CALCINATION OF GIBBSITE

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ABSTRACT. Data are presented showing the changes in physical properties which occur during the calcination of Bayer-process gibbsite at temperatures up to 1400°C. The various stages of the calcination were examined using differential thermal analysis, X-ray diffraction, low-temperature nitrogen adsorption, optical and electron microscopy, and particle-size distribution analyses. The morphology of the gibbsite aggregates was found to be unchanged up to ~ 1100°C, despite the development of several intermediate metastable phases. At higher temperatures, the original gibbsite pseudomorphs become microporous coincident with the development of finely divided alpha-alumina which is formed in a strain-free state. The crystal size and pore size increase with temperature between 1100 and 1400°C. The influence of the parent gibbsite structure on the morphology of the alpha-phase material is demonstrated in scanning-electron micrographs. The effect of various parameters on the milling of high-temperature calcines is also discussed.

Introduction

The production of aluminium on a commercial scale depends on the electrolytic reduction of alumina that is obtained by the calcination of aluminium trihydroxide produced in the Bayer process. In essence, the Bayer process is a purification step in which impure natural bauxite is dissolved in caustic soda liquor and a relatively pure form of $Al(OH)_3$ (gibbsite) is precipitated by seeding. Calcination of the gibbsite furnishes a nominally pure oxide product which may pass either to an electrolytic cell for reduction to the metal or may be used as the raw material for the production of certain ceramics such as refractories, abrasives and high-alumina insulators.

The use of calcined alumina in these fields demands a close control of both the chemical and physical properties. In part, this is achieved by a close control of the calcination conditions.

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This paper examines the development and properties of the various phases produced during the calcination of gibbsite in air at temperatures up to 1400°C.

Experimental

Samples of a commercially available Bayer-process gibbsite, contained in platinum crucibles, were calcined in air at various temperatures for two hours. In all cases, the samples were placed in a preheated electric furnace and were found to reach within 10°C of the stated temperature within eight minutes. The samples were cooled over P_2O_5 in a desiccator prior to examination using standard techniques as noted.

Results and discussion
Phases developed during calcination

Figure 1 shows the differential thermal analysis (DTA) curve obtained for the as-received gibbsite heated in air. The first endotherm at 272°C corresponds to the decomposition of gibbsite at the surface of the aggregates present in the material, whereas the main

FIGURE 1. DTA of as-received Bayer-process gibbsite (heating rate: 12°C/min).

FIGURE 2. Schematic representation of phases formed during the calcination of gibbsite.

peak at 383°C corresponds to the decomposition of the bulk of the gibbsite retained within the centre of the aggregates. The high-temperature endotherm at 556°C indicates the final dehydroxylation of the material.

It has been postulated [1-3] that gibbsite may dehydrate via two mechanisms. Surface material which is free to lose water easily, may decompose to form anhydrous active alumina (chi- and, at higher temperature, kappa-alumina). However, the bulk of the gibbsite inside the aggregate may be subjected to a hydrothermal environment and hence decompose initially to the monohydrate (boehmite) which decomposes via a different reaction path to form progressively gamma-, delta-, theta- and finally alpha-alumina with increasing temperature. This reaction scheme has been confirmed in the present work. X-ray powder photographs were obtained of all samples using a Guinier-De Wolff focusing camera and were the basis for the data presented in Figure 2. The identification of the intermediate phases is made difficult by the basic similarity between the diffraction patterns of the gamma-, delta-, theta- and chi-forms and also by the diffuseness of the patterns. For these reasons, the positive identification of chi alumina was made difficult in the presence of gamma-alumina and hence the chi-form is shown in Figure 2 without any temperature limits for its stability field.

The expected increase in the crystal size of alpha-alumina, produced by calcination at 1100°C and above, was indicated in Debye-Scherrer diffraction patterns by a gradual increase in the sharpness of all diffraction lines. Calcination of samples at 50-degree intervals above 1000°C indicated that a relatively large diffracting unit (> 350 Å) of alpha-alumina is developed directly this phase is formed: resolution of the Co K-alpha doublet in the back-reflection region is observed at all times.[4]
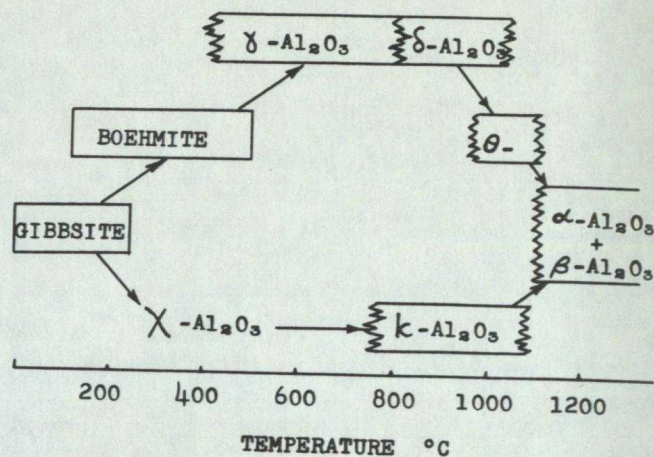
Debye-Scherrer powder patterns were obtained of the 1200-1400°C calcines using an 11.46-cm diameter camera and filtered Co radiation and were used to determine the unit-cell edges of the various calcines. Using the Straumanis technique[5] a series of unit-cell edge values was first obtained and then corrected for the systematic errors of adsorption and divergence of the beam using the Nelson and Riley function.[6] A least-squares analysis was then obtained for a plot of this correction function versus the unit-cell edge values from which extrapolation gave the a_0 and c_0 values. This analysis failed to show any significant variation in the unit-cell edges of the various calcines from that of a fully annealed sample. The values determined were a_0 : 4.7587 ± 0.0002 Å and c_0 : 12.9905 ± 0.0006 Å at 22°C which agree well with the reported ASTM values of 4.758 Å and 12.991 Å respectively.
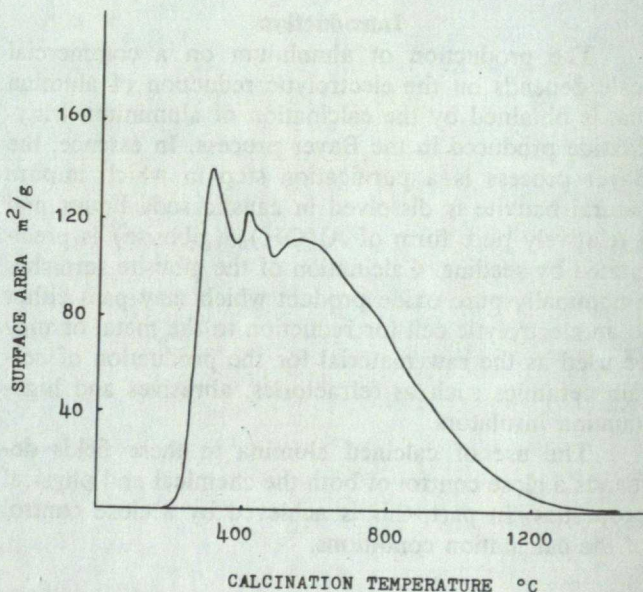

FIGURE 3. Variation of surface area with temperature for as-received Bayer-process gibbsite.

Surface area

In addition to the increased sharpness of X-ray diffraction patterns, the gradual increase in the crystal size of the alpha-alumina with increasing temperature was also shown indirectly by the gradual decrease in specific surface area. The variation of surface area (measured using a Perkin-Elmer Shell sorptometer) with calcination temperature is shown in Figure 3. Comparison of the data in Figures 2 and 3 shows that the maximum surface area is developed at the completion of the gibbsite decomposition at approximately 225°C. The discrepancy between the DTA temperature of 272°C for the decomposition of gibbsite and the figure of 225°C from the X-ray data is due to the different calcination conditions employed. DTA used a dynamic heating rate of 12°C/min whereas samples for X-ray analysis were calcined under isothermal conditions.

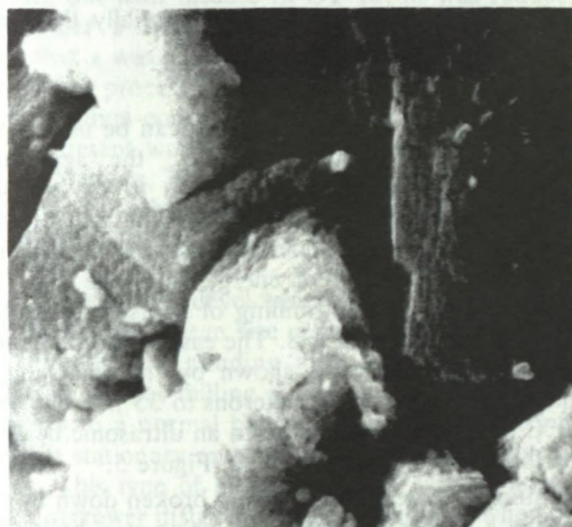A second lower peak in the surface-area curve occurs at approximately 350°C which lies very close to the temperature of formation of gamma-alumina. The third surface-area peak at approximately 550°C does not correlate with any phase change or observable (to a resolution of 250° Å) microstructural change in the
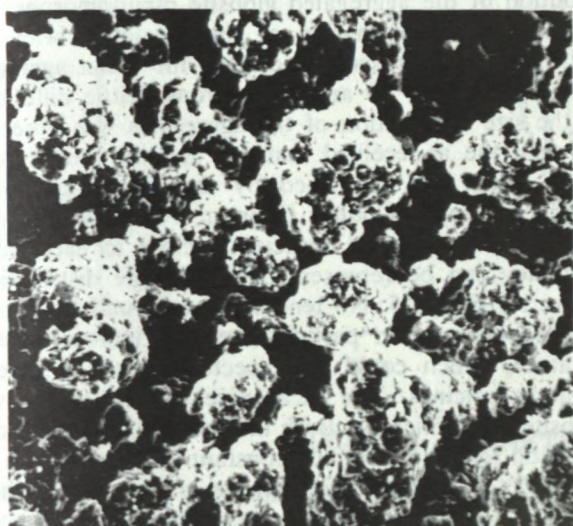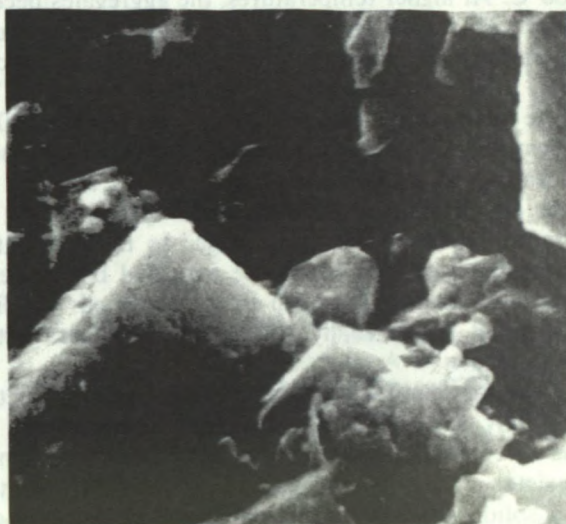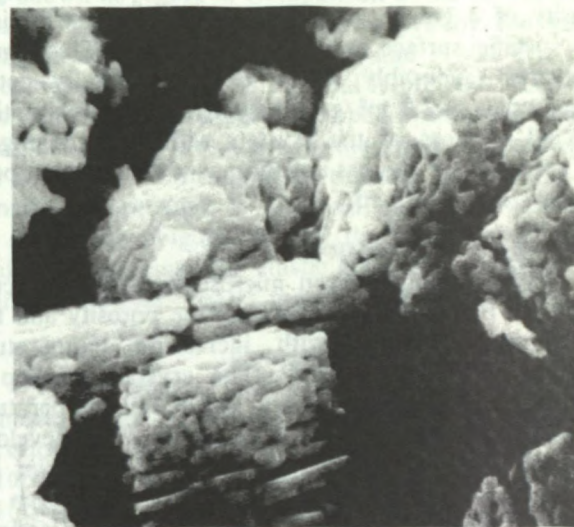

FIGURE 4. SEM micrographs of commercial gibbsite after calcination in air for 2 hrs.

sample. The origin of this effect is not understood. The inflection in the curve at 800°C coincides closely with the transformation of gamma- to delta-alumina and also with the development of the kappa-form from chi-alumina. The final structural change to alpha-alumina at 1100°C is not accompanied by any inflection in the surface-area curve despite the coincident physical change observed in the scanning electron micrographs shown in Figure 4.

Optical microscopy

Optical examination of the calcines with a petrographic microscope does not reveal any changes up to 1100°C. At higher temperatures, the aggregates become darker in transmitted light and the birefringence (kappa-alumina orthorhombic, theta-alumina monoclinic) under crossed polars decreases markedly. The change is most marked between 1100° and 1200°C, the temperature range in which the conversion of theta- and kappa- to alpha-alumina occurs. This effect is due to the development of an open pore system within the aggregate which is effectively closed to the penetration of immersion oil and hence the expected birefringence of the hexagonal alpha-form is not observed: the light is scattered at the many solid-to-air interfaces within the aggregate.

The fact that these aggregates have a pore structure completely open to a gaseous phase is shown by the close agreement between the calculated and experimentally determined surface-area data. It can be shown that for a solid cylindrical prism having a diameter d and aspect ratio* 1:4 the specific surface is given by $12/cd$ where c is the density of the body. Assuming the corundum produced at 1400°C consists of crystals with an equivalent face diameter of 1 micron, and having a density of 4 gm/cc, then for a monosize distribution, the specific surface would be 3 m²/gm. This figure compares favourably with the experimentally determined value of 2.9 m²/gm, showing that the assumption that all surfaces of the crystals within the aggregate are accessible to the gas is valid, i.e. a completely open-pore system is formed.

Scanning electron microscopy

The scanning electron microscope (SEM) micrographs of Figure 4 show that both the porosity and the crystal size increase with increasing temperature between 1200 and 1400°C. The crystals develop a platy habit at all temperatures, but in this temperature range no hexagonal outline is developed. The development of some alpha-alumina at 1100°C, shown by X-ray diffraction, could not be distinguished even at high magnification; only a tendency to develop laminations parallel to the hexagonal face of the original gibbsite crystal was observed. At slightly higher tempera-

*Aspect ratio — the ratio of height to equivalent face diameter for a platy crystal.

tures, these laminations open to form the open-pore system shown clearly in the 1400°C calcine of Figure 4. It has been shown elsewhere[7] that the basis for the pore and crystallite structure is laid at an early stage during the dehydration of several hydroxides including nordstrandite (a polymorph of gibbsite).

Particle-size distribution

The micrographs of Figure 4 confirm the small particle size of the alpha-alumina crystals as suggested by the surface-area data. However, the free-flowing nature of these calcines is due to the particle-size distribution of the aggregated gibbsite pseudomorphs. An initial visual examination of these calcines with the petrographic microscope indicated the mean aggregate size lay between 50 and 80 microns. Little difference in the size distribution of the aggregates was observed between the as-received material and the various calcines. This was confirmed by the size distributions obtained using a Coulter Counter, Figure 5. The size distribution curves lie sufficiently close to each other that they can be represented by a single distribution, Curve A, Figure 5. No tendency was found for a progressive decrease in particle size with increasing temperature, which could be expected for the high-temperature calcines. The mean size for the as-received gibbsite is 62 microns. Both the mean size and the distribution remain essentially constant at temperatures up to 1000°C, and SEM micrographs of the calcines show no change in morphology of the aggregates or the component pseudomorphs. At higher calcination temperatures, the mean particle size is reduced slightly (to 56 microns) coincident with a change in morphology shown in the micrographs of Figure 4. However, the particle-size distribution remains essentially the same.

Milling

Before these calcined materials can be used in the fabrication of high-alumina bodies, the aggregated pseudomorphs must be broken down to the ultimate crystals and thus reduce the porosity. The initial reduction of these aggregates does not require the expenditure of a large amount of energy as is the case, for example, during the ball-milling of coarsely crystalline alumina to 5 microns or less. The ease with which these aggregates break down is shown by the reduction in mean particle size from 56 microns to 35 microns for a 1200°C calcine after exposure to an ultrasonic beam in water for 15 seconds, cf Curve B, Figure 5.

Initially, these materials were broken down by wet milling in a rubber-lined ball mill using steel balls. The milling parameters such as time of milling, charge to water ratio, concentration of surfactant, and grinding medium geometry were varied independently and the effect on the resulting size distribution of material calcined at 1300°C was noted. The greatest effect occurred
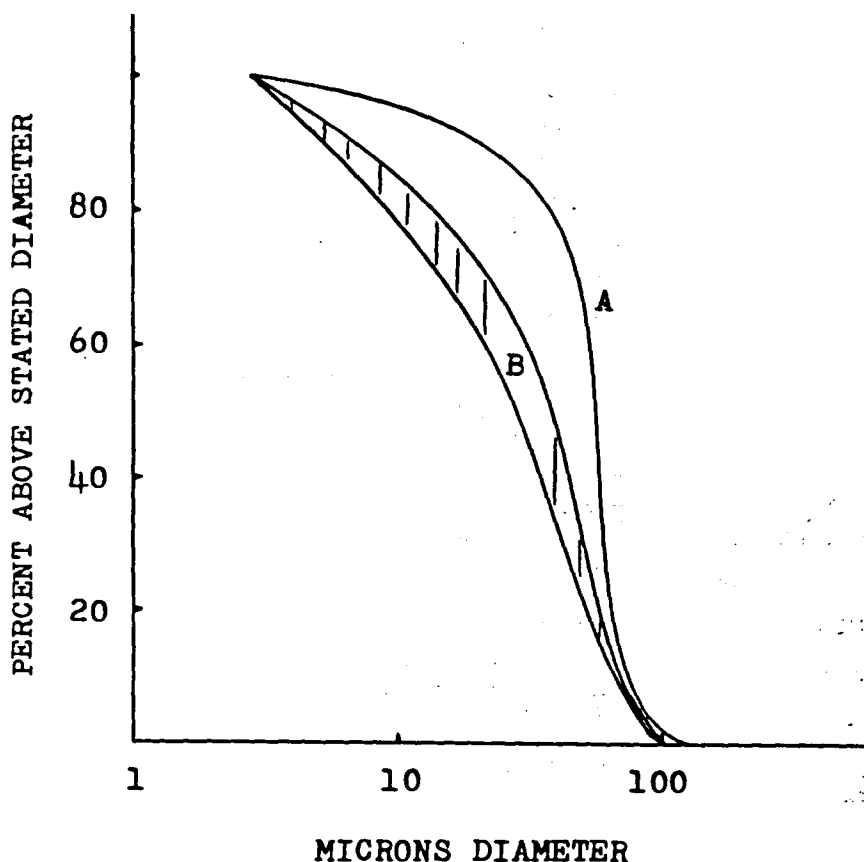
46

Y-axis: PERCENT ABOVE STATED DIAMETER

80
60
40
20

X-axis: 1 10 100

MICRONS DIAMETER

FIGURE 5. Particle-size distribution of calcined gibbsite. A — Size distribution of material calcined between 1000 and 1400°C. B — Size distribution range observed after treating A with ultrasonics in water.

with the use of a surfactant (OT-13, American Cyanamid). Without this grinding aid, a broad-size distribution was produced after ball-milling for 2 hours, in which the mean particle size (m) was 8 microns and the standard deviation (s) was 2.8. Under similar conditions, but with the use of OT-13, m was reduced to just under 3 microns and the distribution narrowed such that s was 1.6. Although this surfactant does aid the milling process significantly, it should be noted that it is a sodium-containing organic material and as used in the present work would contribute 0.12% as Na_2O to the alumina. This could render the material unsuitable for the fabrication of electronic components because the dielectric strength in the fired body would be lowered.

However, the development of a fine-milled alumina having a similar mean size m and distribution s is possible without any grinding aids (surfactants). This is achieved by wet milling using a paddle mill in which, contrary to a normal ball-mill operation, the container remains stationary and the balls are agitated by an impeller. This type of mill produces a smaller mean size and a narrower distribution than a ball mill when operated under similar conditions. For example, the 1300°C calcine developed a size distribution in which m was 8 microns and s 2.8 after milling for 2 hours without any surfactant, whereas m is reduced to 2.5 microns and s to 1.6 after paddle milling for 1 hour without any additive. In general, it was found that the paddle mill produces the same particle-size distribution in half the time and without the use of any surfactant as that which is developed in a ball mill with OT-13.

Typical particle-size distributions obtained after milling the various calcines for 1 hour in a paddle mill are shown in Figure 6. Comparison of the curves shows that a wider distribution is developed by the lower-temperature calcines (1100°C and 1200°C). The presence of more coarse material is probably related to the very small pore size developed within the pseudomorphs which allows the deformation during milling to lie within the elastic limit of the material. As the calcination temperature is increased, so a larger pore size is developed (Figure 4) and the deformation during milling may exceed the elastic limit of the material and consequently less coarse material is retained.

Conclusions

With increasing temperature, alumina formed from gibbsite passes through a series of phase changes before developing the stable alpha-form at approximately 1100°C. No change in morphology was observed up to 1100°C despite the formation of several metastable intermediate phases.

At higher temperatures, the alpha-form is developed initially as very small crystals still retained within the original gibbsite pseudomorph. All the high-temperature calcines consisted of strain-free alpha-alumina; the unit-cell dimensions were found to be identical
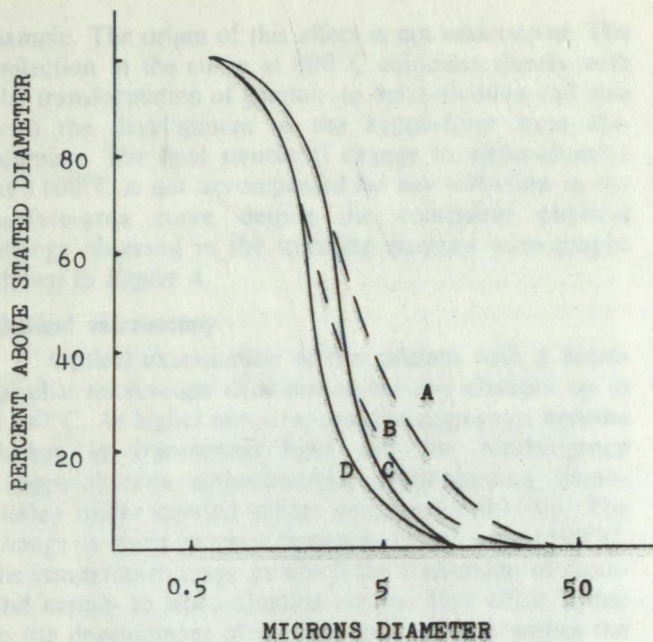
FIGURE 6. Particle-size distribution of calcined
material after wet paddle-milling for 1 hr.
  A – Gibbsite calcined 1100°C in air for 2 hrs.
  B – Gibbsite calcined 1200°C in air for 2 hrs.
  C – Gibbsite calcined 1300°C in air for 2 hrs.
  D – Gibbsite calcined 1400°C in air for 2 hrs.

with those of a fully annealed sample. The pseudo-
morphs become progressively microporous with the
growth of alpha-phase crystals; the pore size increasing
with temperature.

Paddle-milling is much more effective than ball-
milling for the comminution of the alpha-phase cal-
cines. In general, a paddle mill produces a much smaller
mean-particle size and a narrower distribution in less
time than is possible by ball-milling under similar con-
ditions.

Acknowledgments

The author wishes to express his thanks to A. J.
Hanson for his assistance in the experimental stages
of this work.

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