Materials Research, Vol. 12, No. 4, 437-445, 2009

Hydrothermal Synthesis of Well-Crystallised Boehmite Crystals of Various Shapes

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Received: May 26, 2009; Revised: September 10, 2009

Aluminium monohydroxide, also known as aluminium oxyhydroxide (boehmite – AlO[OH]), is water insoluble but crystallises into microcrystals of various shapes. When, by X-ray diffraction, the microcrystals present a basal reflexion ($d_{[020]}$) of 0.611 nm, the crystalline structure is referred to as "well-crystallised" boehmite. Natural and synthetic crystals of well-crystallised boehmite can have a plate-like shape with either a rhombic or hexagonal profile. Synthetic crystals can also be lath-like or ellipsoid in shape. The purpose of this paper is to present a method of hydrothermal synthesis using a single temperature (200 °C) for preparing plate-like crystals of well-crystallised boehmite with ellipsoid, rhombic, hexagonal, and lath-like profiles by using different precursors. Our observations suggest that all of these shapes are stages of growth of the microcrystals of well-crystallised boehmite along the c-axis direction of the rhombic crystals.

Keywords: *aluminium hydroxide, boehmite, pseudoboehmite, fibrillar pseudoboehmite*

1. Introduction

1.1. Well-crystallised vs. poorly crystallised

A crystalline solid is defined as a solid consisting of atoms, ions or molecules packed together in a periodic arrangement[1]. Disturbance of the order and periodicity of the constituent can occur in crystalline solids; the terms "order" and "disorder" refer to the collective nature or degree of such disturbance[1].

The expressions "crystallinity" and "degree of crystallinity" are extensively used, despite the fact that the term "crystallinity" is qualitative and depends on the type of order or disorder, the dimensional nature of the periodicity of the components, and the experimental method for its evaluation[1]. Therefore, "high" and "low" degrees of crystallinity have been used as synonyms for "well-crystallised" and "poorly crystallised", meaning high and low degrees of order in the crystal structure.

Since 2002, the Association Internationale pour l'Étude des Argiles (AIPEA, International Association for the Study of Clays) has recommended the use of the expressions "low-defect" and "high-defect" before the mineral name to describe the structure of a crystalline solid[1]. The AIPEA also states that "low order" is not synonymous with "amorphous" or "non-crystalline"[1]. In addition, the term "amorphous" describes a structure that is amorphous to X-ray diffraction (XRD) or electron diffraction (ED)[1].

1.2. Boehmite

Boehmite is an oxyhydroxide of aluminium (composition, AlOOH or $Al_2O_3.H_2O$). In nature, boehmite always occurs as microcrystals or nanocrystals. Valeton[2] described the occurrence of boehmitic bauxites. Keller[3,4] characterised the presence of boehmite in some high-alumina clays. In 1945, Bohnstedt-Kupletskaya and Vlodavetz[5] described single crystals of boehmite in karst bauxite from the Vishnevye Mountains (Urals, Russia). In 1952, Calvet et al.[6] coined the name "pseudoboehmite" for synthetic pure (pseudocrystallised) aluminium hydroxide gel; its XRD pattern is similar to that of boehmite but with differences in the relative intensities of the peaks; all boehmite reflexions are present, including the basal reflexion ($d_{[020]}$). In 1961, Lippens[7] stated the following: "According to the origin of the ore (bauxite), it can consist of poorly crystallised boehmite (such as that found in France). Well-crystallised boehmite can be found in nature (in some Russian bauxites)." In 1970, Lippens and Steggerda[8] wrote, "In the discussion of boehmite, a clear distinction should be made between well-crystallised boehmite and gelatinous boehmite, sometimes also called pseudoboehmite. Gelatinous boehmite is the principal constituent of European bauxites". The expression "well-crystallised boehmite" continued to be used[9-11]. Boehmite from bauxites (not in Brazil) is an important raw material for the production of aluminium oxide[12]. Misra[13] described the industrial uses of synthetic boehmite, well-crystallised boehmite, and pseudoboehmite. Therefore, the terms "well-crystallised boehmite" and "pseudoboehmite" will be used in this paper.

1.3. Characterisation of well-crystallised boehmite

As a reference for the XRD data of well-crystallised boehmite of AlO(OH) composition and structure, Wefers and Misra[12] adopted the International Centre for Diffraction Data card no. 21-1307, in which the values for the spacings and intensities of the reflexions

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are from a synthetic sample prepared by Alcoa. In particular, the value $d_{(020)} = 6.11$ Å = 0.611 nm must be met. For the material to be classified as well-crystallised boehmite, all peaks must be sharp and intense. Figure 1 is an XRD curve of a well-crystallised boehmite sample meeting the above mentioned criteria. Figure 2 is an XRD curve of a pseudoboehmite sample showing the differences in relation to the well-crystallised boehmite sample, notably, a broadening of the reflexions and a higher $d_{(020)}$ value. The criteria used in order to characterise pseudoboehmite and "fibrillar" pseudoboehmite were those previously described[14].

1.4. Shapes of well-crystallised boehmite crystals

In studies employing transmission electron microscopy (TEM) or scanning electron microscopy (SEM) to evaluate bauxites and high-alumina clays, the XRD data not always indicate whether the materials contain well-crystallised boehmite or pseudoboehmite. Ervin and Osborn[15] and Betejtin[16] demonstrated that that the boehmite found in the Vishnevye Mountains is well-crystallised and occurs as tiny plate-like or lentil-like crystals. Using SEM, Lahodny-Sarc et al.[17] described blocky boehmite crystals in karst bauxite from Monte Negro, Yugoslavia. Mackenzie et al.[18], using TEM, described boehmite microcrystals in bauxite from County Antrim, Ireland, as "euhedral diamond-shaped (rhombic) plates". Keller[4] described natural boehmite crystals in high-alumina Missouri clays as flake-like or plate-like. Souza Santos et al.[14] presented TEM evidence of plate-like hexagonal crystals in boehmite extracted from bauxite found in Yunnan Province, China. These data suggest that natural well-crystallised boehmite more frequently occurs as plate-like rhombic microcrystals, sometimes as hexagonal or lentil-shaped structures.

According to Gitzen[19], synthetic well-crystallised boehmite can be prepared by hydrothermal conversion of Bayer gibbsite, in water or in dilute sodium hydroxide solution at 150 to 300 °C for 106 hours. Ervin and Osborn[15] synthetised well-crystallised boehmite hydrothermally between 200 and 375 °C, using aluminium hydroxide gel from aluminium nitrate plus ammonium hydroxide seeded with hydrothermal crystalline boehmite. The authors presented optical microscopy and TEM images of thin plates with hexagonal or elongated profiles. Turkevich and Hillier[20] provided TEM images showing aluminium oxide monohydrate crystals as ellipsoid plates with sharp points at each end. The structural regularity of the crystal was evidenced by the Bragg reflections in some areas of the plates. According to Gitzen[19], boehmite formed from gibbsite in water heated to 180 to 220 °C produces thin, curve-edged plates, often as coarse as 5 µm. Figure 3 is a TEM image of commercial synthetic well-crystallised boehmite from Bayer gibbsite (Alcoa D-50), showing thin plates (0.10 to 1.50 µm in diameter) with jagged borders, curved profiles, and Moiré patterns. The XRD pattern of this sample is shown in Figure 1.

Lippens[8] prepared boehmite by heating gibbsite in water at 250 °C. The author found that, examined under TEM, the boehmite

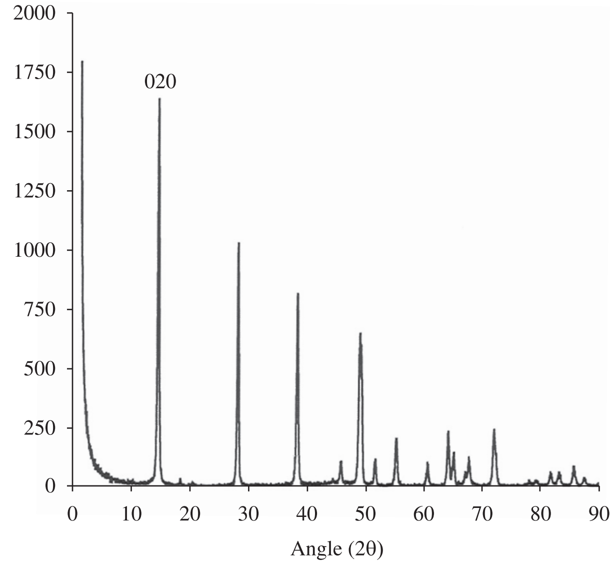

Figure 1. XRD curve of a well-crystallised boehmite (WC-boehmite) showing sharp intense "peaks", especially in the 020 reflexion.

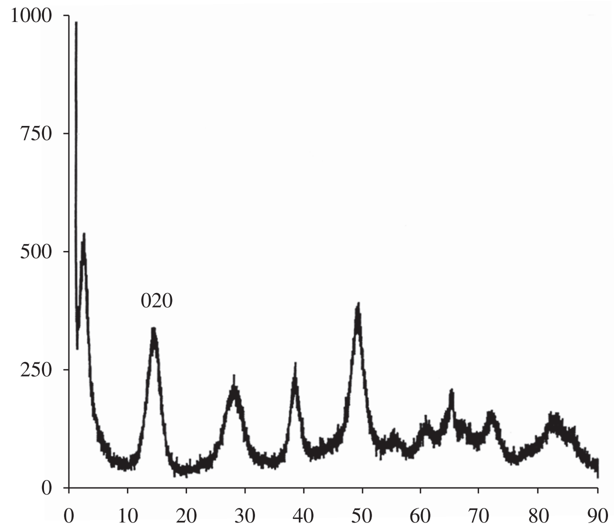

Figure 2. XRD curve of a pseudoboehmite sample, showing the line broadening and lower intensities, especially of the 020 reflexion.

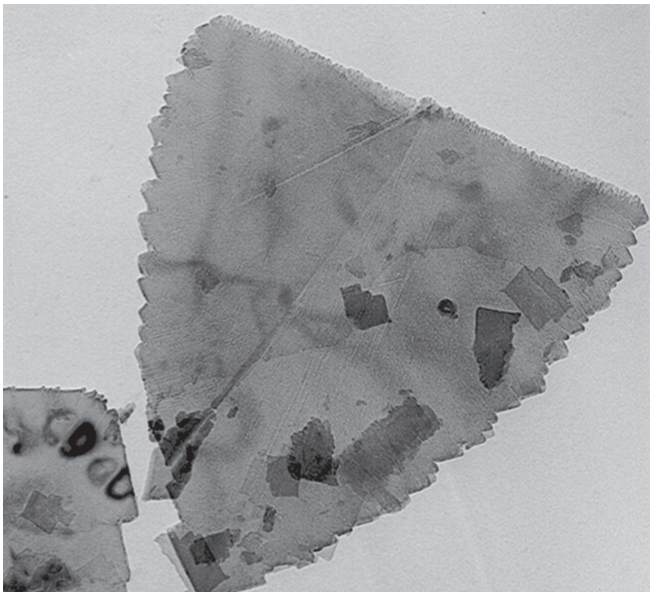

Figure 3. TEM image of commercial synthetic well-crystallised boehmite, showing crystals with a plate-like shape.

consisted of euhedral, plate-like rhombic microcrystals. Wilson[21] described commercial synthetic well-crystallised boehmite (Cera hydrate; BA Chemicals, Buckinghamshire, UK) as microcrystals composed of thin rhombic plates. Wefers and Misra[12] presented TEM evidence that hydrothermally grown boehmite consists of hexagonal laths. Souza Santos et al.[22] described a method of preparing well-crystallised boehmite sols composed of hexagons and hexagonal laths from a pseudoboehmite aqueous sol heated to 200 °C for 8 hours. Buining et al.[23] prepared well-crystallised boehmite dispersions by hydrothermal treatment of an aqueous mixture of several aluminium-alkoxides and hydrochloric acid at 220 °C. The authors showed TEM evidence of elongated, plate-like, thick boehmite microparticles, which have a "flattened" shape and later came to be called "colloidal boehmite rods". These rods are approximately 260 nm in length, 95 nm in width and 8-14 nm in thickness. Synthetic well-crystallised boehmite microcrystals from some commercial boehmite samples have been described variously: as thin plates[21]; as fibrous platelets[13]; as needle-like[24]; as platelets[25]; as thin and acicular[26]; as tiny needles[27]; and as rods[28]. The variety of descriptions indicates that synthetic well-crystallised boehmite microcrystals have different plate-like shapes. However, to our knowledge, there are no experimental methods for preparing well-crystallised boehmite microcrystals with all plate-like shapes: rhombic or diamond-shaped; hexagonal; hexagonal laths; and ellipsoid.

1.5. Examples of ceramic and non-ceramic uses of boehmite

High-alumina refractory products can contain well-crystallised boehmite formed as a result of bonding between tabular alumina and A16SG reactive alumina, autoclaved in saturated water vapour at 190 to 240 °C[24]. Gamma-alumina from well-crystallised boehmite is a precursor for AlON synthesis, because it is isostructural with γ-AlON[26]. Microcrystalline boehmite (Versal pseudoboehmite sol and gel; Kaiser® Aluminum and Chemical Corporation, Cleveland, Ohio, USA) is used in sol-gel processing, catalytic substrates, silicon chips substrates, additives to glass and for high alumina refractory products for ladle metallurgy[30]. Based on the electrokinetic properties of aqueous boehmite, silica and zirconia dispersions, cordierite-zirconia composites were fabricated using colloidal processing[31]. Colloidal or nanometric well-crystallised boehmite samples have been largely used in sol-gel technology in advanced ceramics[25]. Boehmite is the only aluminium hydroxide that, by thermal dehydroxylation, produces the transition γ-alumina series, with specific surface areas ranging from a few $m^2.g^{-1}$ to 300 $m^2.g^{-1}$[32]. The boehmite-transition alumina transformations are pseudomorphic and topotactic in relation to those of pristine boehmite crystals[32]. Currently, synthetic boehmite is produced industrially as nanometric powders and as concentrated aqueous sols (200 $g.L^{-1}$ of boehmite)[25]; several such products were described by Misra[13].

The question remains: why is necessary to know the shape of the particles or monocrystals of a raw material or a precursor for ceramic and non-ceramic uses of a material? The answer is given by Allen[34]: "Particle shape is a fundamental powder property, affecting powder packing and thus bulk density, porosity, permeability, cohesion, flowability, caking behavior, attrition, interaction with fluids and the covering power of pigments." In addition, Ring[30] stated that oxides formed from thermal dehydroxylation of metallic hydroxides are fractal particles.

The purpose of this paper is to present a method of preparing aqueous sols composed of well-crystallised boehmite microcrystals with various morphologies, as determined by the choice of precursor, using a single temperature for hydrothermal treatment.

2. Materials and Methods

2.1. Method

Hydrothermal treatment was performed with saturated water vapour under autogenous pressure at a temperature of 200 ± 5 °C, a residence time of 72 hours at 200 °C, and natural cooling. A polytetrafluoroethylene-lined acid digestion bomb (model 4787; Parr Instrument Company, Moline, IL, USA) was employed. The water-aluminium ratio was 50:1, as used by Nazar and Klein[35] to study the early stages of aluminium hydroxide polymerisation.

2.2. Precursors

Several aluminium hydroxides were used as precursors for the various well-crystallised boehmite crystal shapes: gibbsite-aluminium trihydroxide-powder from aluminium-water/iodine-activated reaction[36]; commercial gibbsite (Hydral 710; Alcoa Chemicals, Reading, Ohio, USA); aluminium isopropoxide; bayerite-aluminium trihydroxide-powder by the Schmäh method[37]; aqueous fibrillar pseudoboehmite sol aged 168 h at 90 °C, prepared as previously described[38]; and crystalline $Al(OH)(CH_3.COO)_2$, prepared according to Xavier et al.[39]

2.3. Characterisation

The crystalline structure, of either the precursors or the dried products, was characterised by XRD using a diffractometer (X'Pert MPD; Philips® Medical Systems, Bothell, WA, USA), copper K-alpha radiation and scanning between 1° (2θ) and 90° (2θ). The morphology was characterised by examination in a transmission electron microscope (CM200; Philips®) operating at 200 kV.

2.4. Procedure

The precursor powder was dispersed in distilled water at a water-aluminium ratio of 50:1, without or with additives. The acid digestion bombs (10 and 100 mL) were used for hydrothermal treatment of the precursors. The dispersion or the aqueous sol was placed in the high-pressure bomb, which was closed and heated to 200 ± 5 °C. The residence time at 200 °C was 72 hours, after which the oven was shut down and allowed to cool overnight. The milky sol was collected and prepared for XRD and TEM by the conventional methods; the drying was conducted at 70 °C. The well-crystallised boehmite sol was found to contain 70 $g.L^{-1}$ of AlOOH.

In some cases, to study their effect on precursors, we added 0.1 M (in relation to the quantity of aluminium) of glacial acetic acid or other additives.

By further vacuum evaporation or heating to 70 °C, the synthetic hydrothermal well-crystallised boehmite sols can be concentrated to 200 $g.L^{-1}$ of AlOOH, which is the usual solid content for $\alpha\text{-}Al_20_3$ nucleation[25] and growth in sol-gel processes in advanced ceramics. The morphologies of the well-crystallised boehmite crystals do not change with the increased concentration to prepare, in parallel, all of those crystals shapes.

3. Results and Discussion

3.1. XRD

All samples presented the XRD pattern of well-crystallised boehmite, with sharp and intense reflexions and a $d_{020} = 0.611$ nm, as would be expected from the temperature of the hydrothermal treatment in saturated water vapour, under autogenous pressure.

3.2. Crystallisation of rhombs

The TEM image of the gibbsite (iodine) precursor microcrystals is shown in Figure 4: plate-like hexagons, 0.8 to 1.8 μm in width. After their hydrothermal treatment with water at 200 °C, the well-crystallised boehmite microcrystals are euhedral plate-like rhombs, 0.17 to 0.33 μm in width. As additives, potassium acetate and sodium hydroxide also produced euhedral well-crystallised boehmite plate-like rhombs: 0.16 to 0.27 μm in width with potassium acetate; and 0.25 to 0.34 μm in width with sodium hydroxide. Figure 5 shows the results obtained with sodium hydroxide.

The Hydral 710 gibbsite microcrystals are plate-like hexagons approximately 1 μm in width[13]. After hydrothermal treatment with water, well-crystallised boehmite is formed as euhedral thick plate-like rhombs, 1.76 to 2.35 μm in width.

Bayerite microcrystals are shown in Figure 6, appearing as pyramid-shaped and hourglass-shaped somatoids, 1.12 to 1.64 μm in width. By hydrothermal treatment with water at 200 °C, euhedral

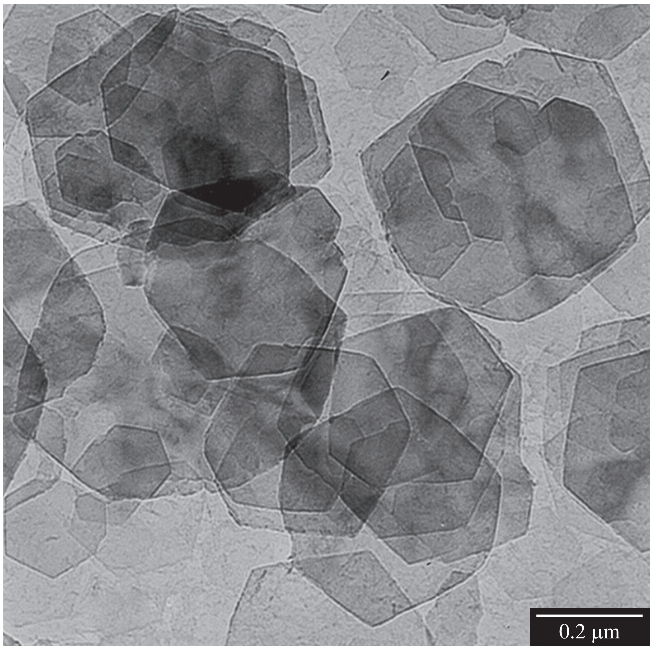

Figure 4. TEM image of plate-like gibbsite crystals used as a precursor for hydrothermal synthesis of well-crystallised boehmite.

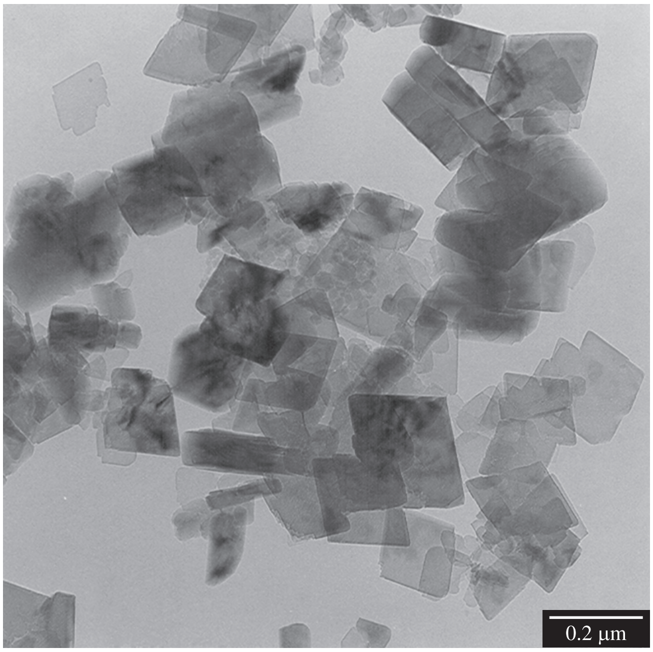

Figure 5. Photomicrograph of plate-like rhombic crystals of well-crystallised boehmite from a gibbsite precursor after hydrothermal treatment (200 °C/72 hours) in NaOH/water solution).

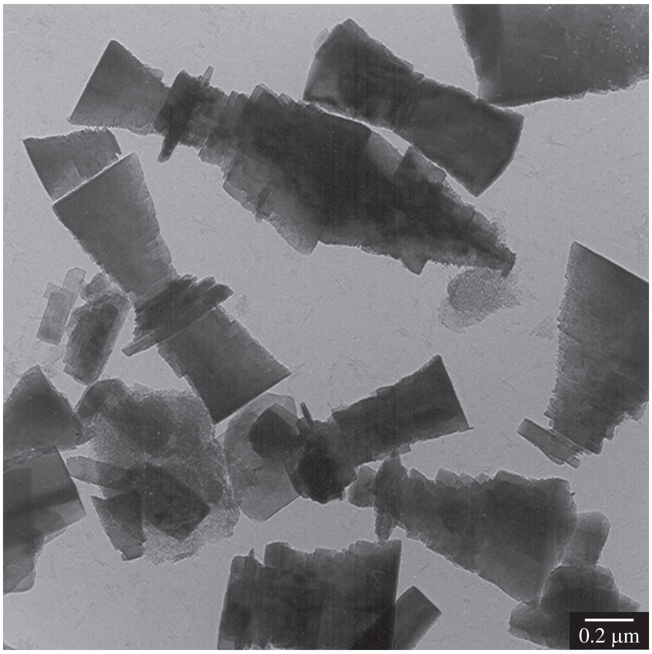

Figure 6. TEM image of bayerite somatoids crystals used as a precursor.

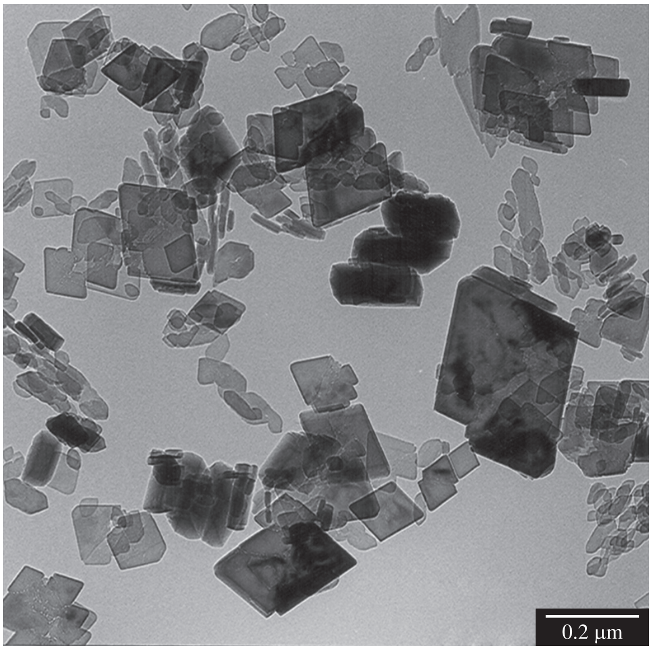

Figure 7. TEM image of plate-like rhombic crystals of well-crystallised boehmite from a bayerite precursor after hydrothermal treatment at 200 °C/72 hours.

well-crystallised boehmite plate-like rhombs, 0.23 to 0.29 μm in width, are formed. Bayerite (iodine) microcrystals appear as plate-like stars and hexagons, 0.86 to 2.14 μm in width. After the same treatment at 200 °C, euhedral plate-like well-crystallised boehmite rhombs are formed, 032 to 1.08 μm in width (Figure 7).

Therefore, all the gibbsite and bayerite precursors produced euhedral well-crystallised boehmite plate-like rhombic microcrystals, of various sizes, ranging from 0.16 to 2.35 μm width. The method for producing the best euhedral well-crystallised boehmite plate-like rhombs is using gibbsite (iodine) in 0.10 M aqueous sodium hydroxide solution as shown in Figure 5. The second best, and the thickest, euhedral rhombs are obtained using gibbsite Hydral 710 in water.

3.3. *Crystallisation of hexagons*

It is common to observe some plate-like hexagons among the rhombic well-crystallised boehmite microcrystals. Preparing non-

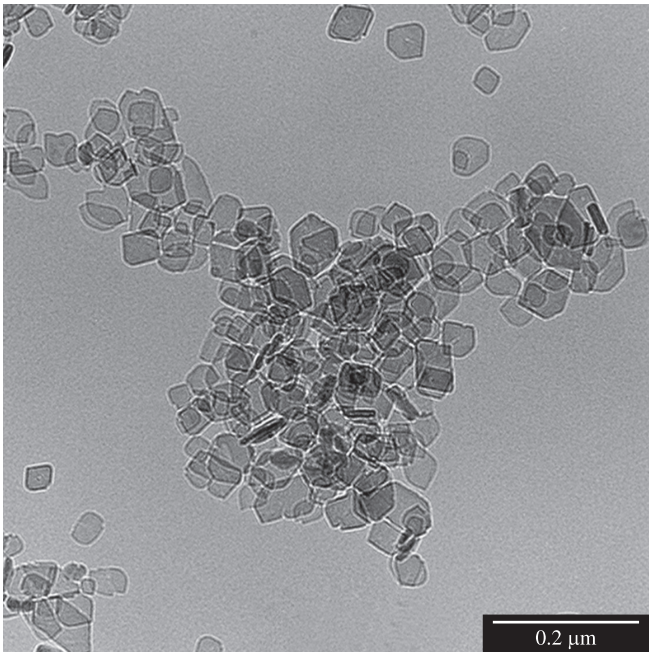

Figure 8. TEM image of plate-like hexagonal crystals of well-crystallised boehmite from amorphous $Al(OH)_3$ gel in water after hydrothermal treatment at 200 °C/72 hours.

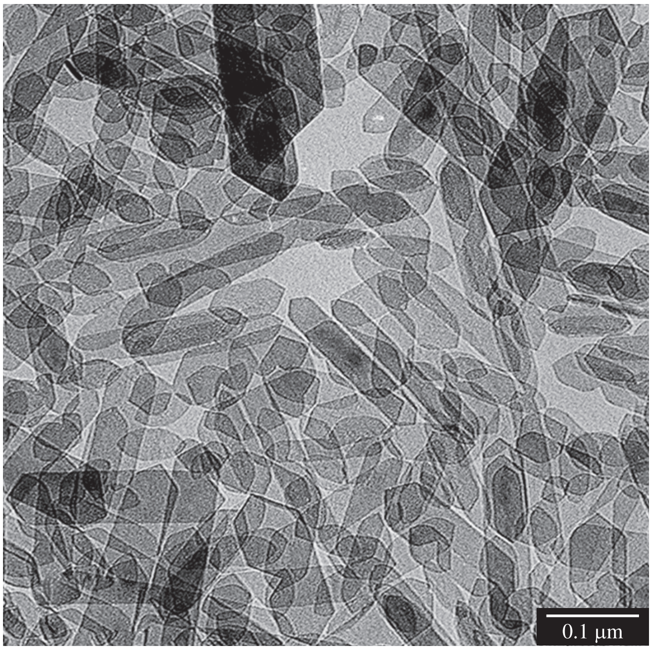

Figure 9. TEM image of laths with hexagonal profile of well-crystallised boehmite from hydrothermal treatment of a fibrillar pseudoboehmite sol at 200 °C/72 hours.

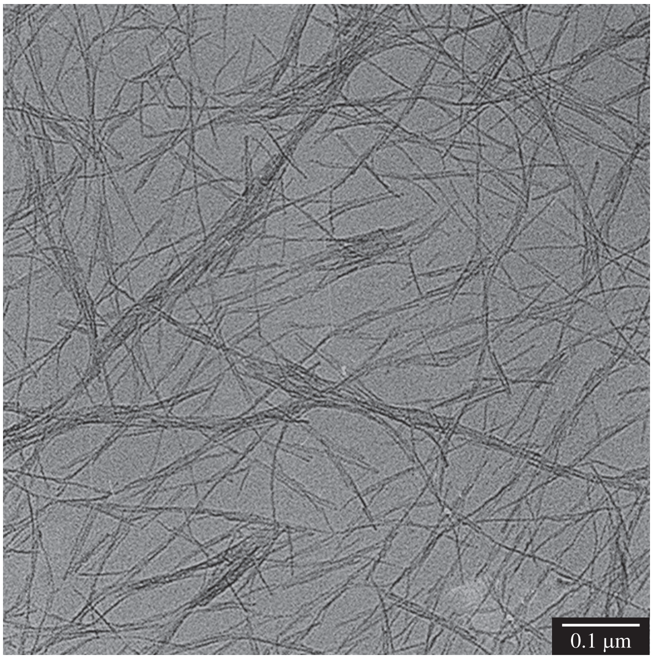

Figure 10. TEM image of fibrillar pseudoboehmite crystals from a 168 h aged sol used as precursor.

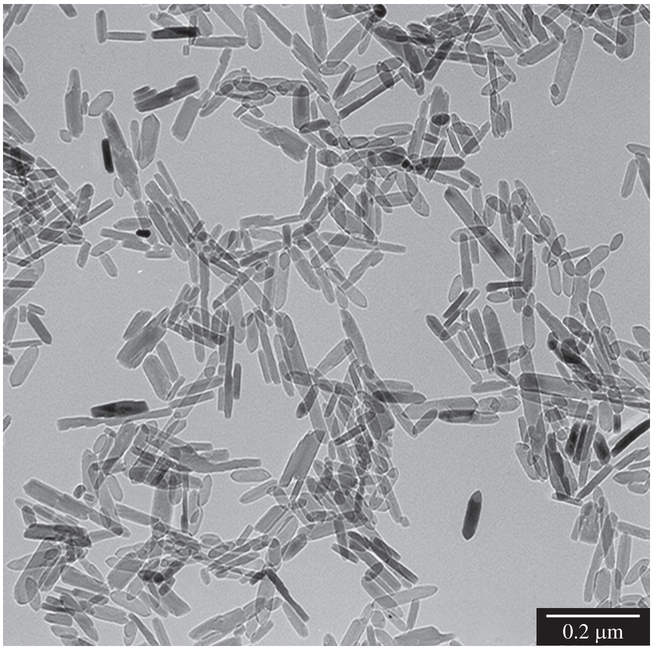

Figure 11. TEM image of lath-like crystals of well-crystallised boehmite from the hydrothermal treatment of the pseudoboehmite sol at 200 °C/72 hours.

crystalline, or amorphous, aluminium hydroxide—$Al(OH)_3$—gel by hydrolysis of aluminium isopropoxide with water and heating the aqueous gel, at the same water-aluminium ratio, hydrothermally to 200 °C (residence time, 72 hours), well-crystallised boehmite was obtained as plate-like hexagon microcrystals, 0.05 to 0.12 µm in diameter, in a sol, as shown in Figure 8.

3.4. Crystallisation of laths

Souza Santos et al.[22] described the preparation of aqueous sols of well-crystallised boehmite composed of lath-like microcrystals, 0.10 to 0,23 µm in length, with hexagonal profiles, and some plate-like hexagonal microcrystals, such as those shown in Figure 9. The precursor was an aged sol of fibrillar pseudoboehmite, hydrothermally treated at 200 °C for 80 hours (crystalline fibrillar pseudoboehmite). Fibrillar pseudoboehmite differs from the other, previously described, precursors (those that produced plate-like rhombic and hexagonal microcrystals) in the following points:

a) It is an aluminium monohydroxide (crystalline fibrillar pseudoboehmite), whereas the other precursors are aluminium trihydroxides, crystalline or non-crystalline (amorphous to electron diffraction);
b) The starting materials for fibrillar pseudoboehmite are aluminium isopropoxide or sec-butoxide and aqueous acetic acid solution; and
c) After hydrolysis, the thermal ageing time for fibrillar pseudoboehmite is 80 hours at 90 °C and at a constant volume.

For the purposes of this study, analogous sols of fibrillar pseudoboehmite were used, containing 70 $g.L^{-1}$ of AlOOH, were prepared as previously described[38] and subjected to thermal ageing for 168 hours at 90 °C. These sols contain longer pseudoboehmite fibrils and the acetic acid content is only for sol stabilisation. Figure 10 presents a TEM image of pseudoboehmite microfibrils from the precursor sol heated in saturated water vapour to 200 °C for 72 hours. A milky sol of well-crystallised boehmite was obtained. Figure 11 shows a TEM image of well-crystallised boehmite lath-like microcrystals, 0.17 to 0.43 µm in length, formed by dissolution/recrystallisation from the pseudoboehmite microfibrils.

A second method of lath production can be used: 1.5 g of water insoluble crystalline $Al(OH)(CH_3.COO)_2$ and distilled water, at a water-aluminium ratio of 50:1, are hydrolysed hydrothermally at 200 °C for

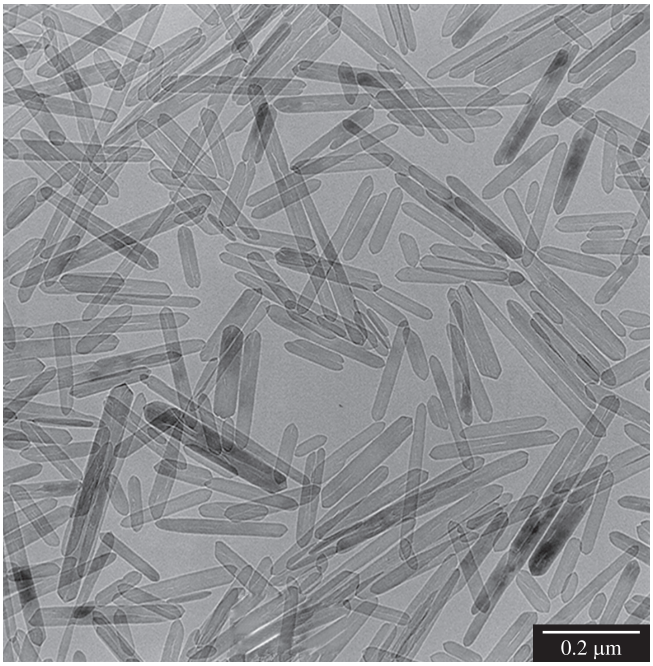

Figure 12. TEM image of lath-like crystals of well-crystallised boehmite from the hydrothermal hydrolysis of aluminium acetate crystals at 200 °C/72 hours.

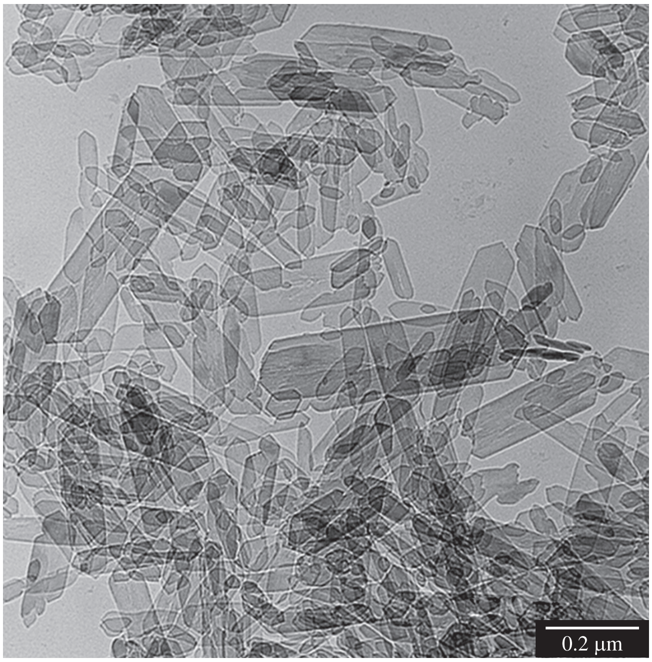

Figure 13. TEM image of lath-like crystals of well-crystallised boehmite from a gibbsite precursor in acetic acid solution after hydrothermal treatment at 200 °C/72 hours.

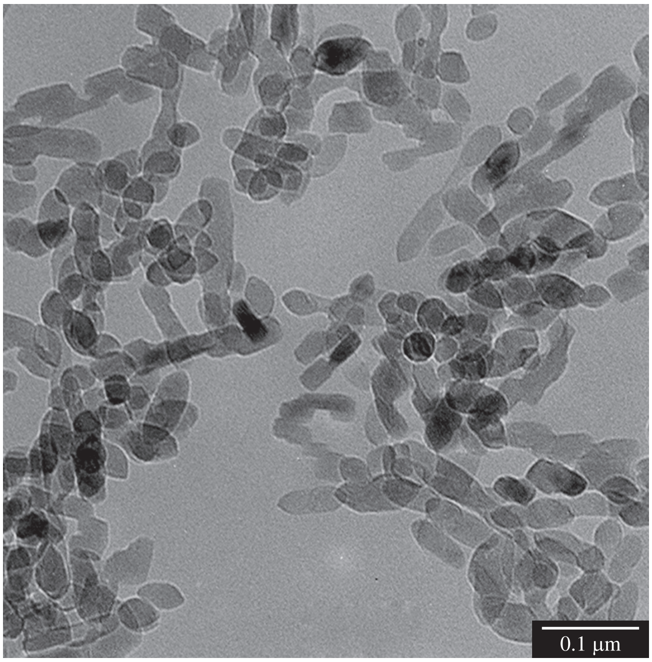

Figure 14. TEM image of ellipsoid plate-like crystals after hydrothermal treatment of the Y-containing pseudoboehmite sol.

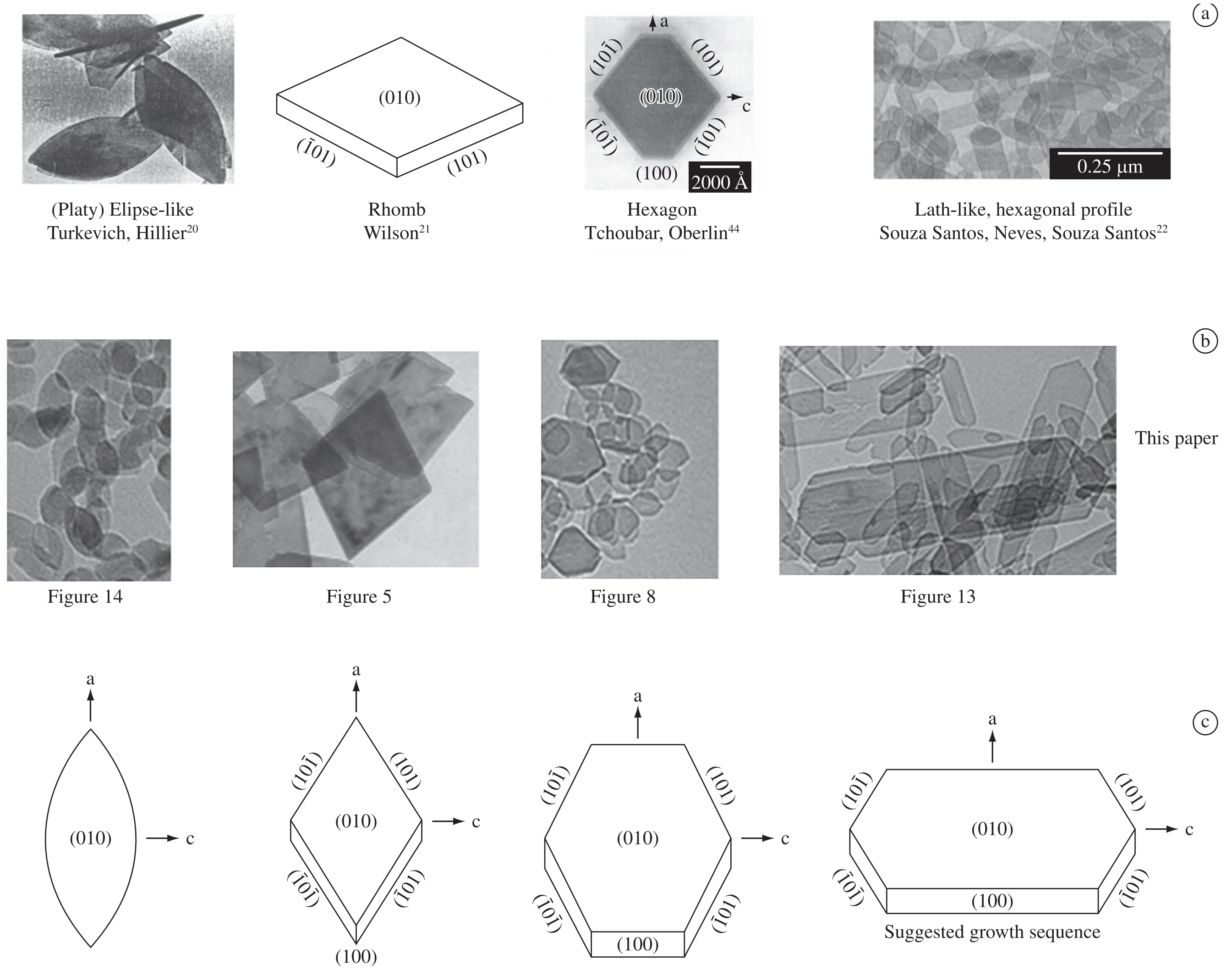

Figure 15. Proposed sequence for the growth of plate-like well-crystallised boehmite crystals in acetic acid solution from gibbsite or pseudoboehmite precursor: a) Crystal shapes of synthetic well-crystallised boehmite described in the literature; b) Crystal shapes of synthetic well-crystallised boehmite prepared by the method described in this paper; and c) Crystallographic relationships during suggested growth sequence.

72 hours, forming a sol of euhedral laths of well-crystallised boehmite, 0,16 to 0.53 µm in length. Figure 12 shows laths by this method.

3.5. Acetic acid as an additive: effect on crystallisation

When acetic acid was used in the precursor synthesis, lath-like crystals of well-crystallised boehmite were formed at 200 °C. Therefore, when only rhombs or hexagons and no laths were formed, we conducted new experiments, adding acetic acid to the precursor dispersion in the bomb, making it 0.1 M in acetic acid. In all cases, only euhedral well-crystallised boehmite lath-like crystals were formed: Figure 13 is a TEM image of lath-like crystals, 0.20 to 0.63 µm in length, from gibbsite (iodine) in acetic acid solution after 72 hours at 200 °C, quite different from the rhombs shown in Figure 5.

Formic, propanoic, citric, hydrochloric and nitric acids, at the same concentrations, had the same effect of forming lath-like crystals, whereas sulphuric and trichloroacetic acids had no such effect on the same precursors.

3.6. Ellipsoid plates

Although the ellipsoid and thin curved-edge plates produced by Turkevich and Hillier have been presented in a number of papers[40-42], we found no information on how these plates were prepared. After trying a variety of additives and modifications of the present method, we were able to produce well-crystallised boehmite plates with an ellipsoid profile using another method. In a reaction at 90 °C in aqueous acetic acid solution with aluminium isopropoxide and yttrium acetate as an additive, the relative molar proportions were 0.95 Al to 0.05 Y and 1 HAc to 50 H_2O. The sol was heated to 90 ± 2 °C (residence time, 500 hours), under reflux and constant volume. The Y-containing aged sol was hydrothermally treated at 200 °C, using the equipment described previously, for 72 hours. The resulting ellipsoid plates of well-crystallised boehmite, 50 to 70 nm in length, are shown in Figure 14. These shapes could be interpreted as incomplete plate-like rhombs.

3.7. Comments on well-crystallised boehmite crystal shapes

Well-crystallised boehmite has an orthorhombic structure, and the crystals have good cleavage according to {010}, which is the basal plane that defines the octahedral layers of the crystalline structure of AlO(OH)[43]. Therefore, it has a layer structure parallel to the xz plane[44]. According to Wilson[21], well-crystallised boehmite has the shape of thin rhombic plates, schematically shown in Figure 15a. Tchoubar and

Oberlin[45], using micro-electron diffraction of well-crystallised boehmite, showed that the plate-like hexagonal crystals have a tendency to grow along the c-axis direction, as shown in Figure 15b.

In this paper, we showed that, in an environment of aqueous acid, especially acetic acid, several precursors and even well-crystallised boehmite rhombs grow to euhedral laths of well-crystallised boehmite, the flat surface of the laths parallel to the (020) plane of well-crystallised boehmite with a spacing of 0.611 nm. Therefore, there are a variety of well-crystallised boehmite shapes, natural and synthetic: ellipsoid plates; plate-like rhombs or "diamonds"; plate-like hexagons and euhedral laths with hexagonal profiles. These can be interpreted as a sequential growth along the c-axis of the crystal according to the environment and temperature, as occurs hydrothermally at 200 °C in this paper.

It is of note that, in terms of structure and varieties of crystal shapes, well-crystallised boehmite is analogous to the clay mineral sodium-montmorillonite, which has an orthorhombic structure, as proposed by Hofmann et al.[46], and has a layer structure (it is a layer silicate and has very good cleavage parallel to {001}, that is, to the basal plane). According to Güven[47], natural crystals have the following habits or shapes: subhedral lamellar; rhombic; hexagonal lamellar or fibrous structure; and lath-like. All of these are shown schematically in Figure 15c.

4. Conclusions

We have described a laboratory method for the preparation of plate-like microcrystals and nanocrystals of well-crystallised boehmite with different shapes or morphologies: plate-like rhomb or "diamonds"; hexagons; and laths with hexagonal profile and different lengths.

The preparation is conducted in a high pressure reactor, at 200 ± 5 °C for 72 hours, in aqueous medium, under autogenous pressure. Distilled water is used, with or without additives to control crystal shapes.

Microcrystals of well-crystallised boehmite in the shape of plate-like rhombs are prepared from microcrystalline gibbsite precursor in distilled water; gibbsite (iodine) and Hydral 710 are good precursors for rhombs. Bayerite somatoids and plate-like microcrystals are also good precursors for rhombs.

Plate-like hexagonal microcrystals of well-crystallised boehmite are prepared from a non-crystalline, or amorphous, hydroxide gel precursor in distilled water. The precursor is prepared by reacting, at room temperature, aluminium isopropoxide in sec-butoxide with water.

Euhedral laths of well-crystallised boehmite, with hexagonal profiles, are prepared from a precursor, which can be an aqueous sol or a gel of fibrillar pseudoboehmite; the most convenient is the sol thermally aged for 168 hours at 90 °C. Another potential precursor is crystalline aluminium hydroxydiacetate in distilled water.

When acetic acid is added to gibbsite, Hydral 710, bayerite somatoids or plate-like microcrystals, as well as when it is added to an aqueous sol or a gel of fibrillar pseudoboehmite, euhedral laths with hexagonal profiles, rather than rhombs or hexagons, respectively, are produced.

The micrometric size of the crystals of the precursors employed facilitates the nucleation and growth of crystals of well-crystallised boehmite.

Rhombs, hexagons, and laths are stages of growth of the plate-like crystals of well-crystallised boehmite along the c-axis direction of the crystal, as shown in Figure 15c.

Acknowledgements

The authors are grateful to Simone P. Toledo for the assistance provided in preparing the figures.

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