that a coherent skeleton of γ -Al₂O₃ with a porous texture is produced. For material fired in air the development of a number of pore systems is described. Of these the most important, as far as the dehydration process is concerned, is a lamellar pore system parallel to (001)_γ, and having a regular spacing of the order of 35-40 Å. A much faster dehydration process is induced by exposure to the electron beam and results in the formation of a more randomly oriented pore structure. The observed microstructure and the calculated internal surface area are compared with the results of previous adsorption studies.

THE ultimate product of thermal treatment of the hydroxides and oxyhydroxides of aluminium is the thermodynamically stable form of aluminium oxide, α -Al₂O₃ (corundum). However, with the exception of diaspore, dehydration of the various species of aluminium hydroxide produces a series of metastable intermediate aluminas before final conversion to α -Al₂O₃. The identity of the transition alumina species found in a particular dehydration sequence is characteristic of the starting material. In the case of boehmite the sequence is (Stumpf *et al.*, 1950; Lippens and de Boer, 1964a):



The temperatures at which these transitions have been observed are somewhat variable, apparently dependent on the crystallinity and previous history of the boehmite and on the conditions of heat treatment (Lippens, 1961). Moreover the time factor is also very important as these are relatively slow transformations. The time-temperature behaviour of an initially amorphous aluminium oxide has been studied by Sirota and Shokhina (1974).

Boehmite (γ -AlOOH) is orthorhombic and has the layered structure of fig. 1a (Milligan and McAtee, 1956; Bosmans, 1966). Within each layer the oxygen packing is cubic close-packed although

this arrangement is disrupted by the stacking of the layers. The hydroxyl groups are on the surfaces of the layers, which are thus linked together by zigzag chains of hydrogen bonds.

Our knowledge of the detailed structures of the transition aluminas is limited by a lack of single-crystal work. γ -Al₂O₃ has a defect spinel structure with a tetragonal distortion (Saalfeld, 1958; Lippens and de Boer, 1964a) and thus is characterized by a close-packed cubic anion lattice. δ -Al₂O₃ has a tetragonal superstructure of the spinel lattice with one unit cell parameter tripled (Lippens and de Boer, 1964a). θ -Al₂O₃ is monoclinic and has the β -Ga₂O₃ structure (Kohn *et al.*, 1957), which is very similar to that of spinel (Katz *et al.*, 1969).

The transformations in the boehmite dehydration sequence are topotactic at least as far as δ -Al₂O₃ (Lippens and de Boer, 1964a) and probably also to θ -Al₂O₃ (Saalfeld, 1958). For the dehydration of boehmite to γ -Al₂O₃ the pseudomorphosis relationships are (using the boehmite parameters of Swanson and Fuyat, 1953):

$$\begin{array}{ll} a_{\text{Bo}} & 3.700 \text{ \AA} \rightarrow [001]_{\gamma} \\ b_{\text{Bo}} & 12.227 \rightarrow [110]_{\gamma} \\ c_{\text{Bo}} & 2.868 \rightarrow [1\bar{1}0]_{\gamma} \end{array}$$

Electron-microscope observation of the microstructure developed during dehydration has been used in a number of studies of hydroxide systems to supplement information from diffraction and adsorption work. In particular, microstructures characteristic of the dehydration process have appeared for bayerite (Lippens, 1961), goethite (McConnell and Lima de Faria, 1961), lepidocrocite (Takada *et al.*, 1964; Giovanoli and Brutsch, 1974), Cd(OH)₂ (Niepce *et al.*, 1977), Co(OH)₂ (Figlarz and Vincent, 1968; Figlarz *et al.*, 1974, 1976), Zn(OH)₂ (Giovanoli *et al.*, 1965), Mg(OH)₂ (Phillips *et al.*, 1978), and CrOOH (Alario-Franco *et al.*, 1972). The microstructure developed in boehmite has also been observed during studies of catalyst support materials

(Bousquet *et al.*, 1970) and of the calcination of gel-derived and crystalline boehmite (Iler, 1961). The main interest in such microstructural studies of aluminium hydroxide systems lies in the importance of the transition aluminas in heterogeneous catalysis, so that any information on the nature of active sites and internal surfaces may aid understanding of catalytic processes. Furthermore the microstructure developed on dehydration may determine the transformation rate and influence the stability of the intermediate phases. The aim of the present work, then, is to provide a full description of the development of microstructure during the low-temperature dehydration of boehmite to γ -Al₂O₃.

Experimental. The synthetic boehmite used in this study was CERA hydrate supplied by the British Aluminium Company Ltd. and having a maximum crystal size of about 5 μ m. Material for examination was furnace-fired isothermally in air in platinum crucibles. X-ray characterization was performed using a Philips powder diffractometer with CuK α radiation.

Samples were prepared for electron microscopy either by crushing, dispersing in alcohol, and depositing on perforated carbon films on copper support grids, or by embedding in resin, sectioning with an LKB microtome, and depositing the thin flakes on to copper grids. Transmission electron microscopy was performed on a Siemens 102 instrument equipped with a double-tilting stage and operated at 100 kV.

Results. The synthetic boehmite used in this study was well crystallized, having the form of thin rhombic plates (fig. 1b) and this morphology was maintained on dehydration to γ -alumina. The

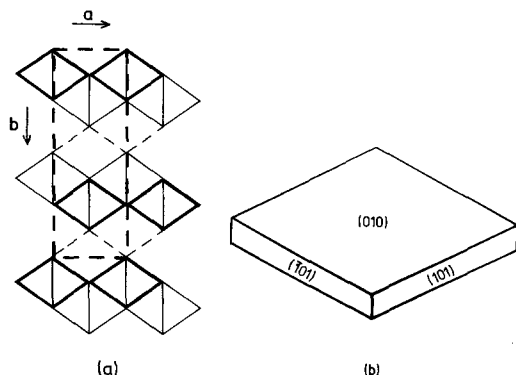


FIG. 1. *a*, idealized structure of boehmite projected along [001]. Thick and thin solid lines outline Al(OH)₆ octahedra joined in layers by edge-sharing. Thin broken lines represent hydrogen bonds linking these octahedral layers. The unit cell is outlined in thick broken lines. *b*, morphology of boehmite crystals.

cleavage plane is parallel to the basal plane of these crystals so that the electron-microscope observations of crushed samples reported here are predominantly of thin fragments having (010)_{Bo}/(110)_γ surfaces. By microtoming resin-embedded samples it was also possible to view fragments in directions making large angles with *b*_{Bo}.

In samples fired for short times (up to 1 day) at 400 °C the predominant microstructural feature is the presence of what apparently are relatively large isolated pores (fig. 2a) with a range of sizes up to about 700 Å across. These are often observed to overlap and, where they do, the contrast in bright-field observation is always additive. Furthermore, tilting the specimen produced no orientations in which the observed contrast was reversed, as would be expected if the features represented a second phase. Thus these features are probably relatively shallow pores locked within the crystal fragments. An SEM study showed no surface features that could be correlated with the microstructure observed in the transmission mode.

These pores were not observed to be present in boehmite itself, but in crystals fired at 400 °C for only 1 h they can be distinguished, although the contrast is low. Increase in the firing time at 400 °C produces an increase in pore density, although no significant change in their average size, and an increase in contrast, and presumably also pore depth, until in the sample fired for 1 day they are quite prominent. Microdensitometer measurements of contrast variations at this stage suggest that these pores have depths corresponding to up to about 30% of the thickness of the crystal fragments. Further increase in firing time leads to the pores being obscured slightly as further microstructural features are developed.

X-ray diffractometer data for boehmite fired for 1 day at 400 °C contained only boehmite reflections while typical electron diffraction patterns are basically [010] boehmite zones, often with disallowed reflections present and sometimes showing traces of the development of the γ -alumina spinel pattern (fig. 2a). Thus at this stage the degree of dehydration is small.

Fig. 2a reveals the interesting fact that these isolated pores are oriented with respect to the crystal structure. In fact their shapes are very similar to those of the original boehmite crystals, and they might be considered as 'negative crystals' within the fragments. They are bounded by {101}_{Bo} planes, and presumably top and bottom by (010)_{Bo} planes.

In some fragments of the sample fired at 400 °C for 1 day it is possible to distinguish traces of microstructural features with a much finer scale.

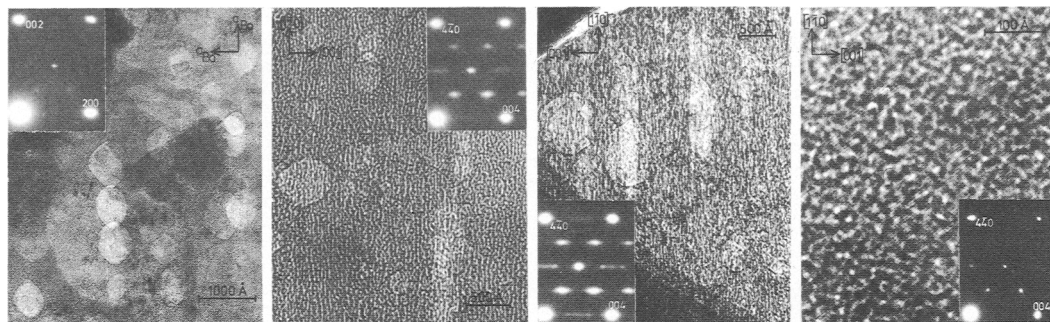


FIG. 2. Microstructures of boehmite fragments at various stages of dehydration together with typical electron diffraction patterns. All are in the same $[110]_B$ orientation. *a*, 400 °C 1 day; *b*, 400 °C 1 week; *c*, 600 °C 1 week; *d*, electron beam induced dehydration.

These are well developed in specimens fired at 400 °C for 1 week (fig. 2*b*). The high contrast observed suggests that we are looking directly down a series of sheet-like pores. The intersection of these pores with the crystal surface produces traces that are approximately linear, although there is evidence of a degree of cross-linking between adjacent pores, and that follow $[001]_{Bo}/[110]_B$ directions. Thus the microstructure can be described as a series of very fine lamellar pores, parallel to $(100)_{Bo}/(001)_\gamma$, cutting through the crystal fragment. The spacing between adjacent pores is remarkably regular and of the order of 35–40 Å.

Electron diffraction patterns from fragments showing such a microstructure are typically $[110]_B$ zones from γ -alumina (fig. 2*b*), developed in a precisely oriented fashion from the original boehmite lattice. The reflections are not sharp, there being a degree of streaking in the c^* direction. Structure factor calculations indicate that the most prominently streaked reflections are those with contributions only from cation positions and not from the oxygen sub-lattice: The direction of streaking is perpendicular to the trace of the lamellar pore system, which is thus the major cause of the streaking effect, although there may be a contribution from the incipient transformation of γ - to δ -alumina which involves tripling the unit cell in the c direction (Lippens and de Boer, 1964*a*).

The X-ray powder pattern from boehmite fired for 1 week at 400 °C contains reflections from both boehmite and γ -alumina but the relative intensities indicate that at this stage the dehydration process is 80–90% complete. The γ -alumina reflections are broad, presumably because of the microstructure, and again reflections with a strong contribution from the cation positions are broadened most significantly. Splittings of 400 and 440-type spinel reflections show that the γ -alumina produced by the dehydration of boehmite under these conditions is tetragonal with $c/a = 0.981$.

In samples fired at 400 °C for longer periods or for short times at 600 °C the lamellar pore system is still well developed but is beginning to appear more complex (fig. 2*c*) and there is evidence that the pores are starting to merge. The original fast-forming large isolated pores are now even more obscured. X-ray powder data show the presence only of γ -alumina with a growing proportion of δ -alumina. Electron diffraction patterns are typically $[110]_B$ zones of γ -alumina, heavily streaked along c^* , showing a gradual coherent transformation to δ -alumina. So for samples with these firing treatments, the dehydration of boehmite is complete and changes in microstructure may be associated with the transformation γ - to δ -alumina or with some sintering process.

In samples in which the dehydration process is incomplete, further, much faster dehydration can be induced by prolonged exposure to the electron beam, which produces well-developed γ -alumina diffraction patterns from boehmite fragments. These different conditions of temperature and water-vapour pressure under which the dehydration is taking place produce microstructures that differ from those of furnace-fired materials. Beam-heating of unfired boehmite crystals does not produce any large isolated pores but eventually a very fine porous microstructure is developed. This behaviour is also observed during the beam-heating of samples previously fired for only a few hours at 400 °C and is already apparent in fig. 2*a*. The orientation of these pores is more random than that of the lamellar pores in furnace-fired samples and they also have a finer scale with spacings of the order of 20 Å. Fig. 2*d* shows such a microstructure, together with γ - Al_2O_3 (111) lattice fringes. The diffraction patterns produced by beam-heating fragments tend to be sharp and to exhibit little streaking.

As stated previously the easy cleavage direction in boehmite-derived crystals produces, in

specimens prepared for electron microscopy by crushing, thin fragments with surfaces parallel to $(010)_{\text{bo}}/(110)_{\gamma}$. By tilting these, diffraction patterns characteristic of other zones can be obtained but since the face viewed is still the same little further microstructural information can be obtained. By embedding samples in resin and microtoming, a small number of fragments were found that could be observed in directions perpendicular to $[110]_{\gamma}$.

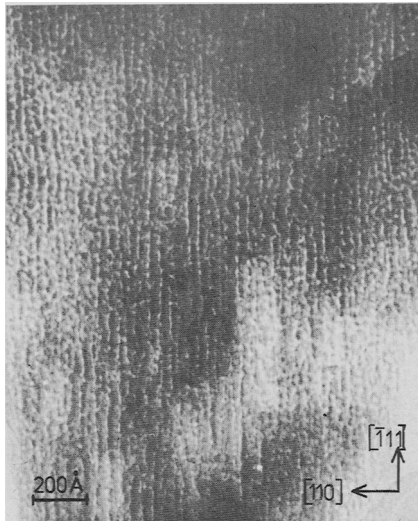


FIG. 3. Microstructure of boehmite fired at 400 °C for 1 week, $[112]_{\gamma}$ orientation.

In the example of fig. 3 a fragment of the sample fired for 1 week at 400 °C exhibits a $\langle 211 \rangle$ type spinel diffraction pattern and has a linear pore system parallel to the straight edges of the fragment running along a $\langle 111 \rangle$ type direction. Analysis of all the possible pseudocubic $\langle 211 \rangle$ zones against the observed pore orientation and crystal shape shows that the microstructure is not due to lamellar $(001)_{\gamma}$ pores. The pattern must be a $[1\bar{1}2]_{\gamma}$ zone (i.e. perpendicular to $[110]_{\gamma}$) with a system of planar pores parallel to $(110)_{\gamma}$. The orientation and scale of the microstructure is again remarkably regular, with a pore spacing of about 35 Å. There is evidence for a considerable degree of cross-linking between pores in the $[110]_{\gamma}$ direction. This may be attributable to intersection with the $(001)_{\gamma}$ planar pores but the small angle between $[1\bar{1}2]_{\gamma}$ and $[001]_{\gamma}$ (35°) would not be conducive to observation of these. The electron diffraction pattern from this fragment is generally diffuse indicating a lesser degree of coherence of the dehydration reaction than that observed when the $(110)_{\gamma}$ face is viewed.

Discussion. The interpretation of the microstructural information presented here in terms of a porous texture for γ -alumina perhaps requires justification, especially in the light of work done on the dehydration of the isostructural lepidocrocite, $\gamma\text{-FeOOH}$, to $\gamma\text{-Fe}_2\text{O}_3$ (Giovannoli and Brutsch, 1974). In this study, linear features about 70 Å wide observed in partially dehydrated lepidocrocite crystals were interpreted as being strings of oriented $\gamma\text{-Fe}_2\text{O}_3$ crystallites extending into undecomposed $\gamma\text{-FeOOH}$ regions. The formation of such a microstructure was envisaged as being caused by collapse of the layered structure of lepidocrocite to form a close-packed cubic oxygen lattice with elimination of H_2O by an internal condensation of protons and hydroxyl groups between the layers. An analogous situation can be imagined for the dehydration of boehmite, but such an interpretation was rejected for a number of reasons. First, beam-heating experiments showed that γ -alumina diffraction patterns developed from aligned boehmite patterns were themselves perfectly aligned, as should be expected from the well-characterized topotaxy of the reaction. Thus in orientations in which boehmite regions are strongly reflecting, regions of spinel structure will also be strongly reflecting since both structures share a similar basic oxygen sublattice, so that in bright-field observation one would not expect high contrast between regions of boehmite and γ -alumina. Secondly, in the event that these linear features might be γ -alumina crystallites incoherent with surrounding boehmite there should be orientations in which the γ -alumina is strongly reflecting and the contrast is reversed, and this has not been observed. Thirdly, in the case of the large, fast-forming pores reported here, overlap is commonly observed and the contrast is always additive. This suggests that the contrast observed is a thickness effect. Fourthly, if the linear features are formed by collapse of the layered structure one would expect their direction of growth to be in the plane of those layers. The evidence here is that the linear features grow down into the crystals from the surface. Finally, fig. 2d shows that the (111) spinel lattice fringes are not restricted to the regions described here as pores, which might otherwise be interpreted as fine crystallites of γ -alumina.

The over-all picture of the microstructural information as interpreted in this study, then, is one in which the dehydration of boehmite leads to a coherent skeleton of $\gamma\text{-Al}_2\text{O}_3$ that is intersected, sponge-like, by a series of pore systems.

The dehydration of boehmite at 400 °C in air was found in this study to be slow, the process being incomplete after 1 week, while at 600 °C the

reaction is complete after 1 day. The early stages of 400 °C dehydration are characterized microstructurally by the formation of relatively large oriented pores, the depth of which increases with time. The fast formation of these features, together with their apparently random positions in the crystal fragments, suggests that their formation may be a nucleated event, perhaps dependent on the presence of dislocations or other defects in the original boehmite crystal. Overlap of these features is commonly observed in transmission micrographs, and the attendant contrast effects indicate that overlapping pores are in fact at different levels within the fragment. This suggests that this type of pore is locked within the crystal lattice and does not emerge at the surface. If this is so, it is difficult to interpret the significance of the formation of these pores with respect to the dehydration process, especially since, at this stage, diffraction data indicate that only a very small degree of dehydration has taken place. The formation of these pores may, however, represent loss of water from defects, consisting of pockets of occluded molecular H₂O, which have been postulated to occur in boehmite crystals (Rouquerol *et al.*, 1966).

The later stages of dehydration are characterized by the formation of a fine lamellar pore system, which is developed only slowly at 400 °C (over a period of about 1 week) and appears to cover the whole of the crystal surface uniformly. The pores are uniquely oriented parallel to (001)_γ planes and the regularity of this orientation as well as that of the spacing between pores is remarkable. The uniqueness of the pore orientation defines an anisotropy in the γ-alumina lattice and this is matched by the observation from X-ray powder data that the spinel lattice of the γ-alumina is in fact tetragonal. Observations of the change in contrast with time suggest that this pore system grows into the crystal in a direction perpendicular to the (110)_γ surface and the time scale over which this occurs (1 day to 1 week at 400 °C) matches that over which the X-ray work indicates significant H₂O loss. Thus this microstructure is characteristic of an important mechanism for the dehydration of boehmite.

Observations of orientations perpendicular to [110]_γ show that fine planar pores parallel to (110)_γ are also formed. The fast-forming large pores observed in [110]_γ orientations may also be associated with this system. Since the process of dehydration is usually considered to advance from the surfaces of a crystal it is reasonable to suppose that different mechanisms may operate on different crystal surfaces. In the case of boehmite it appears that dehydration of (010)_{Bo} faces produces (001)_γ

pores while dehydration of faces perpendicular to (010)_{Bo} produces (110)_γ pores. Again it is reasonable that different dehydration mechanisms may produce different degrees of coherence of the γ-alumina lattice formed.

The lamellar microstructure observed on (110)_γ faces is characteristic, then, of an important mechanism for the dehydration of boehmite since (010)_{Bo} surfaces predominate and since the γ-alumina lattice is formed coherently. By analogy with metallographic eutectic and eutectoid lamellar microstructures, the appearance of the (001)_γ pore system, together with the fact that its growth direction is perpendicular to the (110)_γ surface, suggests that the dehydration mechanism is controlled by a diffusion process perpendicular to the pores, i.e. along [001]_γ. When dehydration is induced by beam heating, different conditions, including those of temperature and pressure, apply and the reaction is much faster, taking minutes rather than days as at 400 °C in air. The pore structure developed under these conditions is much finer in scale and is more randomly oriented. This observation is compatible with a dehydration mechanism controlled by a diffusion process. The possibility that detailed mechanistic information may be derived from evidence provided by microstructural observations will be discussed in a future study.

It is instructive to compare the results of this work with the data provided by the adsorption work of de Boer *et al.* They found, for samples of well-crystallized boehmite fired at various temperatures for times in the range 6–24 h, that the surface area increases up to a maximum of 65.7 m²/g Al₂O₃ for heat-treatment at 580 °C followed by a decrease for higher temperatures (de Boer *et al.*, 1962). This increase in surface area was found to be coincident with substantial loss of H₂O from the material and was attributed to the formation of a large number of narrow pores (de Boer and Lippens, 1964). This behaviour should be compared with the development of the fine microstructure observed in the present study. A study of the pore-size distribution (Lippens and de Boer, 1964b) revealed that after treatment at 450 °C 29%, and for 580 °C 50%, of the total surface area is provided by pores with widths less than about 18 Å. Calculations of mean widths for these narrow pores (Lippens, 1961) gave values of 8.4 and 10.9 Å for material treated at 450 and 580 °C respectively. Again these values compare favourably with the microstructure illustrated in fig. 2b. Discrepancies between the temperatures necessary for the development of the fine porosity observed in the work of de Boer and in the present study can be attributed to

the short firing times used in the former study.

Assuming a figure of 8 Å for the mean pore width of the fine microstructure of fig. 2b and thus a mean width of 30 Å for the regions of γ -Al₂O₃, a figure of about 180 m²/gAl₂O₃ can be calculated for the internal surface area assuming complete development of the fine porous texture.

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