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Crystallization of nordstrandite in ethylene glycol / water solutions: electron microscopic studies

Research Article

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Abstract: The present work shows the growth of nordstrandite microcrystals observed by transmission and scanning electron microscopy. Nordstrandite was synthesised from non-crystalline aluminium hydroxide reacted in 20% ethylene glycol/water solution, at room temperature. This material was characterized by TEM, SEM, SAED, XRD and EDS/TEM, during six month and revealed the formation and growth of nordstrandite. Fibrillar pseudoboehmite is the only aluminium hydroxide which could be identified during the first two weeks. The nuclei grow, from complete dissolution/recrystallization of pseudoboehmite fibrils, into platy rectangular microscrystals of nordstrandite. Some tabular microcrystals recrystallise, forming after six months only the multi-point nordstrandite stars. This electron-optical study suggest that the star shape results from the overlapping of rectangular plates, and pseudoboehmite fibrils act as the precursor of nordstrandite crystallisation in ethylene glycol/water solution.

Keywords: *Aluminium hydroxide • Crystal growth • Electron microscopy • Nordstrandite*

1. Introduction

Crystalline $Al(OH)_3$ exists as three polymorphs: gibbsite, bayerite and nordstrandite. Of these, gibbsite is the most common polymorph found in nature, occurring in bauxites, high-alumina clays and various soil types. It crystallises in the monoclinic system [1]. Both natural and synthetic gibbsite microcrystals appear as hexagonal plates [2,3].

Bayerite and nordstrandite rarely occur in nature. Bayerite crystallises with monoclinic symmetry [4]. Synthetic bayerite crystallises as hour-glass shaped microcrystals known as somatoids [5,6]. Nordstrandite, first described in 1956 by Van Nordstrand *et al*. [7], crystallises in the triclinic system [8]. Under transmission electron microscopy (TEM), synthetic nordstrandite appears as platy rectangular crystals [9] or as platy crystals in characteristic multi-point star shapes [10]. Nordstrandite is used in the manufacture of several catalytic products [11].

Due to the structural similarities among the three, nordstrandite exhibits a combination of the structures and properties of gibbsite and bayerite [12], although the respective synthetic microcrystals are distinctly different in shape.

Several factors may affect the structure and shape of the crystals of each synthetic polymorph. These factors include pH, OH/Al ratio, and the presence, nature and

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concentration of organic or inorganic ligands, as well as the rate of stirring of the solution in which they crystallise [13-18].

In most procedures, nordstrandite crystallises when mixed with gibbsite and bayerite. Pure nordstrandite microcrystals have been synthesised by ageing non-crystalline aluminium hydroxide in an aqueous medium in the presence of ethylenediamine [19], or ethylene glycol [18], or sodium aluminate solution [20].

The purpose of this study was to present, in detail, the process of ageing non-crystalline aluminium hydroxide in ethylene glycol/water solution. The evolution of nordstrandite microcrystals is described from nucleation until the appearance of the final star-shaped form. Such comprehension represents relevant information about crystal growth as well as control of the size and morphology of the crystal.

2. Experimental Procedures

2.1 Preparation of the $Al(OH)_3$

Nordstrandite was synthesised based on the method described by Aldcroft and Bye [19], but using other chemicals, as described by Antunes *et al.* [18]. The reaction and ageing were conducted at room temperature (20ºC/25ºC) instead of 60ºC, as used by Aldcroft and Bye [19], in order to have a lower rate of growth of nordstrandide microcrystal. First, a "gelatinous" precipitate of non-crystalline aluminium hydroxide was obtained in water. Pieces of Alcoa aluminium foil (2-3 g) were cut into sections, polished, degreased and lightly amalgamated in 0.1-N mercury(II) chloride solution. They were thoroughly washed with distilled water until Cl^--free and placed into one litre of $C0_2$-free distilled water. After 5 minutes, the water was changed to eliminate the first products of the reaction; the aluminium foil sections were washed several times with distilled water and allowed to react in 20% (v/v) ethylene glycol/water solution at room temperature until all aluminium dissolved and a greyish precipitate formed, which changed to a white "gelatinous" precipitate containing the non-crystalline aluminium hydroxide. Left to stand and age at room temperature, it crystallised into a white powder (the aluminium hydroxide nordstrandite) in the ethylene glycol/water solution [18]. The ageing of the precipitate in the ethylene glycol/water solution was observed for 6 months at room temperature (20°C - 25°C).

2.2 Methods of characterisation

To monitor the crystallisation process during this period, small samples of the precipitate were periodically collected and examined. The sample (an aqueous suspension of the precipitate) was air dried or diluted in distilled water into an appropriate concentration for each procedure. Conventional techniques of preparation were employed for each of the characterisation methods. After air drying, samples were observed under TEM using a Philips CM200 unit (Philips Electron Optics, Eindhoven, The Netherlands) operating at 200 kV. The same device was also used for selected area electron diffraction (SAED) and for energy dispersive spectroscopy/TEM (EDS/TEM) microanalysis. The samples were also observed with a scanning electron microscope (SEM) operating at 25 kV (model 840A, JEOL, Peabody, MA, USA). The X-ray diffraction (XRD) was conducted in a model X-Pert diffractometer (Philips), using copper K-alpha radiation and operating at 40 kV and 40 mA, the sample being scanned between 1° (2θ) and 90° (2θ).

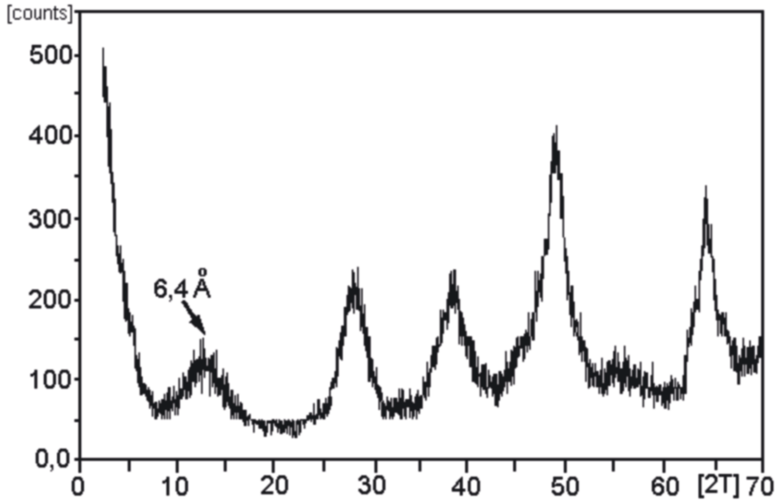

Figure 1. Five-day-old pseudoboehmite X-ray diffraction (XRD) curve.

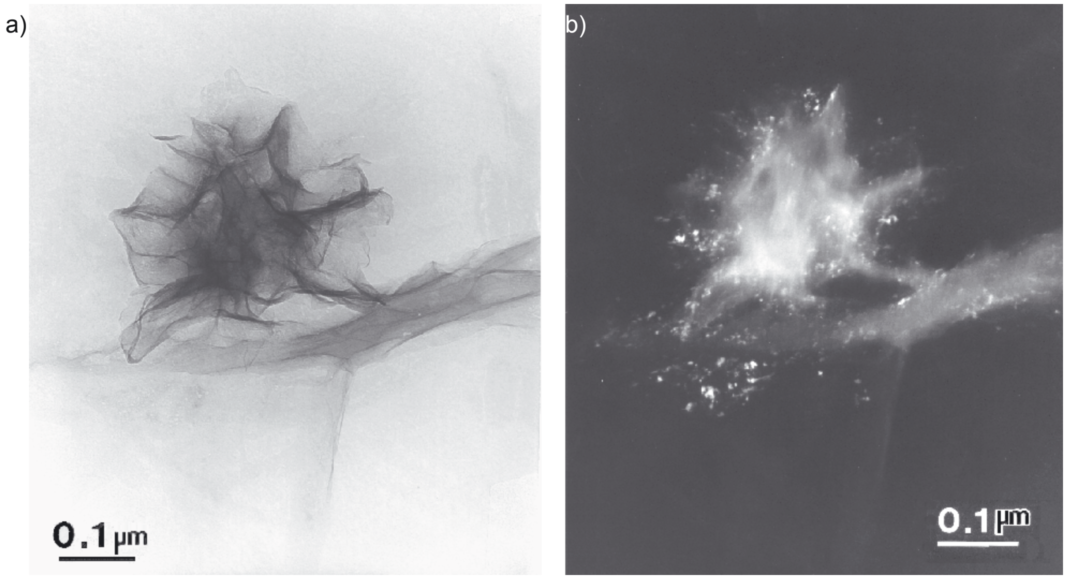

Figure 2. (a) Five-day-old pseudoboehmite transmission electron micrograph. (b) Dark field image indicates its crystallinity.

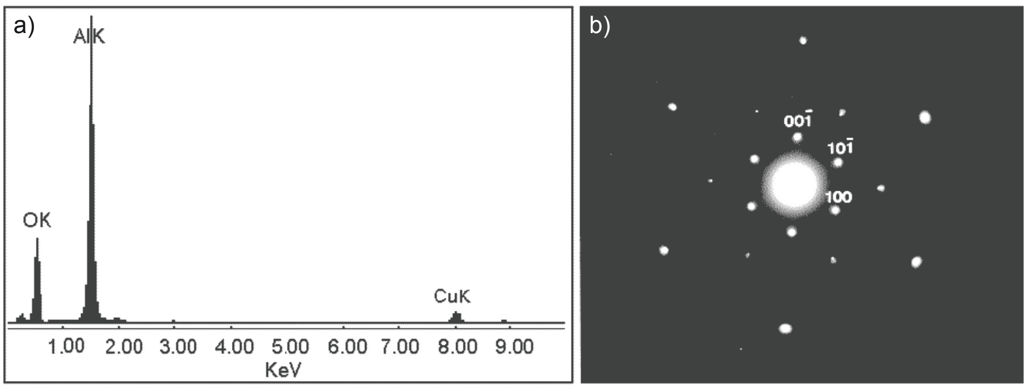

Figure 3. (a) The energy dispersive spectroscopy/transmission electron microscopy (EDS/TEM) microanalysis shows that the sheets (Fig. 2b) are composed of only aluminium and oxygen. (b) Corresponding selected area electron diffraction (SAED) shows nordstrandite reflections.

3. Results and discussion

During the six-month study period, the results of TEM, SEM, SAED, XRD and EDS/TEM studies revealed the formation and growth of nordstrandite microcrystals. XRD analysis showed characteristic nordstrandite basal reflection (0.479 nm) only after 30 days of ageing at room temperature. From the first day, only pseudoboehmite was observed as the 0.64 nm characteristic basal reflections (Fig. 1). Pseudoboehmite is defined as the poorly crystallised Al(III) compound, composed of $Al_2 O_3 .\times H_2O$ (2.0 > x > 1.0), with interplanar spacing increased in the [020] direction up to 0.670 nm, in comparison to 0.612 nm for well-ordered boehmite - AlOOH [21]. Pseudoboehmite occurs most frequently in the form of microfibrils [22].

During the first week of ageing, TEM images revealed the presence of fibrils, mostly in groups of curled and crumpled sheets, in the white precipitate. The EDS/TEM microanalysis showed only the presence of Al and O. The SAED technique did not provide clear reflections due to the small amount of material within the diffraction field. The XRD curve was from pseudoboehmite. Therefore, the first stage of crystallisation occurred during the first two weeks and there was only formation of fibrillar pseudoboehmite. Figs. 2a and b show TEM images of five-day fibrillar pseudoboehmite sheets in bright and dark fields, confirming the crystallinity of the crumpled sheets.

After 15 days of ageing, XRD revealed only pseudoboehmite reflections and no nordstrandite. However, under TEM, some electron-dense granules with rectangular and round profiles, approximately 200 nm in length, were seen. Using EDS/TEM only Al and O were identified, although SAED showed that these particles presented in the crystalline structure of nordstrandite (Figs. 3a and b). It is essential to note that all of these particles were directly connected to fibrils. In some instances, this continuity appeared to exist between bundles of parallel fibrils and the surface of a given particle (Fig. 4).

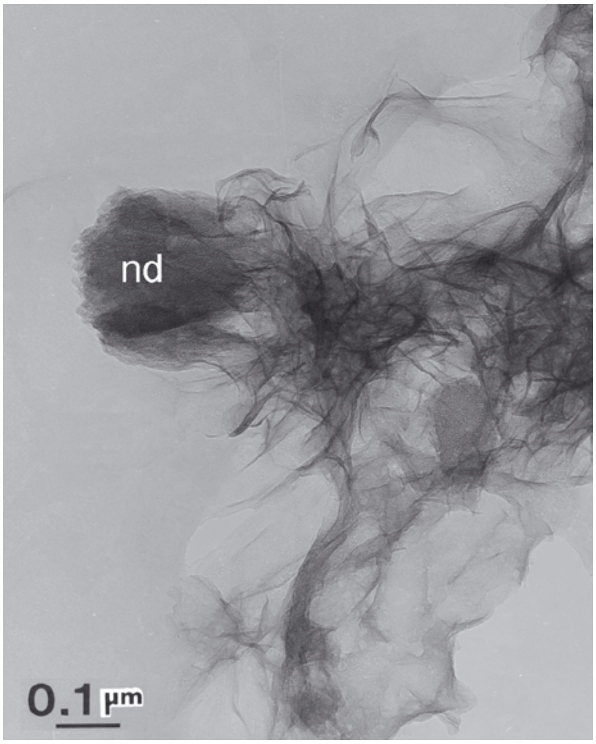

Figure 4. After 15 days, electron-dense nordstrandite granules appear connected with fibrils; here we can see that the nordstrandite particles (nd) and pseudoboehmite fibrils are intimately connected

The TEM analysis showed that pseudoboehmite decreased with further ageing, and, in the XRD, several nordstrandite reflections began to appear. After 30 days, nordstrandite was well characterised by SAED and XRD, although pseudoboehmite was still present (Fig. 5). In TEM, some nordstrandite microcrystals still appeared in continuity with the pseudoboehmite fibrils (Fig. 6), and many single nordstrandite fibril-free rectangular crystals with rounded corners were observed.

After 2 months of ageing, there was a further decrease in the number of pseudoboehmite fibrils, as observed in XRD and TEM analyses. Most of the nordstrandite microcrystals were fibril-free and had acquired a well-defined rectangular profile (Fig. 7). Through XRD and SAED, these rectangular microcrystals were identified as nordstrandite. However, at this second stage of ageing (when nordstrandite had been well characterised by both methods), no multi-point, star-shaped platy crystals were detected under TEM and SEM.

At four months of ageing, nordstrandite was the only aluminium trihydroxide characterised by XRD and SAED, and XRD and TEM showed only traces of pseudoboehmite or complete absence of pseudoboehmite fibrils. Under TEM, the rectangular nordstrandite crystals presented changes in their profiles, as shown in Fig. 8. Thin rectangular plates, with sharp corners, appeared to overlap the rectangular particles. However, close examination of the crystals revealed that these plates, which were either rectangular or triangular precursors of the final multi-point star-shaped platy crystals, were actually outgrowths from the lateral surfaces. In the SAED analysis, these developing rectangular crystals were identified as nordstrandite. This was the third stage of ageing; the fourth and last stage occurs in the fifth and sixth months of ageing.

After five months of ageing, no pseudoboehmite was detected in the XRD, and very few fibrils were observed under TEM. The nordstrandite star-shaped crystals had grown (to 1 µm in diameter), probably through re-crystallisation of the rectangular crystals. The nordstrandite crystals had acquired the characteristic well-developed multi-point platy star shape described in [10,18,19]. In Fig. 9, it can be seen that the multi-point star profile results from the overlapping of thin, rectangular and triangular platy crystals, likely developing from one thick rectangular crystal rather than from the stacking together of separate free platy crystals. The SAED data indicate that the various planes of the plates are perpendicular to the b-axis of the nordstrandite crystal. Aldcroft and Bye suggested that spiral growth is the origin of the outgrowth of the plates from the rectangular nordstrandite crystal.

Fig. 10 shows six-month-old nordstrandite crystals with all star corners formed, many from a 60° angle and some presenting 120° re-entrant angles. The twinning suggested by the 120° re-entrant angles of the stars was not detected by SAED during the ageing period, thus confirming observations made by Aldcroft and Bye [19].

Based on these findings, a model for the development and growth of the multi-point platy star-shaped microcrystals of nordstrandite in ethylene-glycol/water solutions is proposed:

(a) From zero to 15 days of ageing in ethylene glycol/ water solution, non-crystalline aluminium hydroxide changes to fibrillar pseudoboehmite, the fibrils growing by chain polymerisation.

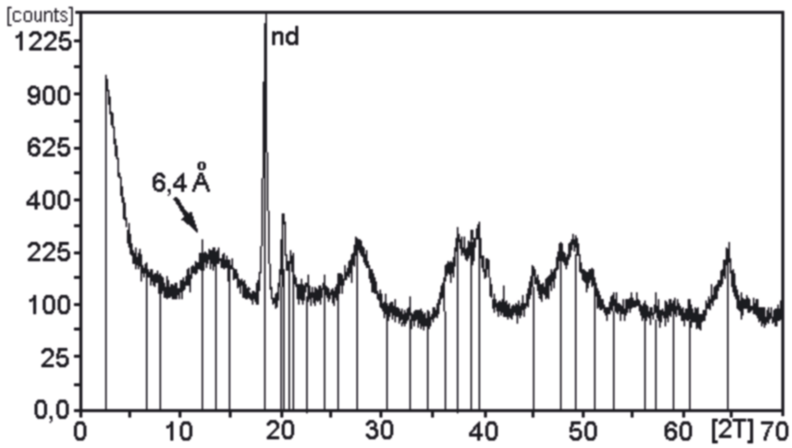

Figure 5. The X-ray diffraction (XRD) curve shows nordstrandite reflections as well as the pseudoboehmite reflections.

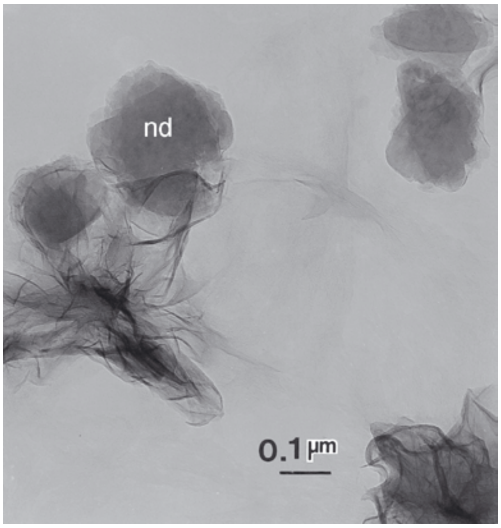

Figure 6. Nordstrandite particles (nd) and pseudoboehmite fibrils are still connected. However, there are less fibrils and the particles are larger.

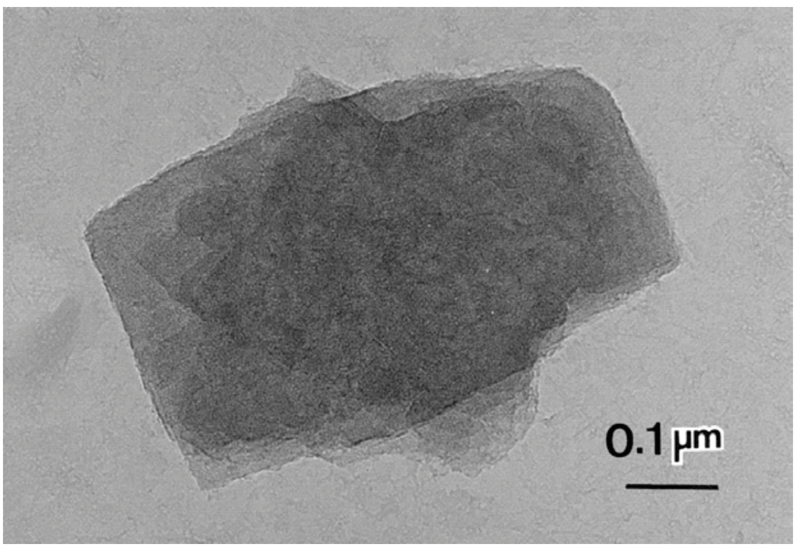

Figure 7. The nordstrandite particle acquires a more well-defined rectangular profile and is completely fibril-free.

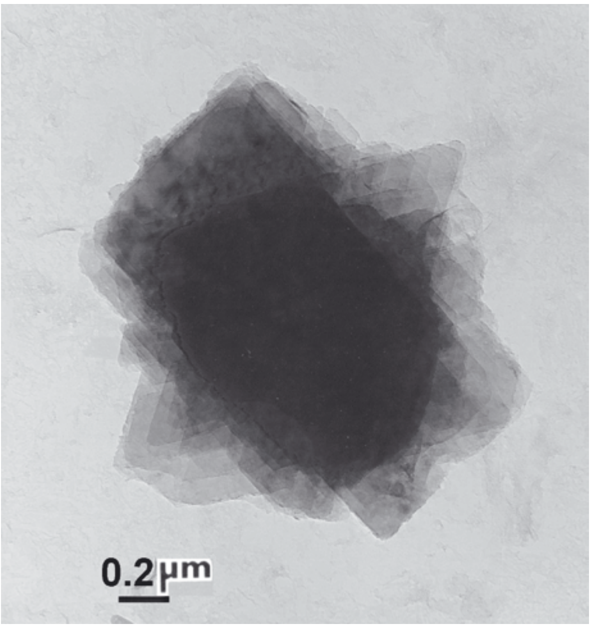

Figure 8. At four months of ageing, the nordstrandite particles present a star-shaped configuration.

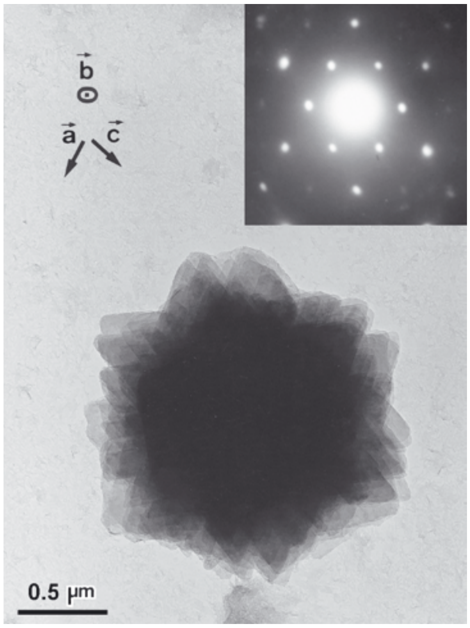

Figure 9. Final stage of the development of the nordstrandite particles into a star-shaped configuration. The selected area electron diffraction (SAED) insert indicates that the various planes of the plates are at right angles to the b-axis.

(b) By day 15, there is spontaneous formation of nordstrandite nuclei, followed by the development and growth of the nuclei from the aluminium cations in the solution.

(c) Between days 15 and 30, the nordstrandite nuclei continue to grow as a result of depolymerisation of the pseudoboehmite fibrils, followed by dissolution of the Al and OH ions in the solution. The crystallizing nuclei increase in size and become rectangular in shape. Therefore, nordstrandite first crystallizes as rectangular particles resulting from fibrillar pseudoboehmite depolymerisation and dissolution, that is, by a dissolution/re-crystallization process.

(d) After two months of ageing, only rectangular fibril-free nordstrandite microcrystals exist in the solution, but no star-shaped crystals yet have formed. The rectangular crystals are the precursors of the crystallization of the multi-point star-shaped crystals of nordstrandite.

(e) Upon further ageing, there are more outgrowths of platy rectangular and triangular crystals from the lateral faces of the rectangular nordstrandite crystals (perpendicular to the b-axis). This outgrowth is the mechanism for the formation of the multi-point nordstrandite stars.

(f) After five months of ageing, all pseudoboehmite fibrils and the majority of the rectangular nordstrandite crystals have disappeared, and only star-shaped platy crystals are observed. Therefore, the multi-point star-shaped nordstrandite crystals are formed from rectangular nordstrandite crystals, probably by a dissolution/re-crystallization process.

(g) After six months of ageing, the crystallisation of well-formed, multi-point, star-shaped nordstrandite microcrystals is complete.

This model is presented in Fig. 11.

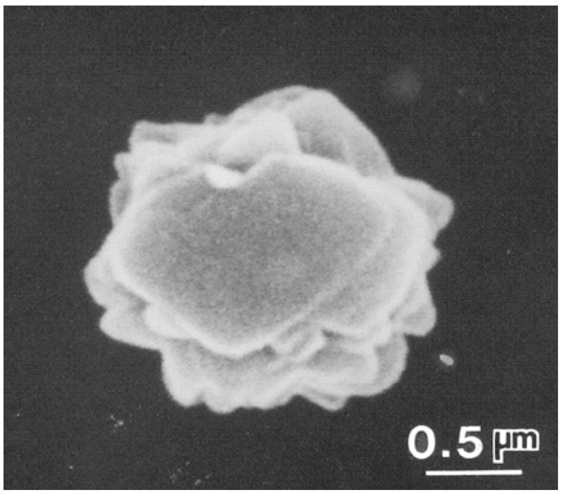

Figure 10. Scanning electron microscopy (SEM) micrograph showing that the final stage of crystal growth is composed of plate stacking, resulting in a star shape.

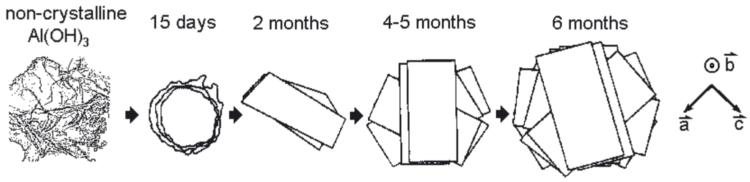

Figure 11. Representation of nordstrandite crystal development in ethylene-glycol/water solutions.

4. Conclusions

This electro-optical study of ageing of non-crystalline aluminium hydroxide in ethylene glycol/water solutions has shown that fibrillar pseudoboehmite microcrystals, characterized by XRD and TEM, at room temperature, are the only aluminium hydroxide crystals formed after the first fifteen days of ageing.

In the second week, 200 nm electron-dense granules have nucleated spontaneously, they are characterized by SAED as nordstrandite. The fibrillar pseudoboehmite bundles and the nordstrandite nuclei are always in close proximity.

After six months, only well-formed, multi-point, star-shaped platy microcrystals of nordstrandite are observed, and fibrillar pseudoboehmite has disappeared. Fibrillar pseudoboehmite, in ethylene glycol/water solution, acts as the precursor for the nordstrandite crystallisation, from nucleation to the full growth of the well-formed star-shaped crystals, by dissolution/ re-crystallization processes.

The well-formed nordstrandite crystals appear by TEM and SEM as resulting from the irregular overlapping of rectangular and triangular plates (perpendicular to the b-axis), thereby resulting in the characteristic multi-point stars. However, by SAED, it is shown that the multi-point stars are monocrystals.

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