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SIMULTANEOUS DTA AND DTG MEASUREMENTS ON ALUMINIUM OXIDE MONOHYDROXIDES

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Simultaneous DTA and DTG curves (Mettler TA-2) have been measured for one diaspore and four different boehmites at temperatures up to 750° in a flow of dried argon. The crystallographic structures of the materials were assessed by X-ray diffraction and the degree of clustering of the elementary particles by scanning electron microscopy. To get straight base-lines a calibration curve was used to correct the DTA curves. The usefulness of the correction was established by comparison with DTA curves obtained with a Mettler TA-2000.

The diaspore contained occluded water. Expulsion of the water at 300–350° brought about fragmentation of the crystals. The DTA and DTG peaks that correspond to the dehydration to alumina both lie at 560°.

There is a noticeable spread in the DTA and DTG peaks for the different boehmites in the temperature range 455–530°. All the DTA peaks lie close to the corresponding DTG peaks. One of the boehmites displayed a double peak (470° and 502°). To trace the origin of the variation in peak temperature, the porous structure of the boehmite having its peak at 530° was varied by ball-milling and by dispersion into water, neither of which markedly affected the crystallographic structure and the crystallite size. Whereas ball-milling did not change the peak temperature much, dispersion into water brought about a transition from a single peak at 530° to a double peak at 450° and 490°. Prolonged storage in air led to a shift of the peaks to 480° and 520°. It is concluded that the porous structure of boehmites can profoundly affect the appearance and the temperature of their dehydration peaks.

Two different modifications of AlOOH are known, *viz.* diaspore and boehmite. [1]. The mineral diaspore, which is slightly more stable than boehmite, is often found as crystals some mm in size. Boehmite is generally less well crystallized. Most synthetic boehmites contain crystallites some tenths of a micron in size that are intimately clustered.

At temperatures above about 400° the aluminium oxide monohydroxides lose water and transform to alumina. As is to be expected, the dehydration temperature depends on the water vapour pressure. Imelik et al. [2] observed boehmite to dehydrate at 360° at 10^{-3} mm Hg, while in air marked dehydration proceeded only at 400°. De Boer et al. [3] reported dehydration of boehmite at a water vapour pressure of 4.6 mm Hg at 425°. Stumpf et al. [4] mentioned a shift in the dehydration temperature from 390–440° to 450–550°, when they changed the atmosphere from dry air to steam.

In DTA experiments, where the temperature is raised continouously, dehydration proceeds at more elevated temperatures. For diaspore an endothermic peak at 540 – 580° has been reported [5]. The peak temperatures for boehmite, which has been studied more frequently, range from 530 to 590° [6]. Since the water vapour pressure determines the dehydration temperature, the rate of transport of water out of the sample may be expected to influence the peak temperature. When a high internal vapour pressure is required to drive the water rapidly out of the sample, the peak temperature will be higher. As water, moreover, decreases the rate of dehydration of boehmites, the water vapour pressure will affect the peak temperature even more strongly. Eyraud and Goton [7] and Callister Jr. et al. [8] reported the negative effect of water on the rate of dehydration of boehmite.

As dealt with, for example, by Garn [9], effects of transport of evolving gases on DTA peaks can be minimized by flowing a gas over the sample and by using small samples. While a small sample reduces the transport resistance inside the material, the gas flow provides for a rapid transport of gaseous reaction products from the sample. With boehmites, however, it may be difficult to avoid the transport resistance within the sample determining the peak temperature. Wakao and Smith [10] published experimental results which demonstrate that the rate of transport of gases through boehmites strongly depends on the porosity and the mean pore size. Lippens and Steggerda [11] reviewed the porous structure of dehydrated boehmites. The BET surface area of boehmites consisting of small crystallites increases only slightly or even decreases on dehydration, whereas that of well-crystallized boehmites increases. The nitrogen sorption isotherms indicate the formation of slit-shaped pores with an average size of about 22 Å.

In view of these observations it may be expected that the structure and distribution of the macropores within boehmites containing small crystallites will be retained during dehydration. Since, as said above, boehmites of varying porosity and macropore size display different transport properties, the internal vapour pressure required to promote a rapid transport of water, and, hence, also the peak temperature, can vary. With boehmites containing large crystallites, the macroporous structure will also be retained. With larger crystals, transport of water through the narrow slit-shaped pores formed by the dehydration may also determine the overall rate of transport of water.

To establish whether the porous structure of boehmites can influence the temperature of the dehydration peak, the packing of the elementary particles can be altered by ball-milling and by dispersion in water. Especially dispersion into water can markedly affect the porous structure of finely-divided solids, as has been dealt with, for example, by Iler [12]. The temperature of the dehydration peak may also depend on the size of the crystallites, because of either the higher stability of larger crystallites [13] or the more difficult transport through longer narrow slits.

We therefore decided to investigate four different boehmites, two of which consist of small crystallites, and a diaspore of a large crystallite size. The crystallographic structures of the solids have been accurately determined. In these experiments the pore structure of one of the boehmites was varied by ball-milling and also by dispersion in water.

Experimental

Methods

Simultaneous DTA-DTG measurements were carried out in a Mettler TA–2 [14]. Nickel crucibles (diameter 0.5 cm, height 0.6 cm) and sensitive Ni/NiCr thermocouples, which had been calibrated with indium (156.6°) and zinc (472°), were used. The weight of sample and reference (dead-burnt alumina) was about 30 mg. To obtain a reproducible packing of the powdered samples, a vibrator with spatula (Mettler) [14] was used.

The samples were placed in a quartz furnace with a corrosive gas inlet. To ensure an equal heat flux to sample and reference, a nickel cylinder that surrounded sample and reference was mounted inside the furnace. The cylinder was closed at the top by a flat lid. To obtain a rapid exchange of gas, the cylinder and the lid contained a number of holes.

Sample and reference were kept in flowing argon dried by passing through three columns filled with molecular sieve 4A (1/16″ pellets) previously baked out at 330–360°. The flow rate through the inlet for corrosive gases was 10 ml min^{-1}. After passing through the balance, the second stream of argon (50 ml min^{-1}) entered the nickel cylinder at the bottom. Flow controllers kept the flows accurately at the above values. Before entering the balance, the argon was heated to 300 K, the temperature at which the housing of balance was thermostated. The previous heating of the argon prevented thermal disturbances that lead to spurious effects on the weight recording.

In all experiments the heating rate was 5° min^{-1}. Though the temperature *vs.* time curve was not completely linear, it reproduced exactly. Previously we ran the temperature program with an empty sample and a filled reference crucible. Provided the furnace and the small circular discs onto which the crucibles were placed [14] were mounted in the same orientation, each run yielded curves displaying the differential temperature and the apparent weight that were precise duplicates. In addition to a correction for the weight [15], we could therefore also correct for a small difference in heat flux to sample and reference. To assess the usefulness of the DTA correction, we compared the corrected curves of the TA–2 with curves recorded with a Mettler TA–2000 DTA apparatus. A flow of carefully-dried nitrogen was passed through the TA–2000. The sample and the reference were kept in open aluminium pans.

A camera (diameter 114.83 mm) was used to record X-ray patterns of the materials studied on photographic films. With an accurate automatic photometer the values of the lattice spacings were determined. The profiles of broadened diffraction maxima were also measured by the photometer; the size of the crystallites were calculated from the widths of the maxima [16]. The materials were studied in a Cambridge Stereoscan microscope.

Materials

The diaspore investigated (Dia) was obtained from the Billiton Corporation. The following boehmites were studied:

BoI – synthetic boehmite from the British Aluminium Corporation;
BoII – BoI ground for 1 hr in an agate ball-mill;
BoIII – synthetic boehmite hydrothermally prepared by Dr. J. van Dijk (Delft, Netherlands);
BoIV – synthetic boehmite from the Ormet Corporation;
BoV – synthetic boehmite from Matiswerk;
BoVI – BoI dispersed into water, filtered and dried for 16 hr at 110°.

Results

X-ray diffraction and electron microscopy

The diffraction pattern of the diaspore contained spots instead of the usual Debye-Scherrer rings. The spot pattern is due to large crystals of diaspore (minimum size of crystallites about 0.5 mm). After grinding, fully-developed Debay-Scherrer rings were obtained. The directions of the spot reflections of the original diaspore coincide with the positions of the Debye-Scherrer rings of the ground material.

The *d* values measured for the diaspore are collected in Table 1, which also includes values from the literature [17]. The diaspore investigated here displayed spacings that are 0.03 to 0.7 Å larger than those of the literature. The agreement is nevertheless satisfactory.

Table 1

X-ray diffraction of diaspore
(Cu Kα radiation; $\lambda = 1.54$.A)

d [17]	*I* [17]	*d* (this work)
4.70	3	4.745
3.97	8	4.040
3.20	3	3.243
2.54	6	2.567
2.37	2	
2.33	8	
2.32	6	

Table 2 contains the *d* values measured for the boehmites, together with two sets of data from the literature [17, 18]. The differences between the experimental and the literature values are generally small; BoIII and BoIV did not show some of the weak reflections. Comparison of the data for BoI, BoII and BoVI shows that the crystallographic structure was not affected by grinding or dispersion in water. BoVI had lost only three weak reflections. Neither grinding nor dispersion gave rise to a marked broadening of the reflections. Hence, the crystallite size was not decreased to below about 0.1 μ.

Table 2

X-ray diffraction of boehmites
(Cu Kα radiation; λ=1.54 A)

Reflection	[18]		[17]		BoI	BoII	BoIII	BoIV	BoV	BoVI
	d	*I*	*d*	*I*	*d*	*d*	*d*	*d*	*d*	*d*
020	6.11	100	6.112	100	6.103	6.103	6.090	6.046	6.088	6.122
120	3.164	65	3.160	53	3.150	3.159	3.164	3.151	3.209	3.152
140 031	2.346	53	2.343	50	2.341	2.344	2.343	2.335	2.335	2.341
131	1.980	6	1.979	6	1.977	1.979	—	1.973	1.973	—
051	1.860	32	1.857	24	1.857	—	1.854	—	—	—
200	1.850	27	1.847	17	—	1.847	—	1.848	1.850	1.848
220	1.770	6	1.768	8	1.769	1.770	—	1.763	1.764	—
151	1.662	13	1.661	14	1.662	1.661	1.660	1.656	1.659	1.657
080	1.527	6	1.526	9	1.528	1.526	1.525	1.522	1.523	—
231	1.453	16	1.452	14	1.446	1.447	1.448	1.448	1.449	1.448
002	1.434	9	1.435	7	1.434	1.432	1.432	1.431	1.432	1.430
—	—	—	1.430	7	—	—	—	—	—	—
180	1.412	—	1.410	1	—	—	—	—	—	—
022	1.396	2	1.402	3	—	—	—	—	—	—
171	1.383	6	1.382	9	1.386	1.381	1.381	1.380	1.380	1.380
260	1.369	2	—	—	—	—	—	—	—	—
251	1.312	15	—	—	1.314	1.309	1.307	1.307	1.308	1.308

BoIII and BoV exhibited a (020) reflection (d = 6.1 Å), that was broadened. From the profile of the (020) reflection a weight-mean dimension normal to the (020) planes of 870 Å for BoIII and of 860 Å for BoV was calculated. These sizes were confirmed from electron micrographs. At a magnification of 9,000, BoIII showed the presence of clustered thin platelets. The thickness of the platelets varied between 500 and 1,000 Å. The lateral dimensions of the platelets were between 3,000 and 6,000 Å (0.3 – 0.6 μ). At a magnification of 10,000, BoV displayed highly-clustered particles of the order of 1,000 Å. Most particles of BoV were spherical in nature, but some appeared to be platelets.

At a smaller magnification, the size of the conglomerates of boehmite crystallites could be established. BoIII showed conglomerates of 15 – 40 μ. The conglomerates of BoV were smaller. Besides small conglomerates of 1 – 3 μ, larger ones of 7 – 10 μ could be seen.

Thermal analysis of diaspore

DTA curves measured with the nickel crucibles displayed a small exothermic peak at 340 – 350°. This is due to the fact that the mass of the reference crucible was slightly larger than that of the sample crucible. As nickel loses its ferromagnetism at the Curie temperature (358°), this results in an exothermic signal. Alloying of the nickel caused the transition temperature to be slightly below the Curie temperature of pure nickel.

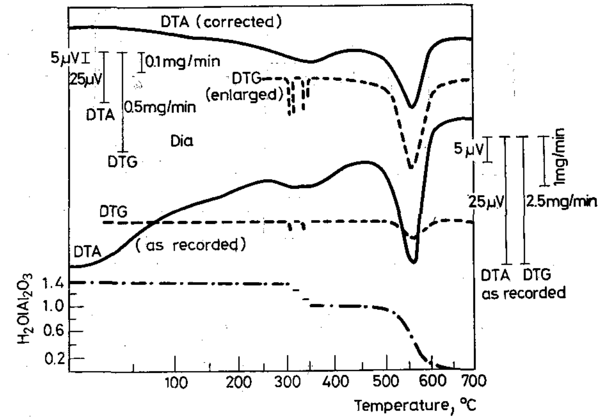

Fig. 1. Simultaneous TG DTA of diaspore. Mettler TA-2; heating rate 5° min^{-1}. Correction DTA curve, see text; H_2O/Al_2O_3 calculated from corrected TG curve

The results obtained with the diaspore are shown in Fig. 1 (note the small exothermic peak at 350° due to nickel). The base-line of the DTA curve shows a positive slope, which is eliminated by the correction. Loss of water led to an endothermic DTA peak and a negative DTG peak at 560°. This temperature agrees well with those quoted in the literature, *viz.* 540 – 585° [5] and 572° [19]. With the DTA curve the onset of the reaction becomes apparent at a markedly lower temperature than with the DTG curve, which shows the loss of water from about 500°.

The DTA curve exhibits a broad endothermic maximum at about 350°. The crystallites of the diaspore decrepitated in the temperature range 300 – 350°. Blow-out of solids was prevented by grinding, which led to smaller crystallites. The curves of Fig. 1 were obtained with a ground sample. As can be seen from the DTG curve, the sample lost water in two distinct steps. The DTG curve shows two high and narrow peaks, whereas the DTA curve displays a broad maximum. Apart from the loss of material, the unground diaspore showed the same curves as ground samples.

The H_2O/Al_2O_3 ratio is plotted against temperature at the bottom of Fig. 1. The data were calculated by assuming that the sample had lost all water at about 800°. Samples kept for 6 hr at 1100° in atmospheric air showed a smaller weight loss, which is presumably due to readsorption of water during cooling. Figure 1 shows that the material had the theoretical composition of diaspore ($Al_2O_3 \cdot H_2O$) after the two releases of water below 350°. The composition $Al_2O_3 \cdot H_2O$ remained stable up to about 500°.

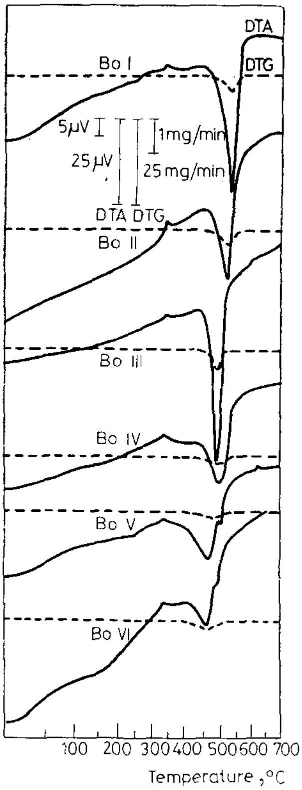

Fig. 2. Simultaneous DTA, DTG of boehmites, Mettler TA-2; heating rate 5° $\min^{-1}$; DTA and DTG curves as recorded experimentally. ——— DTA; ------ DTG

As the aluminium trihydroxides, gibbsite and bayerite, decompose at about 300°, we considered the possibility that the diaspore contained some trihydroxide. The composition $Al_2O_3 \cdot 1.4H_2O$ should, however, correspond to a fraction of trihydroxide of about 25% by weight. After dehydration of the trihydroxide the composition should have been $Al_2O_3 \cdot 0.8H_2O$ instead of $Al_2O_3.1.0H_2O$. During dehydration of gibbsite and bayerite, hydrothermal conditions have been postulated inside large crystals [3]. These conditions lead to formation of boehmite, which also has the composition $Al_2O_3 \cdot H_2O$. An amount of gibbsite or bayerite equivalent to about 25 wt.% should, however, have been detected in the X-ray diffraction pattern. We therefore believe that 11 wt.% of water was occluded in the large diaspore crystallites. The *d* values (Table 1) of the diaspore, which are consistently larger than those published in the literature, may be explained by the presence of occluded water. The DTA curve indicates that water was released above about 300°, but could escape from the crystallites only after the pressure had increased sufficiently to fragment the crystallites.

Thermal analysis of boehmites

Figure 2 shows the DTA and DTG curves as recorded for the boehmites. The DTA curves have the small exothermic peak at about 345° and an upward drift of the base-line analogous to the experimental DTA curve of Fig. 1. The corrected DTA curves are presented in Fig. 3 together with the DTG curves drawn on a larger scale. The correction procedure yielded straight base-lines, except with BoVI, where the crucibles were presumably not correctly positioned.

Table 3

Peak temperatures of boehmites, °C

Sample	Mettler TA—2		Mettler TA—2000
	DTG	DTA	DTA
BoI	540	530	530
BoII	520	520	528
BoIII	498	498	498
BoIV	510	500	502
BoV	480	470	470
	510	502	505
BoVI	460	455	480
	495	490	520

Table 4

Published peak temperatures of boehmites, °C

Author(s)		DTA	Author(s)		DTA
De Boer et al.	[3]	590	Murat	[23]	560
Calvet et al.	[20]	590	Mackenzie	[5]	550
Arakelyan et al.	[21]	580	Arakelyan et al.	[21]	550
Mackenzie	[5]	560	Smykatz-Kloss	[19]	545
Trambouze et al.	[22]	560	Eyraud et al.	[24]	530

As with the diaspore, the peaks in the DTA and DTG curves almost coincide; the peaks of the DTG curves are at a slightly higher temperature than those of the DTA curves. It is evident that the different boehmite samples displayed widely-differing peak temperatures. BoI exhibited the highest peak temperature (530–540°), which is markedly lower than that of the diaspore (560°). The widths of the peaks displayed by the different boehmites also vary. BoV and BoVI showed double peaks.

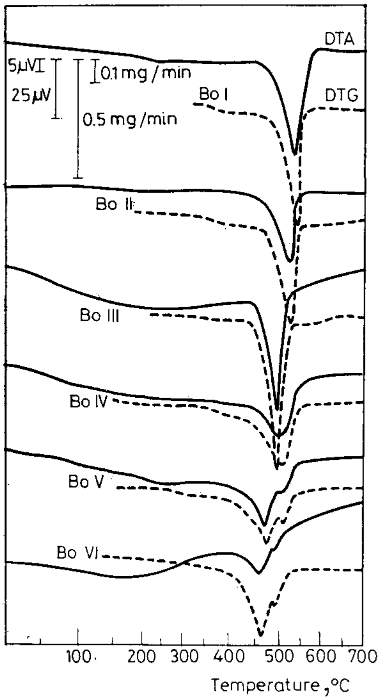

Fig. 3. Simultaneous DTA, DTG of boehmites; Mettler TA-2; heating rate 5° min^{-1}, DTA curves corrected as described in text. DTG curves on larger scale; ——— DTA; --- DTG

The DTG curves have a shoulder to the main peak at lower temperatures. With BoI to BoIV the shoulder appears at about 350°, whereas with BoV and BoVI it is less sharp and appears at lower temperatures. The DTA curves do not clearly show the shoulder both before and after correction.

Measurements with the TA-2000 are shown in Fig. 4. The curves resemble the corrected DTA curves of Fig. 3, though the return to the base-line could not always be recorded as the maximum temperature of the TA-2000 was about 550°. The curves in Fig. 4 show a slow development of the main peak at about 360°. This temperature roughly corresponds to those where the shoulders to the DTG curves in Figs 2 and 3 set in.

The peak temperatures have been collected in Table 3. The temperatures of the DTA peaks measured with the TA-2 and the TA-2000 are seen to agree very well, except for the values for BoVI. The shapes of the DTA curves recorded for BoVI with the TA-2 and TA-2000 also differ. In Fig. 3 the second peak is much smaller than the first, whereas in Fig. 4, the second peak is slightly higher than the first. The difference in the curves for BoVI in Figs 3 and 4 may be accounted for by the time lapse between the two measurements. The BoVI was stored for about 3 months in a stoppered bottle after the measurements of Fig. 3 had been made. During the storage the solid particles partly returned to the state of BoI and BoII, which show a single peak at 520 – 530°.

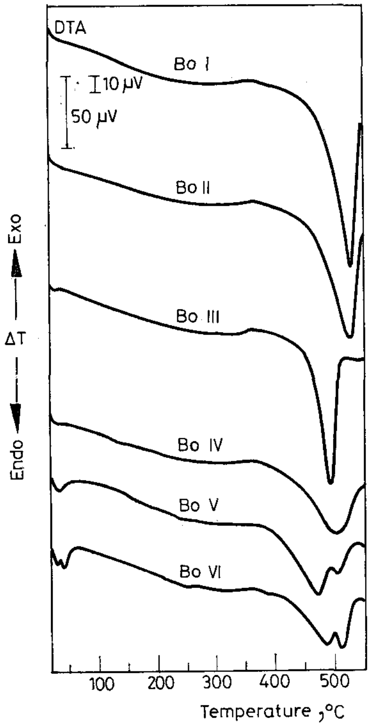

Fig. 4. DTA of boehmites; Mettler TA-2000; heating rate 5° min^{-1}, Curves as recorded experimentally

Discussion

Peak temperatures published in the literature for boehmites are listed in Table 4. It is evident that only the peak temperature of BoI falls within the range of temperatures in Table 4 (530 – 590°). The other samples investigated in this study showed peak temperatures considerably below 530°. DTA curves with double peaks have not been published in the literature. On studying hydrothermally-treated pseudoboehmite, Papée et al. [25] observed analogous thermogravimetric curves that contain a very short plateau during the dehydration. The two peak temperatures were about 490° and 570°.

The X-ray diffraction patterns of Table 2 indicate that the large variation in the peak temperatures of Table 3 cannot be due to differences in crystallographic structure. With identical crystallographic structures, a variation in peak temperature is generally ascribed to varying crystallite size [26]. Since nucleation of a new solid phase and evolution of a gaseous component can generally proceed more easily at the surface of a solid, the temperature at which the reaction proceeds rapidly may be lower with smaller crystallites.

Evidence has been published that the size of the crystals influences the rate of dehydration of boehmite. Hill and Zimmermann [27], investigating the dehydration of boehmite crystals of about 2 mm on the hot-stage of a microscope, observed decomposition only above 540°. Using the same technique, Saalfeld [28] reported dehydration of polycrystalline boehmite of a much smaller crystallite size to proceed already at 430°.

The broadening of the (020) reflection shows that BoIII and BoV contain crystallites of a dimension of about 900 Å. This dimension was also found with the electron microscope. The presence of small crystallites in BoIII and BoV could explain the low peak temperatures (BoIII 498°; BoV 470° and 500°). The double peak of BoV could be due to the presence of smaller crystallites in addition to larger ones. A considerable fraction of crystallites smaller than 900 Å was not apparent, however, in the electron micrographs of BoV.

The experimental data of BoI, BoII and BoVI demonstrate more convincingly that the crystallite size is not the main factor in determining the temperature of the dehydration peak. By grinding, BoI was transformed into BoII, which did not show a broadened (020) reflection. Accordingly, the peak temperature of BoII is only 10° below that of BoI. The onset of the dehydration peak is at a lower temperature and less sharp with BoII than with BoI. The (020) reflection of BoVI is not broadened either, which is to be expected, as dispersion into water is not likely to decrease the crystallite size markedly. Nevertheless, BoVI exhibits a double peak with temperatures as low as 455° and 490°, which are below those of BoIII and BoV that contain small crystallites. Storage of the dispersed material led to a shift of the higher peak back to the temperature of BoI, viz. 530°. A slow growth of crystallites during storage is just as unlikely as a reduction of the crystallite size by dispersion in water.

As pointed out by Garn [9], transport of a gaseous reaction product out of the sample can strongly affect the peak temperature. Since we were using small samples and passed a flow of dried argon over the samples, transport of water from the external surface of the samples to the flowing gas was rapid. As a result, our peak temperatures are below those quoted in the literature. Our experimental results demonstrate that the rate of transport of water through the sample can also determine the peak temperature. We therefore ascribe the difference in peak temperatures shown by BoI (530°) and by BoII and BoIV (about 500°) to a lower porosity and the presence of narrower pores in BoI. BoV contained regions of different porosity and pore size distribution. The different transport resistance led to the double peak.

Grinding slightly improves the transport of water out of the samples. The less sharp onset and the lower peak temperature of BoII indicate a lower transport resistance. As expected, dispersion in water affected the stacking of the conglomerates of small crystallites much more. The resulting material contained regions of different transport resistance; both regions have a higher porosity and wider pores than BoI. During storage the liquid water present in narrow pores slowly evaporated from BoVI. The capillary forces due to the receding water meniscus [12] appreciably decreased the porosity and the mean pore size. Since water was transported markedly more slowly from regions where the liquid water had evaporated during storage, the peak shifted to a higher temperature.

As mentioned above, dehydration of boehmite should proceed already at about 400°. When the reaction is carried out at a temperature which is continuously increasing, at a rate, for example, of 5° min^{-1}, the maximum rate of reaction may be expected at a temperature considerably above 400°. The onset of the reaction, however, should be observed at a temperature not far above that where the reaction shows a marked rate at a constant temperature. With calcium oxide, onset of the reaction with CO_2 and decomposition of $CaCO_3$ at decreasing and increasing temperatures, respectively, was experimentally observed at the temperatures calculated from thermodynamic data [29].

With highly-porous materials, where the stacking of the elementary particles does not dramatically change on decomposition with formation of a gaseous product, a slow transport of the reaction product out of the sample can be expected. With boehmites the evolving water not only increases the thermodynamic equilibrium temperature, but also decreases the rate of dehydration. As a result, the temperature of the dehydration peak can be considerably above the thermodynamic equilibrium temperature as calculated from the water vapour pressure of the surrounding gas. The peak temperature will, moreover, depend on the porous structure of the sample.

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RÉSUMÉ — Les courbes ATD et TGD d'une diaspore et de quatre boehmites différentes ont été enregistrées simultanément (Mettler TA-2) jusqu'à 750°, sous circulation d'argon desséché. La structure cristallographique de ces composés a été examinée par diffraction des rayons X et le degré de compacité a été évalué par microscopie électronique à balayage. Une courbe d'étalonnage a été utilisée pour corriger les courbes ATD et obtenir des lignes de base droites. L'utilité de cette correction est démontrée en comparant avec les courbes ATD obtenues à l'aide d'un appareil Mettler-TA-2000.

La diaspore contenait de l'eau d'inclusion. L'élimination de l'eau à 300—350° a entraîné la fragmentation des cristaux. Les pics ATD et TGD qui correspondent à la déshydratation en oxyde d'aluminium se trouvent tous deux à 560°.

Un étalement des pics ATD et TGD est perceptible pour les différentes boehmites dans l'intervalle de température 455—530°. Tous les pics ATD sont proches des pics TGD correspondants. L'une des boehmites a donné un pic double (470 et 502°). Afin de trouver l'origine de la différence de température entre les deux pics, la structure poreuse de la boehmite dont le pic se situait à 530° a été modifiée par traitement dans un broyeur à boulets et par dispersion dans de l'eau; ni l'un ni l'autre de ces deux traitements n'influence de façon apparente la structure cristallographique et la taille des cristaux. Alors que le traitement au broyeur à boulets ne change pas beaucoup la température du pic, la dispersion dans de l'eau fait apparaître le passage d'un pic unique à 530° à un pic double à 450 et 490°. Le stockage prolongé dans l'air provoque un déplacement des pics à 480 et 520°. On en conclut que la structure poreuse des boehmites peut influer profondément sur l'apparition et la température de leurs pics de déshydratation.

ZUSAMMENFASSUNG — Simultane DTA- und DTG-Kurven (Mettler TA-2) wurden für ein Diaspor und vier verschiedene Boehmite bei Temperaturen bis zu 750° in einem Strom von getrocknetem Argon aufgenommen. Die kristallographische Struktur der Substanzen wurde mittels Röntgendiffraktion und der Anhäufungsgrad der Elementarpartikel mittels Raster-Elektronenmikroskopie bestimmt. Um gerade Grundlinien zu erhalten wurde eine Eichkurve zur Korrektur der DTA-Kurven verwendet. Die Nützlichkeit der Korrektur wurde durch Vergleiche der in einem Mettler TA-2000 Gerät erhaltenen DTA-Kurven festgestellt.

Der Diaspor enthielt eingeschlossenes Wasser. Das bei 300 bis 350° erfolgte Abspalten des Wassers brachte eine Fragmentierung der Kristalle mit sich. Die DTA- und DTG-Peaks, welche der Dehydratisierung zu Aluminiumoxid entsprechen, liegen beide bei 560°.

Im Temperaturbereich von 455 bis 530° läßt sich ein Verbreitern der DTA- und DTG-Peaks der verschiedenen Boehmite wahrnehmen. Einer der Boehmite zeigte einen Doppelpeak (470° und 502°). Um dem Ursprung der Änderungen der Peak-Temperaturen festzustellen wurde die poröse Struktur des Boehmits mit einem Peak bei 530° mit Hilfe einer Kugelmühle und durch Dispersion in Wasser verändert. Keine dieser Behandlungen änderte merklich die kristallographische Struktur und die Kristallgröße. Während das Vermahlen in der Kugelmühle die Peak-Temperatur nicht wesentlich änderte, erbrachte die Dispergierung in Wasser einen Übergang von einem einzigen Peak bei 530° zu einem Doppelpeak bei 450 und 490°. Längeres Lagern an der Luft führte zu einer Verschiebung der Peaks nach 480° und 520°. Es wird gefolgert, daß die Porösstruktur von Boehmiten das Erscheinen und die Temperatur ihrer Dehydratisierungspeaks stark beeinflussen kann.

Резюме — Одновременно были измерены кривые ДТА—ДТГ (Меттлер ТА-2) для одного диаспора и четырех различных боэмитов при температурах до 750° в токе сухого аргона. Кристаллографическая структура этих материалов была определена рентгено-диффракционным методом, а степень образования кластеров элементарных частиц — сканирующей электронной микроскопией. Имеющаяся калибровочная кривая базисной линии была использована для коррекции кривых ДТА. Пригодность такой коррекции была установлена путем сравнения с кривыми ДТА, полученными на приборе Меттлер ТА-2000. Диаспор содержит окклюдированную воду. Выталкивание воды имеет место при 300—350°C, сопровождаясь разрывом кристаллов. Оба ДТА—ДТГ пики, соответствующие дегидратации окиси алюминия, находятся при 560°. Заметный разброс проявляется среди ДТА- и ДТГ пиков различных боэмитов в области температур 455—530°. Все ДТА пики лежат близко к соответствующим ДТГ пикам. Один из боэмитов проявляет двойной пик (470° и 502°). Чтобы установить причину изменения температурного пика, этот боэмит пористой структуры и имеющий пик при 530°C был изменен путем размола на шаровой мельнице и диспергированием в воде. Ни один из этих методов не затрагивает заметно его кристаллографическую структуру и размер кристаллитов. В то время как размол на шаровой мельнице не изменяет температурный пик, диспергирование в воде — вызывает переход от одного пика при 530° к двойному — при 450° и 490°. Продолжительное выдерживание на воздухе приводило к сдвигу пиков до 480° и 520°. Сделано заключение, что пористая структура боэмитов может глубоко затрагивать как вид пиков, так и температуру их дегидратации.