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The effect of grinding on the thermal decomposition of alumina monohydrates, α- and β-$Al_2O_3 \cdot H_2O$

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Abstract

Well-crystallized alumina monohydrates, two boehmites and a diaspore, were ground in air for 0–24 h in a planetary ball mill. The effect of grinding on the texture, structure and thermal behaviour of dehydration and α-transformation was examined by means of XRD, TG, DTA, SEM and ^{27}Al MAS-NMR. It was found that after 24 h of grinding, the boehmites changed entirely to an amorphous hydrated alumina, part of which transformed to alumina by an additional mechanochemical dehydration, while diaspore did not.

Keywords: Alumina; Boehmite; Decomposition; DTA; Grinding; TG

1. Introduction

The reactivity of solids is strongly influenced by mechanochemical treatment. Therefore, mechanochemical processing is widely used in the chemical industry where solids are involved. In a previous paper [1], the mechanochemical phenomena of two alumina trihydrates, gibbsite and bayerite which are very important ceramic materials, were mainly studied by grinding.

The purpose of the present study is to investigate the effect of mechanical grinding on the particle size, morphology, and temperatures of dehydration and transformation to α-Al_2O_3 (i.e. α-transformation) of the well-crystallized alumina monohydrates, boehmite and diaspore, which were synthesized under hydrothermal conditions.

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2. Experimental

Two boehmites (α-$Al_2O_3 \cdot H_2O$) were hydrothermally synthesized from gibbsite (Nippon Light Metal Co., BHP39 high-purity aluminum hydroxide, α-$Al_2O_3 \cdot 3H_2O$) in an autoclave (internal volume of 125 ml) under the following conditions: vapour pressure 700 kg cm^{-2}, at 370°C for two days in (A) water and (B) 1N NaOH solution. These will hereafter be referred to as boehmite (A) and boehmite (B). A diaspore (β-$Al_2O_3 \cdot H_2O$) was obtained by the hydrothermal synthesis of gibbsite mixed with a natural Chinese diaspore ore as a seed crystal under a vapour pressure of 1000 kg cm^{-2}, at 390°C for two weeks [2]. By using the resulting diaspore for the subsequent experiments, the purer diaspore was synthesized. All the alumina monohydrates obtained were washed with distilled water and then dried at 100°C.

The alumina monohydrates were dry-ground in air for 0–24 h in a P-7 planetary ball mill (Fritsch). Two grammes of sample and four alumina balls 12 mm in diameter were placed in a 12 ml alumina jar. The grinding was interrupted every hour, and the sample was scraped from the balls and the sides of the jar and then reloaded to continue grinding for 0–8 h. For 12–24 h of grinding, a 12 ml agate jar and four agate balls 12 mm in diameter were used.

Powder X-ray diffraction (XRD) patterns, scanning electron microscopy (SEM), simultaneous TG-DTA and particle size distribution were measured by the same procedures reported previously [1]. ^{27}Al MAS-NMR spectra were recorded on a Bruker MSL-400 high-resolution NMR spectrometer at a resonance frequency of 104.262 MHz and a magnetic field strength of 9.4 T. The spinning rate was 4 kHz. Pulses of 5 μs with a 0.4 s recycle time were used. Chemical shifts were recorded with respect to an aqueous solution of $Al(H_2O)_6Cl_3$ used as an external standard.

3. Results and discussion

Figs. 1 and 2 show the XRD patterns and SEM photographs of boehmites and diaspore synthesized hydrothermally. Evidence for a single phase of each alumina monohydrate can be seen in Fig. 1, as all the diffraction lines were assigned on the basis of the JCPDS powder diffraction lines. Boehmites (A) and (B), and diaspore are composed of granular, lamellar and acicular microcrystals, respectively. The morphology of these particles is reflected in the XRD patterns in Fig. 1, therefore proving that the well-developed plane of the lamellar particles of boehmite (B) corresponds to the (020) plane and the longest crystal axis of diaspore correspond to the *c*-direction. The difference in the morphology between boehmite (A) and boehmite (B) probably depends on the solvent used for the hydrothermal synthesis. In particular, in the course of the crystal growth of boehmite (B), the predominant adsorption of Na ions was assumed to occur on the *ac* planes and inhibit crystal growth towards the *b*-direction, which may produce the lamellar particles shown in Fig. 2(b).

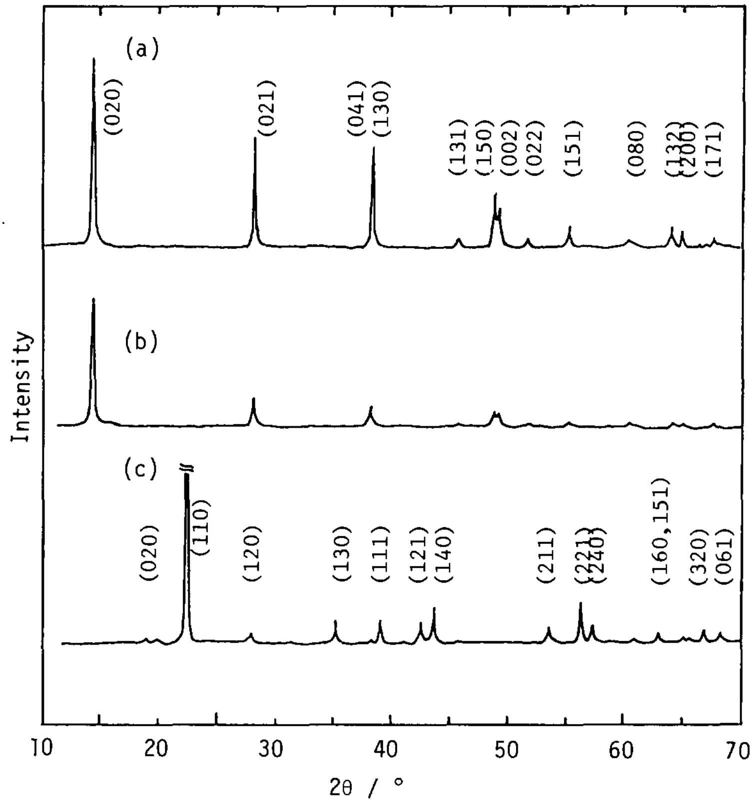

Fig. 1. X-ray diffraction patterns of (a) boehmite (A), (b) boehmite (B) and (c) diaspore.

Fig. 3 shows the variation of XRD patterns of boehmites and diaspore with grinding time. As the grinding time increases, a decrease in the intensity of the diffraction lines is observed. In particular, considerable changes occurred during 12 h grinding. After 24 h grinding, boehmites (A) and (B) changed entirely to an amorphous phase. Alumina trihydrates, gibbsite and bayerite also changed to an amorphous phase after only 4 h grinding [1]. These alumina trihydrates have a layered structure and readily allow the adjacent layers linked by hydrogen bonds to slip over each other, and then the whole structure to break down under grinding. However, the decreases in intensity of the three main diffraction lines of the alumina monohydrates during grinding differ from one another (Fig. 4). As can be seen in Figs. 3 and 4, while the intensity of the (020), (021) and (041, 130) lines of boehmite (A) decreased almost equally and monotonously with an increase in grinding time, that of the (020) line of boehmite (B) decreased significantly in comparison. In the case of diaspore, a significant decrease in the intensity of the (110) line and a relative increase in the intensity of the (111) line were observed. This behaviour can be understood from the SEM photographs in Fig. 5, which

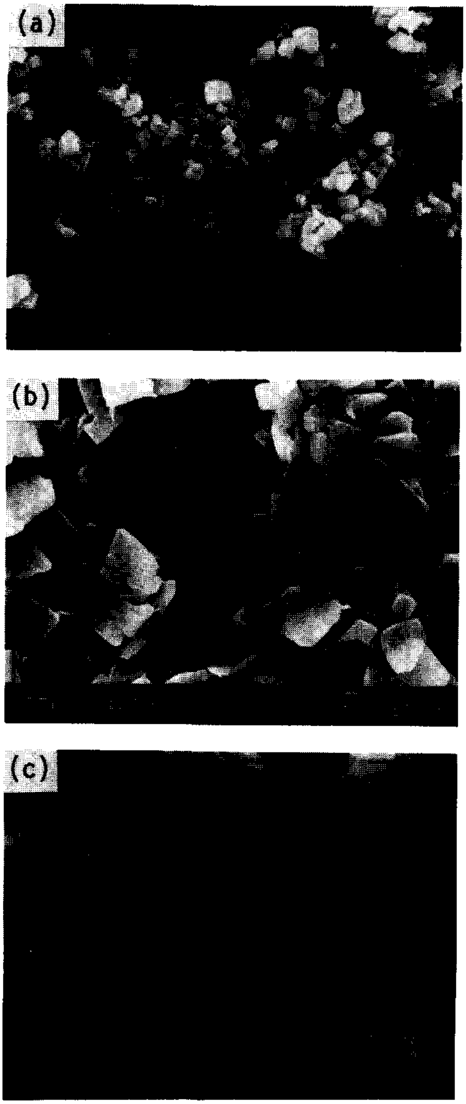

Fig. 2. Scanning electron micrographs of (a) boehmite (A), (b) boehmite (B) and (c) diaspore. The original magnifications are given on the micrographs.

shows that the (020) planes of the boehmite (B) and the longest crystal axes of the diaspore were predominantly broken by grinding.

Fig. 6 shows the variation of the median size (d_{50}) of the boehmites and diaspore with grinding time. The median size is equal to the diameter at 50% of the cumulative size distribution (Stokes diameter) curve. The initial values of d_{50} were reduced steeply to the half values during the first hour of grinding and then levelled

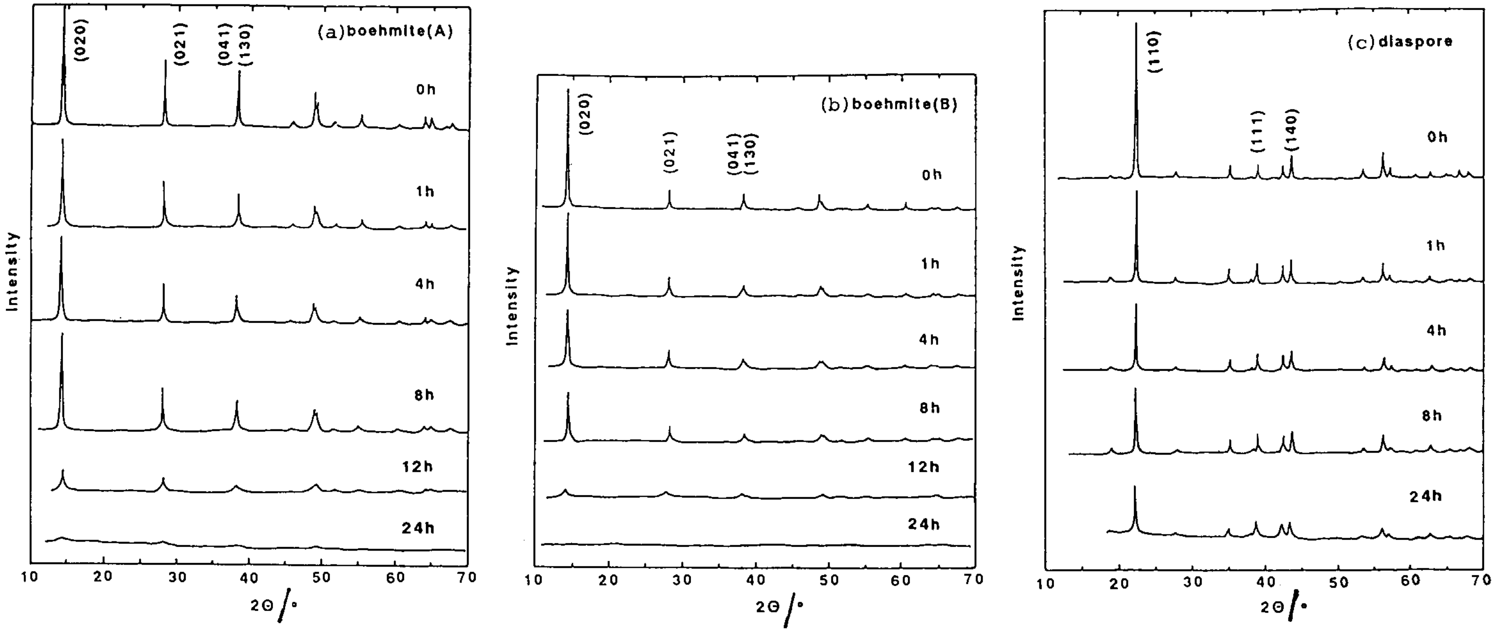

Fig. 3. Variation of X-ray diffraction patterns of (a) boehmite (A), (b) boehmite (B) and (c) diaspore with grinding time.

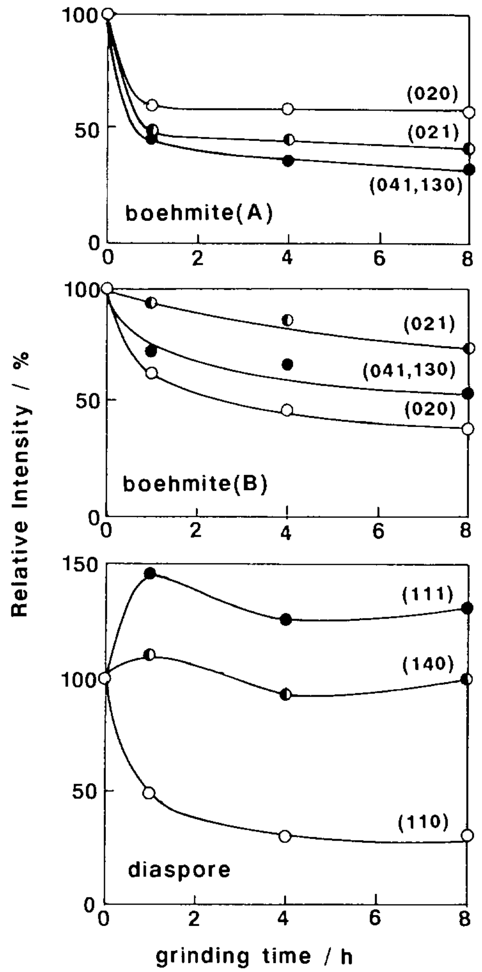

Fig. 4. Variation of the intensity of diffraction lines with grinding time.

off, indicating the establishment of a grinding equilibrium, in which size diminution and aggregation of particles counteract each other. In addition to a decrease in particle size by grinding, a roughening of the surface of the ground particles can be observed in Fig. 5. This appears to result from the adhesion of the more finely ground or amorphized particles on to the surface of the ground particles.

^{27}Al MAS-NMR spectra of unground, 8 h and 24 h ground boehmites and diaspore are shown in Fig. 7. The spectra of unground samples show a central peak at 7–9 ppm, and first-order spinning side bands at 48–52 ppm and −32 to −35 ppm, which are assigned to octahedrally coordinated Al (Al_{oct}). The spectra of the 8 h ground samples are entirely similar to those of unground ones. However, in the 24 h ground boehmites (A) and (B) an additional peak is observed as a shoulder at

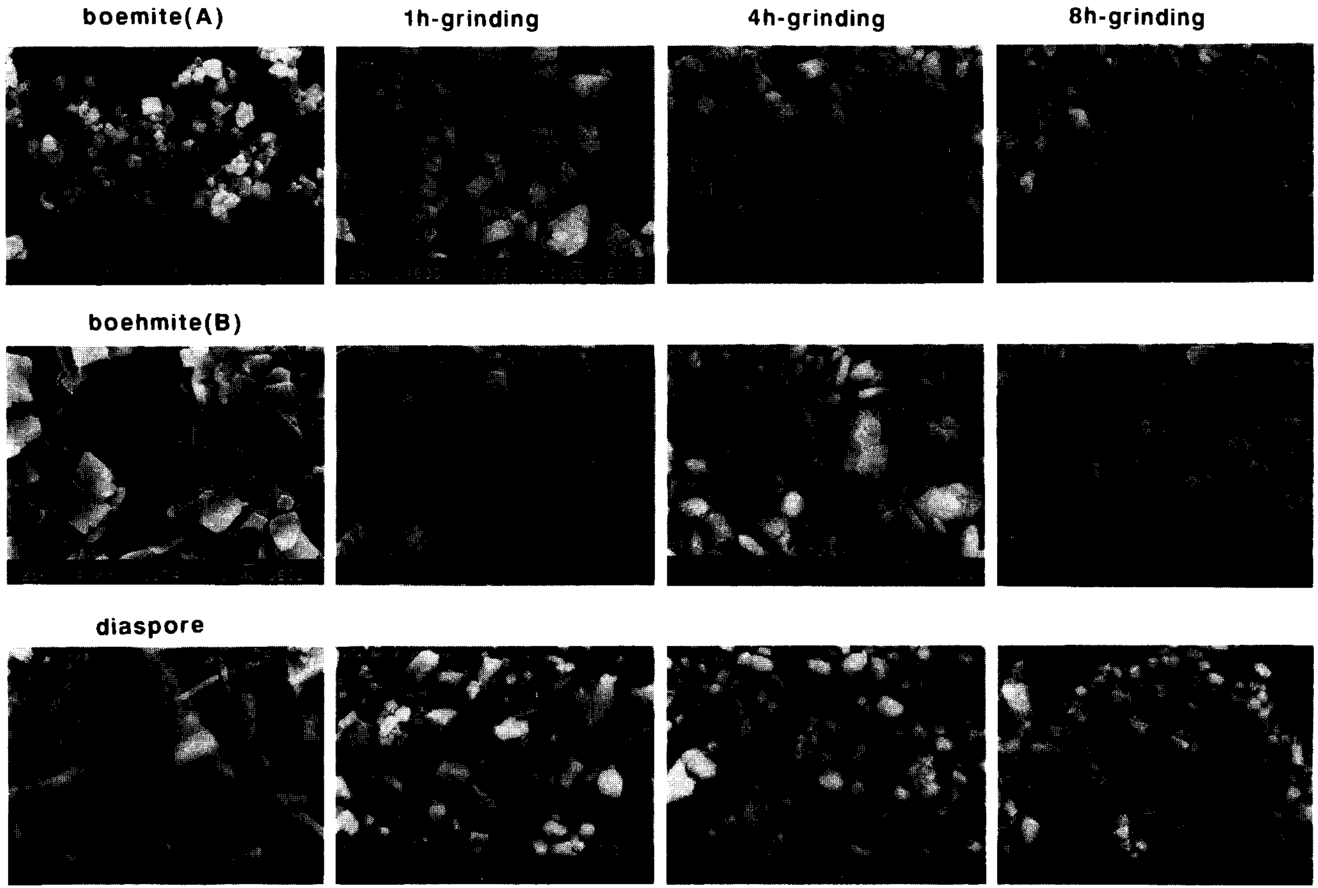

Fig. 5. Scanning electron micrographs of boehmite (A), boehmite (B) and diaspore ground for various times. The original magnifications are given on the micrographs.

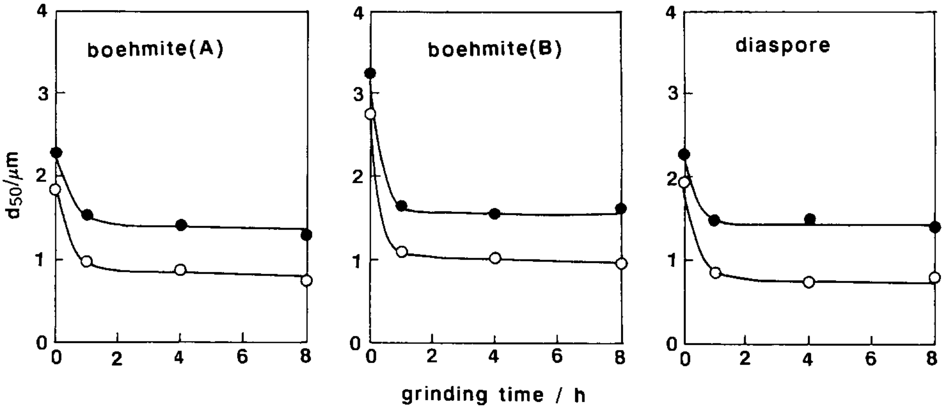

Fig. 6. Variation of median size (d_{50}) with grinding time: ●, an equivalent volume diameter; ○, an equivalent surface diameter.

around 75 ppm, which is assigned to tetrahedrally coordinated Al (Al_{tet}) [3–5]. All transition aluminas are known to show resonances of both Al_{tet} and Al_{oct} in their ^{27}Al MAS-NMR spectra. Therefore, it is considered that mechanochemical dehydration occurred to form some alumina on parts of the surface of 24 h ground boehmite (A) and (B) particles. This alumina can be regarded as an amorphous phase, because the XRD patterns of the 24 h ground samples showed an amorphous phase (Fig. 3). In contrast, diaspore did not show a peak attributable to Al_{tet} even when ground for 24 h. Although the mechanochemical dehydration of diaspore to α-Al_2O_3 could be expected [6], it was not possible to confirm this by NMR because α-Al_2O_3 shows only Al_{oct} spectral features, as does diaspore. In fact, it was proved that the mechanochemical dehydration of diaspore did not occur under the present experimental conditions from the results of XRD and TG-DTA experiments.

Fig. 8 shows TG and DTA curves of boehmites and diaspore ground for different amounts of time. The forms of alumina identified by XRD after being heated to various temperatures and then quenched to room temperature are shown on the DTA curves. The unground boehmites (A) and (B) showed an endothermic peak due to the dehydration at 535 and 545°C, and formed γ-Al_2O_3. On further heating, γ-Al_2O_3 transformed to α-Al_2O_3 via δ- and θ-Al_2O_3, showing a small exothermic peak at about 1200°C. The unground diaspore showed an endothermic peak due to the dehydration at 510°C and transformed directly to α-Al_2O_3. The difference in the transition sequence between boehmite and diaspore depends on the oxygen ion packing in their structures [7]. In boehmite, the structure as a whole is not close-packed, but within a layer the oxygen ions are cubic close-packed. In diaspore, oxygen ions are arranged in hexagonal close-packing. Therefore, it is considered that such a structural similarity between diaspore and α-Al_2O_3, which have a hexagonal close-packed oxygen ion lattice, caused a topotactic transformation from diaspore to α-Al_2O_3 at a temperature as low as 510°C [2].

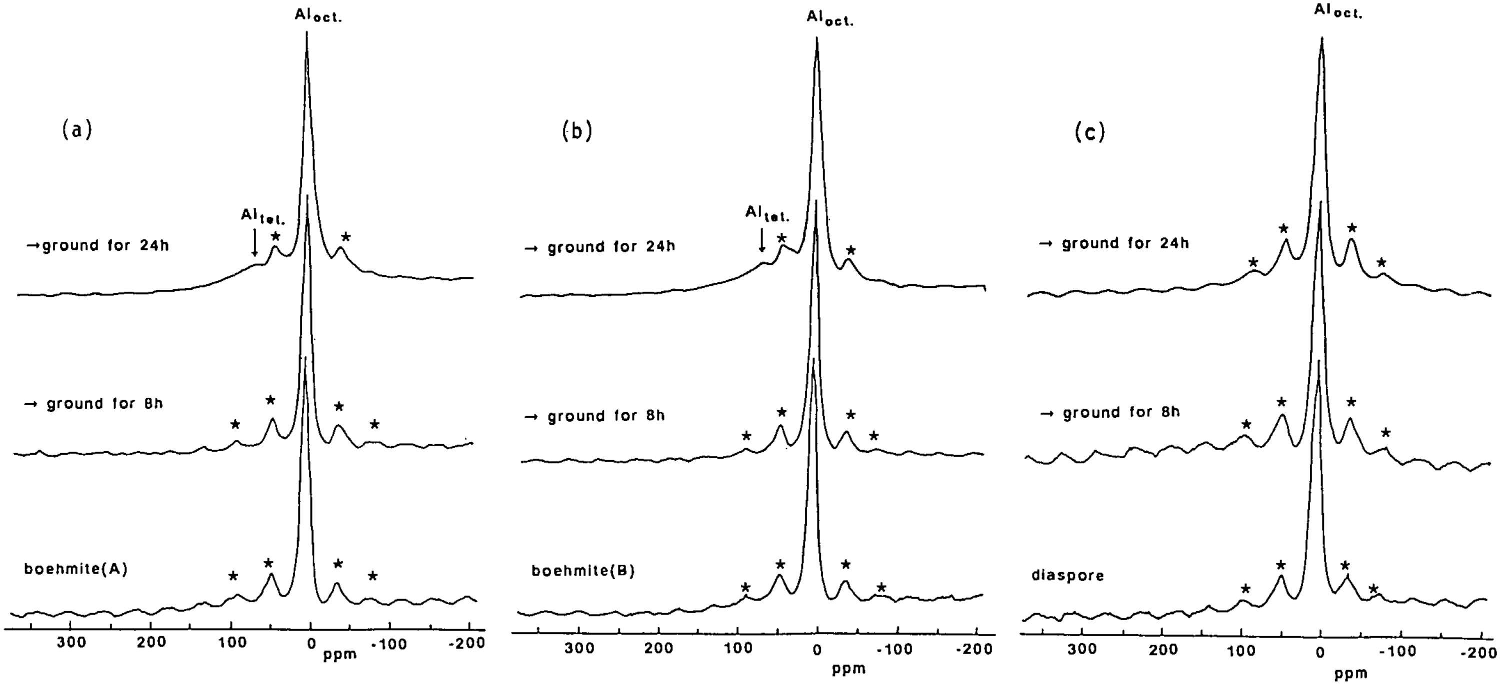

Fig. 7. ^{27}Al MAS-NMR spectra of (a) boehmite (A), (b) boehmite (B) and (c) diaspore ground for 0, 8 and 24 h. The asterisk signifies spinning sidebands.

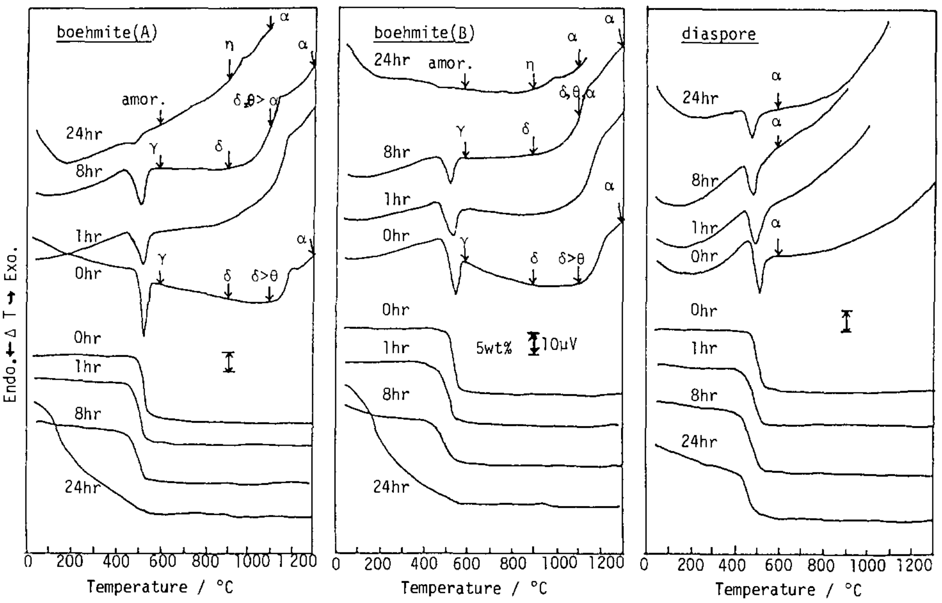

Fig. 8. TG and DTA curves of boehmite (A), boehmite (B) and diaspore ground for various times.

With an increase in grinding time, the temperatures of dehydration and the α-transformation peaks were lowered. After 24 h grinding, the dehydration peaks of boehmites (A) and (B) had almost disappeared and an additional broad endothermic peak appeared at around 150°C, in contrast to the diaspore which still showed an endothermic peak at 480°C. This behaviour is also reflected in the TG curves. The weight loss in the TG traces began at lower temperatures with increasing grinding time. On heating to 1300°C, the overall weight losses in boehmites (A) and (B) ground for 8 h and in diaspore ground for 24 h were approx. 15 wt%, which were equivalent to the stoichiometric weight loss (15.0 wt%) of these samples. This suggests that, in these cases, no mechanochemical dehydration occurred. In contrast, most of the amorphous phase obtained by 24 h grinding of boehmites (A) and (B) was estimated to be hydrated alumina on the basis of ^{27}Al MAS-NMR spectra (Fig. 7), which were almost the same as the spectra for unground boehmites except for the appearance of an Al_{tet} line, and of the TG and DTA curves (Fig. 8) showing a weight decrease due to dehydration. On heating, this amorphous hydrated alumina transformed to amorphous alumina, to η-Al_2O_3 and then to α-Al_2O_3, showing a small exothermic peak due to the α-transformation at 950°C, i.e. an identical transformation sequence to that observed for an amorphous hydrated alumina obtained by the grinding of gibbsite and bayerite. Moreover, the weight losses in boehmites (A) and (B) ground for 24 h on heating to 1300°C were 24.9 and 27.5 wt%, respectively. As described above, from the results of XRD (Fig. 3) and ^{27}Al MAS-NMR spectroscopy (Fig. 7), mechanochemical dehydration was induced on parts of the surface of amorphous hydrated alumina particles by

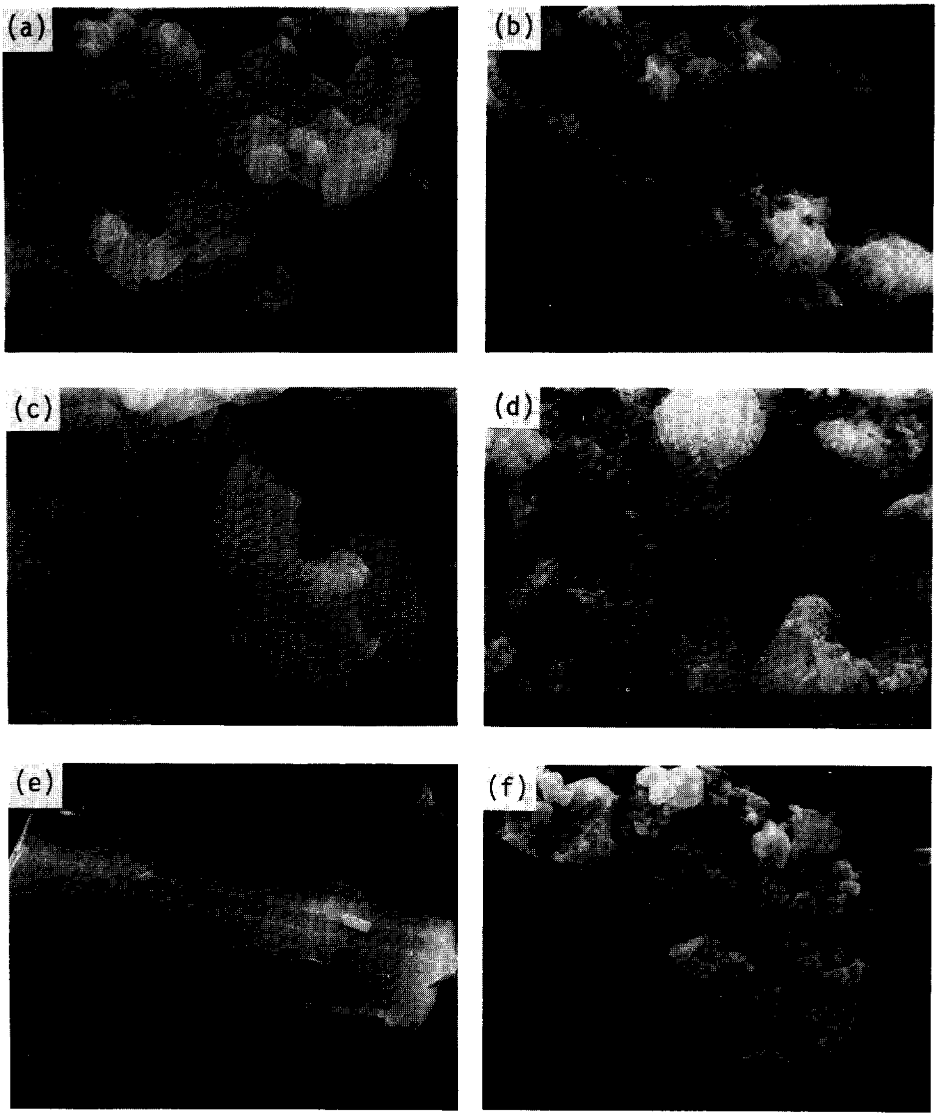

Fig. 9. Scanning electron micrographs of (a,b) boehmite (A), (c,d) boehmite (B) and (e,f) diaspore calcined at 1300°C. a, c, e: unground. b, d, f: ground for 8 h. The original magnifications are given on the micrographs.

prolonged grinding. The amorphous alumina thus resulting can be expected to be more reactive, and therefore adsorb water molecules from a surrounding atmosphere, which leads to an increase in the total weight loss under TG analysis. Finally, the formation of finely dispersed or amorphized particles by grinding led to a lowering of the temperatures of dehydration and α-transformation.

The SEM photographs shown in Fig. 9 are obtained for α-Al_2O_3 by the heating of unground and 8 h ground boehmites and diaspore to 1300°C. In unground samples, the external shape of each particle was retained in spite of the formation of some cracks and pores. In contrast, in 8 h ground samples the formation of vermicular-like particles by the sintering of the more finely ground materials was observed on the surface of the ground particles. This actually supports the formation of more finely ground or amorphized particles on the surfaces of the particles of ground boehmites and diaspore. A study of the relationship between the surface textures of particles modified by mechanochemical treatments and their surface reactivity, such as catalytic reactions, are presented in the next paper [8].

References

[1] T. Tsuchida and N. Ichikawa, React. Solids, 7 (1989) 207.
[2] T. Tsuchida and K. Kodaira, J. Mater. Sci., 25 (1990) 4423.
[3] V.M. Mastikhim, O.P. Krivoruchiko, B.P. Zolotovskii and R.A. Buyanov, React. Kinet. Catal. Lett., 18 (1981) 117.
[4] C.S. John, N.C.M. Alma and G.R. Hays, Appl. Catal., 6 (1983) 341.
[5] D. Plee, F. Bong, L. Gatineau and J.J. Fripiat, J. Am. Ceram. Soc., 107 (1985) 2362.
[6] Y. Arai, T. Yasue and I. Yamaguchi, Nippon Kagaku Kaishi, (1972) 1395.
[7] A.F. Wells, Structural Inorganic Chemistry, 4th edn., Clarendon Press, Oxford, 1975, p. 528.
[8] T. Tsuchida, Sayuri Ohta and Kumi Horigome, J. Mater. Chem., 4 (1994) 1503.