Journal of the European Ceramic Society **14** (1994) 77–83

Phase Transformations and Control of Habit in Lyothermal Synthesis of α-Al_2O_3

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(Received 4 November 1993; revised version received 10 February 1994; accepted 28 February 1994)

Abstract

The phase transformation of gibbsite to corundum (α-Al_2O_3) in 1,5-pentanediol (glycothermal treatment) was investigated between 270 and 450°C and between 10 and 50 MPa. The kinetics of transformation to corundum in this range are hindered. Only the formation of microcrystalline tohdite (5 $Al_2O_3 : 1H_2O$) can be observed. The lowering of the nucleation energy of corundum by adding α-Al_2O_3 seeds enables the synthesis of microcrystalline corundum at 330°C. The size of the gibbsite particles and the size and quantity of the α-Al_2O_3 seeds are important for the homogeneity and particle size of the resulting corundum. The particle size and the morphology of glycothermal α-Al_2O_3 powders were compared with the results of hydrothermal synthesis of α-Al_2O_3.

Die Phasenumwandlung von Gibbsit nach Korund (α-Al_2O_3) wurde in 1,5-Pentandiol (Glykolthermalsynthese) zwischen 270°C und 450°C und zwischen 10 und 50 MPa untersucht. Die Kinetik der Reaktion von Gibbsit zu Korund ist in diesem Bereich gehindert. Stattdessen wird die Bildung von mikrokristallinem Tohdit ($5Al_2O_3 \cdot 1H_2O$) beobachtet. Nur durch die Zugabe von α-Al_2O_3-Keimen konnte die Keimbildungsenergie des Korund herabgesetzt werden, so daß bei 330°C mikrokristalliner Korund synthetisiert werden konnte. Die Größe der eingesetzten Gibbsitpartikel und die Größe und Menge der α-Al_2O_3-Keime hat einen bedeutenden Einfluß auf die Homogenität und die Partikelgröße des gebildeten α-Al_2O_3. Die Partikelgröße und die Morphologie der Korundpulver aus der Glykolthermalsynthese wurden mit hydrothermal synthetisierten Korundpulvern verglichen.

La transformation en plusieurs phases du gibbsite en corindon (α-Al_2O_3) a été examinée dans du pentanediol-1,5 (synthèse glycolthermale) entre 270 et 450°C et entre 10 and 50 MPa. La cinétique de la réaction gibbsite–corindon est empêchée dans ce domaine. On peut simplement observer la formation de tohdite microcristallin (5 $Al_2O_3 . 1H_2O$). Ce n'est qu'en ajoutant des germes α-Al_2O_3 que l'énergie nécessaire pour la formation des germes du corindon a pu être réduite et que le corindon microcristallin a ainsi pu être synthétisé à 330°C. La taille des particules de gibbsite utilisées, de même que la taille et la quantité des germes α-Al_2O_3 ont une influence considérable sur l'homogénéité et sur la taille des particules du α-Al_2O_3 ainsi formé. La taille des particules des poudres de corindon et leur morphologie, qui ont fait l'objet d'une synthèse glycothermale, ont été comparées avec des poudres de corindon synthétisées hydrothermalement.

Introduction

The sintering temperature and the microstructure of ceramics strongly depend on the powder characteristics of the raw materials.[1] The synthesis of α-Al_2O_3 powder with small particle size, narrow particle size distribution and controlled particle morphology is an important prerequisite for the improvement of Al_2O_3 ceramics.[2]

Two main aspects will be considered in this paper. First there is a need to lower the formation temperature of corundum, α-Al_2O_3. For the transformation of gibbsite ($Al(OH)_3$) to corundum by calcination via the series of metastable aluminas, temperatures over 1000°C are usually necessary. Under hydrothermal conditions many materials can be synthesized at significantly lower tempera-

Journal of the European Ceramic Society 0955-2219/94/$7.00

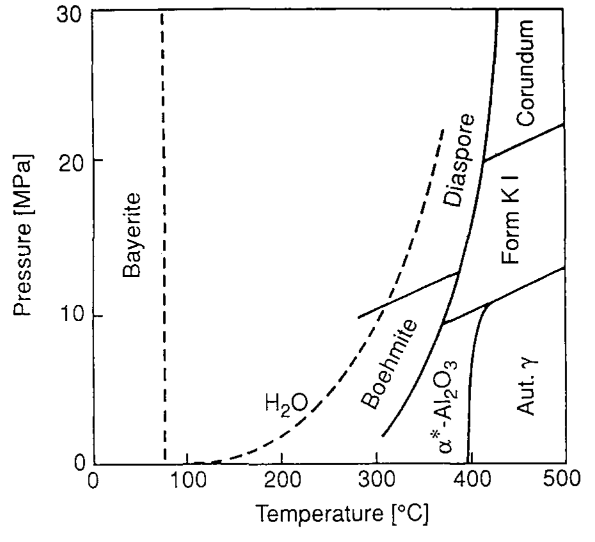


Fig. 1. p,T Diagram of the system Al_2O_3–H_2O from Ref. 6.

tures. By this method the formation of corundum is possible at temperatures of about 450°C and pressures of 20 MPa.[3-5] The results of hydrothermal oxidation of aluminium metal between 350 and 400°C obtained by Torkar & Krischner[6] are shown in Fig. 1. These authors found several apparently metastable forms of aluminium oxides. Their phase 'KI' was shown by Yamaguchi *et al.* [7] to be equivalent to the mineral tohdite. The 'α^*-Al_2O_3' is a highly reactive form of α-Al_2O_3, which contains about 0·15 mol H_2O/mol Al_2O_3. A similar form was later also found by Inoue *et al.*[8] in glycothermal experiments and called 'microcrystalline α-Al_2O_3'. A further polymorph found by Torkar & Krischner[6] was called 'autoclave γ'.

A second important point, namely the effects of reaction parameters on growth and habit of the alumina crystals, merits closer examination. The hydrothermal synthesis normally yields individual corundum crystals of uniform size. These particles are hexagonal {001} platelets with grain diameters over 10 μm. Little is known about the thermal reaction of aluminium hydroxides (especially to yield corundum) under pressure in other solvents and the effect of solvent on habit formation.[8-10]

Buining *et al.*,[9] studied the effect of hydrothermal conditions on the morphology of colloidal boehmite particles. Fibrous boehmite was synthesized by heating basic aluminium chloride solutions under constant stirring. The temperature and the Al_2O_3:Cl molar ratio caused variations of the average particle length between about 100 nm and 500 nm and the aspect ratio of the boehmite fibrils. In most cases complete dehydration to corundum could not be reached and the reaction stopped at boehmite. Intercalation compounds of boehmite were synthesized from gibbsite in methanol and ethylene glycol. Kubo & Uchida[10] supposed that during the reaction in methanol, methoxide groups were incorporated between the layers of boehmite. Inoue and coworkers[11,12] investigated the reaction of gibbsite in ethylene glycol and found similar structures with ethylene glycol molecules located between the boehmite layers. Inoue *et al.*[8] described the synthesis of a nearly spherical 'microcrystalline α-alumina' at 300°C in 1,6-hexanediol and other derivatives of ethylene glycol. Inoue *et al.* postulated that the low transformation temperature is caused by the relative instability of an intermediate boehmite intercalation compound compared with stable boehmite in water.

In the present paper results on the phase transformations of gibbsite in different solvents autoclaved between 270°C and 500°C will be presented (in general terms this is called lyothermal treatment, where reaction in 1,5-pentanediol is termed glycothermal treatment, and in water, hydrothermal treatment). Pressures between 10 MPa and 50 MPa (compared to lower pressures used in similar experiments by Inoue *et al.*[8] and seeding by α-Al_2O_3 were applied in glycothermal treatment. Correlations between properties, such as phase composition, grain size and morphology of the alumina powders and the conditions of synthesis will be given.

2 Experimental section

2.1 Pressure vessels

The experiments were carried out at temperatures up to 500°C and pressures of 100 MPa with a cold seal-cone closure vessel analogous to that used in earlier experiments by Matthes.[13] Small sealed silver capsules contained the material to be studied. In this way, contamination by vessel material is prevented. The vapour pressure within the autoclave was measured with a manometer. Initial pressurisation, up to 20 MPa can be applied through the use of a connected nitrogen cylinder before heating the vessels.

2.2 Materials

The starting materials were: commercial gibbsite (Apyral 120, Vereinigte Aluminium Werke (VAW), Na_2O, max. 0·6%; Si_2O, max. 0·05%; Fe_2O_3, max. 0·035%, grain size 0·8, μm), α-Al_2O_3 seeding material (AES-11C, Sumitomo, Na_2O, 0·03%; SiO_2, 0·04%; Fe_2O_3, 0·01%, grain size 0·4 μ m) and 1,5-pentanediol (Aldrich). α-Al_2O_3 seeds smaller than 0·1 μm were obtained by dispersing a commercial α-Al_2O_3 (A16-SG, Alcoa) in a nitric acid–water solution and removing the larger particles and agglomerates.[14] The grain size of the starting gibbsite was reduced to less than 0·4 μm by wet grinding in ethanol.

Table 1. Starting materials, reaction parameters and products for the synthesis of $\mathrm{Al_2O_3}$ in (a) 1,5-pentanediol and (b) 0·1 N NaOH (0·1 N $\mathrm{NH_4OH}$)

Number	*Educts*	*Reaction parameters*	*Products*
	Starting material: (seeding material)[a] *average particle size (μm)*	*Temperature (°C); pressure (MPa); time (h)*	*Main product (by product)*
(a) Solvent: 1,5-pentanediol			
(1)	Gibbsite; 0·4	270–330; 10–50; 5	Boehmite (Tohdite)
(2)	Gibbsite; 0·4	330–70; 10–50; 5	Tohdite (Boehmite)
(3)	Gibbsite; 0·4	370–420; 10–50; 5	Tohdite
(4)	Gibbsite; 0·4	420; 50; 96	Tohdite
(5)	Tohdite; <0·4 (α-$\mathrm{Al_2O_3}$; 0·3)	350; 25; 12	Tohdite
(6)	Gibbsite; 0·4 (α-$\mathrm{Al_2O_3}$; 0·3)	270–320; 25–50; 12	Corundum (Boehmite)
(7)	Gibbsite; 0·8 (α-$\mathrm{Al_2O_3}$; 0·3)	330; 25; 12	Corundum
(8)	Gibbsite; 0·4 (α-$\mathrm{Al_2O_3}$; <0·1)	330; 25; 12	Corundum
(b) Solvent 0·1 N NaOH ($\mathrm{NH_4OH}$)			
(9)	Gibbsite; 0·8	500; 50; 12	Corundum
(10)	Gibbsite; 0·8 (α-$\mathrm{Al_2O_3}$; 0·3)	500; 50; 12	Corundum

[a] α-$\mathrm{Al_2O_3}$ seeds (1 wt%) (with regard to weight of gibbsite) were used.

2.3 Preparation

Gibbsite (5 g) was dispersed in 50 g 1,5-pentanediol and stirred for 5 min with an high frequency stirrer (Ultra-Turrax, TP1ON, Janke and Hunke). Dispersions for hydrothermal experiments were prepared in the same way in 0·1 N NaOH and 0·1 N $\mathrm{NH_4OH}$. For experiments with α-$\mathrm{Al_2O_3}$ seeds, 0·05 g additional α-$\mathrm{Al_2O_3}$ (max. grain size. 0·3 μm) was added before stirring. The stock solution was treated for 5 min ultrasonically (Sonorex RK103, Bandelin electronics, HF power 160 W, *f*: 50–60 Hz). 1–3 cm^3 of the dispersions were enclosed in the silver capsules. The different experiments are shown in Table 1 and a flow chart of the preparation route of alumina is given in Fig. 2.

2.4 Reaction conditions

1,5-Pentanediol (0·1 N NaOH, or $\mathrm{NH_4OH}$) was placed in the space between the autoclave and the silver capsule. The free space in the autoclave was filled with nitrogen. If required, external nitrogen pressure was applied. The autoclave was heated up to a maximum of 500°C for hydrothermal experiments and 450°C for 1,5-pentanediol. The final pressure resulted from the (vapor) pressure built up by the solvent and the added nitrogen pressure. The reaction time was varied from 5 to 96 h. The resulting alumina powders were isolated, filtered, washed with water and methanol and then dried at 100°C.

2.5 Sample characterization

The powders were characterized by X-ray powder diffraction (XRD) on a Philips diffractometer PW1050/80 with Ni-filtered CuK_α radiation. The alumina powders were crushed in a mortar and uniformly distributed on a Si single crystal with (100) orientation.

The measurements of surface area and nitrogen adsorption isotherms were made on an instrument ASAP 2400 (Micrometrics). Surface areas were computed by the BET method. Before measurement the samples were degassed at 120°C.

The alumina samples were prepared for thermal analysis by drying at 120°C. The specimens were heated at a rate of 10°K/min to 1300°C under air

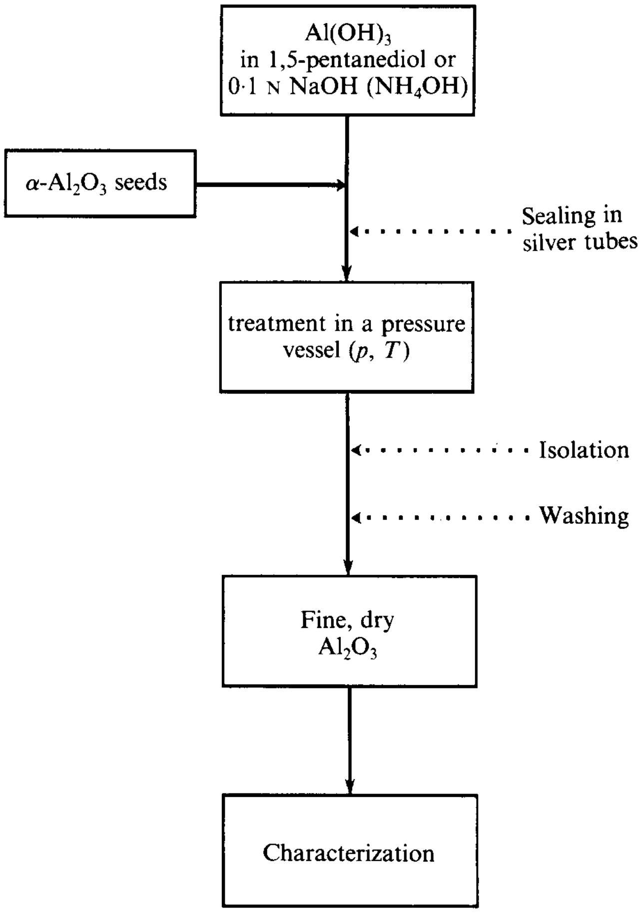


Fig. 2. Schematic of the preparation route for alumina powders by synthesis in 1,5-pentanediol, 0·1N NaOH or $\mathrm{NH_4OH}$.

or argon atmosphere by using the simultaneous thermal analyser STA-429 (Netzsch).

SEM photographs with magnifications up to 30 000 were made on a Hitachi S-800 field emission electron microscope. The particle size was measured by photon correlation spectroscopy (PCS) with the Malvern spectrometer PCS-K7023, after suspending the samples in ethanol and deagglomerating them ultrasonically. Powders with grain sizes greater than 1 μm were measured in ethanol by laser diffraction with the Malvern 2600c droplet and particle sizer. IR spectra were measured on a Perkin Elmer 283 using the KBr technique.

3 Results

3.1 Phase transformations in 1,5-pentanediol

First the results of the phase transformations of gibbsite (0·8 μm) in 1,5-pentanediol were studied; the influence of this solvent on particle size and habit formation was also investigated. Following Inoue *et al.*[8] who synthesized a 'microcrystalline α-alumina' in 1,6-hexanediol, the authors tried to achieve complete dehydration of gibbsite to corundum in 1,5-pentanediol. For this purpose, higher pressures (10–50 MPa) and longer reaction times (5–96h) were applied. Selected results, arising from about 30 experiments, with reaction parameters and the resulting aluminium oxides are summarized in Table 1. At low reaction temperatures, below 270°C, boehmite was obtained. With increasing reaction temperatures (between 270°C and 370°C) an increasing amount of tohdite, 5 Al_2O_3 : $1H_2O$, appeared besides the boehmite phase (numbers 1 and 2). At 370°C pure tohdite (number 3) was obtained. Its XRD pattern agreed with that reported in the literature,[7,15] (Fig. 3) and its temperature/pressure conditions of formation agree with those given by Torkar & Krischner (Fig. 1). Higher reaction temperatures of 420°C at pressures of about 50 MPa as well as long reaction times (96 h) did not lead to complete dehydration to corundum (number 4).

In control experiments evidence was found for the extreme stability of tohdite in the system Al_2O_3–1,5-pentanediol. When corundum seeds (0·3 μm) were added to the tohdite powder, in a further experiment (number 5) the transformation to corundum at temperatures at 350°C (and 25 MPa) in 1,5-pentanediol was impossible.

3.1.1 Specific surface area

Between 270 and 330°C the amount of tohdite increased with increasing reaction temperature. Concomitantly the specific surface area decreased from 114 to 45 m^2/g and the average pore radius increased from 5 to 19 nm. This can be explained by the densification process, which occurs upon transformation from boehmite (d = 3·01 g/cm^3) to tohdite (d = 3·77 g/cm^3), accompanied by the loss of water. The pure tohdite samples, synthesized between 380 and 420°C, have a specific surface area between 35 and 45 m^2/g.

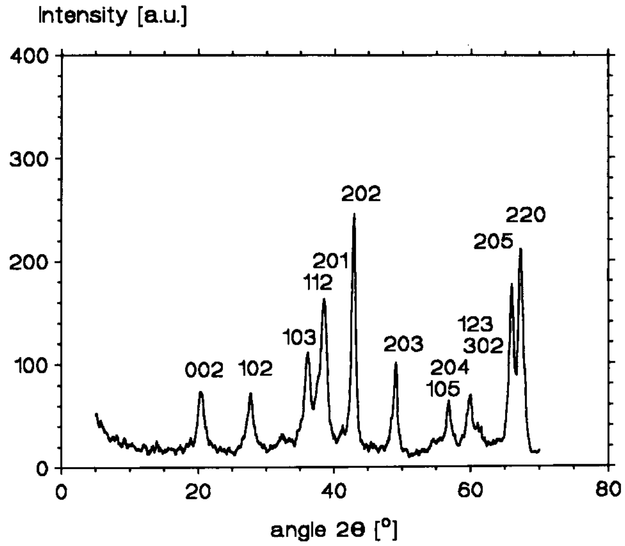


Fig. 3. X-Ray diffraction pattern of tohdite synthesized in 1,5-pentanediol (indexing from Ref. 15).

3.1.2 Water content

Thermogravimetric measurements (TG) of tohdite (number 3) indicate a weight loss of 4%, between 500 and 1200°C. From these results a molar ratio Al_2O_3/H_2O of 0·24 was calculated (the value expected for tohdite is 0·2).

3.1.3 Particle size and crystallite size

Photon correlation spectroscopy (PCS) of tohdite powder (number 3) dispersed in ethanol revealed broad particle distributions between 200 and 700 nm with an average diameter of 330 (± 130 nm). Particle sizes between 200 and 500 nm were determined from SEM (Fig. 4).

The crystallite size of the tohdite was calculated with Scherrer's formula[16] from the half-maximum peak-width values of the (203) reflections of the XRD pattern. This gave a value of 30 nm. This means that the particles measured by photon correlation spectroscopy (PCS) consist of agglomerated primary crystallites.

3.1.4 Stability of tohdite

Tohdite synthesized at 390°C (number 3) showed a strong exothermic peak at about 1200°C in its DTA which corresponded to the transformation to α-Al_2O_3 (corundum). Samples were held at a given temperature in the 500–1200°C range and analyzed by X-ray diffraction after cooling. The transformation to the structurally related κ-Al_2O_3

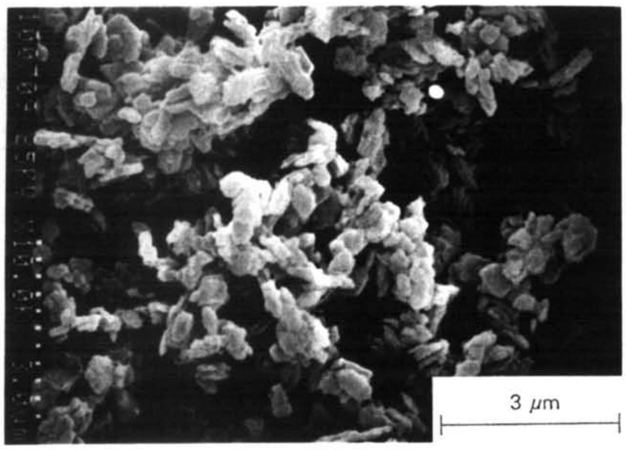


Fig. 4. SEM micrograph of tohdite (3) synthesized in 1,5-pentanediol (T = 390°C, p = 25 MPa) (scale bar = 3 μm).

takes place at temperatures between 800 and 900°C. The complete dehydration to α-Al_2O_3 occurred between 1100 and 1200°C.

3.2 Synthesis of corundum in 1,5-pentanediol

The transformation of gibbsite to corundum in pure 1,5-pentanediol did not occur in the range between 250 and 450°C and 10 and 50 MPa but resulted in tohdite. In order to lower the activation energy for the transformation, corundum seeds were added. The results of different experiments in 1,5-pentanediol and the products obtained are also given in Table 1. Corundum seeds (1 wt% relative to gibbsite) of particle size 0·3 μm were added to the stock solution. After short reaction times (5 h), at temperatures below 330°C, a mixture of boehmite and corundum (number 6) was obtained. Only corundum (number 7) was detected by X-ray diffraction (Table 1) after a reaction for 12 h, at 330°C and 25 MPa. This product can be distinguished clearly from the 'α -Al_2O_3' by Torkar & Krischner, because it is not soluble in hot sulfuric acid and shows sharp and intense diffraction lines. The specific surface area is about 4 m^2/g.

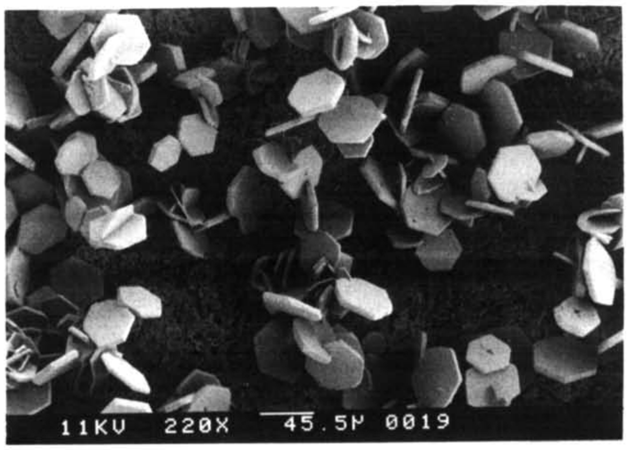


Fig. 5. SEM micrograph of hydrothermally synthesized hexagonal α-Al_2O_3 platelets (scale bar = 45·5 μm).

3.3 Hydrothermal experiments

In agreement with previous studies[5,15] it was found that the transformation of gibbsite at temperatures above 450°C and pressures between 20 and 50 MPa, after 12 h, in NaOH or NH_4OH leads to corundum (number 9). SEM micrographs show regular hexagonal platelets of corundum with diameters of about 50 μm and a thickness of about 5–10 μm (Fig. 5). By seeding the gibbsite powder with small 0·3 μm Al_2O_3 seeds the average particle size of the resulting corundum (number 10) is reduced to 5–15 μm. The platelets are less regular but the morphology remains unaltered.

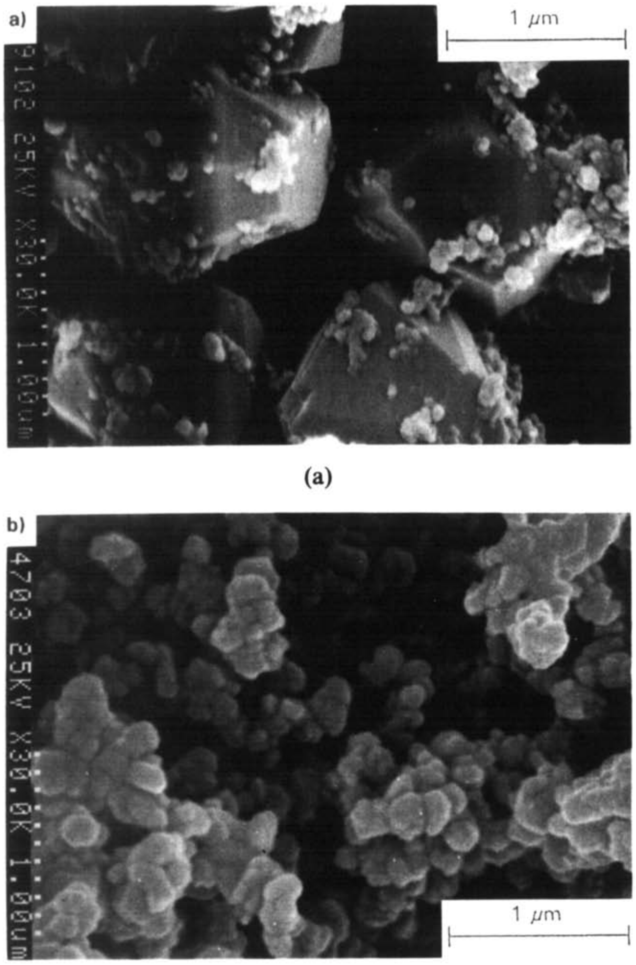
3.4 Influence of solvent and seeding on particle size and morphology of α-Al_2O_3

The influence of solvent and seeding on particle size and morphology of the α-Al_2O_3 resulting from the dehydration of $Al(OH)_3$ is summarized in Table 2. Replacing the solvent water by 1,5-pentanediol reduces the particle size of the α-Al_2O_3 powder by more than a factor of 10. The morphology of the powder particles changed from hexagonal platelets (number 10) in water to bipyramids (number 7) in 1,5-pentanediol

Table 2. Influence of solvent and educts on particle size and morphology of α-Al_2O_3 resulting from the dehydration of gibbsite

Educts		*Solvent*	*Reaction parameters*	*Products (corundum)*	
Average particle size (μm)			*Temperature (°C); pressure (MPa); time (h)*	*Average particle size (μm)*	*Habit*
Gibbsite	*α-Al_2O_3[a]*				
0·8	No seeds	0·1N NaOH	500; 50; 12	50	Hexagonal platelets (Fig. 5, (number 9))
0·8	0·3	0·1N NaOH	500; 50; 12	10	Hexagonal platelets (number 10)
0·8	0·3	1,5-Pentanediol	330; 25; 12	1·5	Bipyramids (Fig. 6(a)) (number 7)
<0·4	<0·1	1,5-Pentanediol	330; 25; 12	0·2	Nearly spherical (Fig. 6(b)) (number 8)

[a] α-Al_2O_3 seeds (1 wt%) (with regard to weight of gibbsite) were used.



(a)

(b)

Fig. 6. SEM micrograph of corundum (scale bar = 1 μm). (a) Bipyramids synthesized in the presence of 1 wt% corundum seeds (grain size of seeds = 0·3 μm); (b) spheres synthesized in the presence of 1 wt% fine corundum seeds (grain size of seeds <0·1 μm).

(Fig. 6(a)). Using seed crystals with a size less than 0·1 μm resulted in homogeneous, almost monodispere α-Al_2O_3 powders (number 8) with an average particle size of 0·2 μm. (Figure 6(b)). The morphology of the particles is nearly spherical.

A nucleation and growth process often determines the process temperature and process time, the particle size and the chemical phase development in ceramic powder synthesis.[2] The above-mentioned microstructural development of the α-Al_2O_3-powders in 1,5-pentanediol can be explained by the different number of seeds attainable in the solution. The growth process is enhanced and results in 1·5 μm α-Al_2O_3 bipyramids, if 1 wt% 0·3 μm α-Al_2O_3-seeds are used. By using 1 wt% seeds smaller than 0·1 μm, the number of seeds is increased. As a consequence smaller and more homogeneous corundum particles are formed.

4 Summary

The dehydration of $Al(OH)_3$ (gibbsite) in 1,5-pentanediol was studied in a wide temperature range between 270 and 450°C and under pressures between 10 and 50 MPa. The transformation kinetics of gibbsite to corundum are hindered in this range. Only the formation of microcrystalline tohdite with the composition 5 $Al_2O_3 \cdot 1H_2O$ can be observed. The transformation of gibbsite to corundum was possible in 1,5-pentanediol at about 330°C by seeding with α-Al_2O_3. Corundum powders consisting of 1·5 μm particles with a habit of bipyramids were obtained from gibbsite through the addition of 1 wt% 0·3 μm α-Al_2O_3 seeds. By reducing the seed crystallite size from 0·3 to 0·1 μm and thus increasing the concentration of seeds, almost spherical α-Al_2O_3 powders with a particle size of about 0·2 μm were formed.

For the powder synthesis of α-Al_2O_3 from solution, the size and quantity of seeds are important to the homogeneity and particle size of the resulting α-Al_2O_3. This means that seeding is a promising method to enhance kinetics and to control the development of the α-Al_2O_3 phase and the microstructure of the product.

Acknowledgements

The authors thank G. Müller for his comments on the text and T. Heinrich (Physikalisches Institut der Universität Würzburg) for technical assistance and helpful discussions of the X-ray results. Thanks are also due to M. Okrusch (Institut für Mineralogie der Universität Würzburg) for allowing the authors to use his autoclave facilities and W. Böhm for technical help.

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