

Standard Transition Aluminas. Electron Microscopy Studies

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The aim of this paper is to present the results of characterization of the particle shapes of six standard transition aluminas samples using transmission and scanning electron microscopies; selected area electron diffraction, in parallel with X-ray powder diffraction were used for confirmation of the different transition aluminas types. The transition aluminas - chi; kappa; gamma; theta; delta; and eta were supplied by ALCOA Central Laboratory. The chi-; kappa-; gamma- and delta-Al₂O₃ microcrystals are pseudomorphs from their respective precursors gibbsite and boehmite. However, theta-Al₂O₃ microcrystals are not pseudomorphs after the standard delta-Al₂O₃ sample. Also, eta-Al₂O₃ are not pseudomorphs after bayerite somatoids.

Keywords: *transition aluminas, alumina precursors, gibbsite, electron microscopies*

1. Introduction

1.1. Corundum

A crystalline element or a solid inorganic chemical compound formed by a geological process is a mineral and therefore receives a specific name. Natural crystalline aluminum oxide or alumina (Al₂O₃) is named corundum; the monocrystals* are colorless and transparent. If they contain, intimately mixed, microcrystals of magnetite (Fe₃O₄) or hematite (Fe₂O₃), they are called emery. If the corundum monocrystals contain some elements in isomorphic substitution for Al³⁺ in their structure, gemstones and semi-precious gemstones are formed, also receiving specific names for their colors: (a) sapphire - blue (Fe, Ti); (b) ruby - red (Cr); oriental topaz - yellow (Fe³⁺, Fe²⁺); amethyst - purple (Fe, Mn, Ti); oriental emerald - green (Fe²⁺).

Since, by definition, a mineral is formed in Nature, the expression "synthetic mineral" may be criticized. However, it is used for synthetic rubies and sapphires that are industrially produced today by the Verneuil (oxi - hydrogen flame) or by hydrothermal processes².

It is a common practice in X-Ray Crystallography to take the crystalline structures of some minerals (and also of some chemical compounds) as standards, these structures receiving the name of the mineral. The crystal structure of

corundum is called corundum structure, but also is called α -Al₂O₃ or alpha-alumina structure (Krebs³).

1.2. Alpha-alumina

It was an old recommendation in gravimetric chemical analysis to heat the white gelatinous precipitate of aluminum hydroxide at temperatures above 1200 °C to "stabilize" it for weighing the alumina formed at lower temperatures; the aluminas, if not heated above 1200 °C, adsorbed water vapor very fast and no equilibrium was reached for the weighing. The alumina heated above 1200 °C was named alpha-alumina in 1916 by Rankin and Merwin⁴; the use of Greek letters was an old common practice in Chemistry to distinguish between compounds with exactly the same composition, but having different physico-chemical properties. These authors also proposed a new beta-alumina, which will be discussed later. The name β -Al₂O₃ was also given by Rankin + Merwin⁴ to a Na - containing alumina. The α -alumina prepared by heating aluminum hydroxides is a finely divided powder constituted by micrometer sized particles. After the Debye-Scherrer X-ray powder method was developed in 1916, soon it was shown that the α -alumina particles are micro-crystals with the same crystalline structure of the mineral corundum. Today, the expression more frequently used is α -alumina crystalline structure. Presently, α -Al₂O₃ has many

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**A (mono) crystal consists of a three dimensional periodical arrangement of atoms, each of which will scatter an incident X-ray beam¹.

uses in Traditional and Advanced Ceramics; particularly, is an important substrate for the growth of the superconductors and semiconductors by molecular beam epitaxy.

1.3. Transition Aluminas

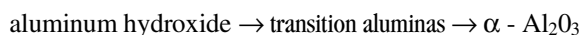
The aluminas, heated at temperatures under 1100 °C, were considered in the early days of X-ray powder diffraction method as amorphous or non-crystalline materials, in spite of the fact that they have important adsorptive and catalytic properties; in other words, they were considered very ill defined and complex materials, that above 1100 °C changed into crystalline α -alumina; sometimes, they were loosely called “gamma-alumina” by Ulrich⁵.

Later, it was recognized⁶ the existence of five crystalline aluminum hydroxides: gibbsite; bayerite; nordstrandite; diaspore; and boehmite; they have crystals varying from micro to millimetric size; their dehydroxilation occurs by heating between 300 °C and 600 °C and aluminas are formed, all as micrometer sized powders; these fine grained powders change their structure at 1100 °C, but remain as powders; increasing the temperatures from 1100 °C up to near the melting point of α -Al₂O₃ (2050 °C), the powder particles start to coalesce, sinter and recrystallize as microplatelets of hexagonal profile or even hexagonal prisms with α -Al₂O₃ structure; they are called “tabular crystals” of aluminas and must not be confused with the commercial product patented under the name “tabular alumina”. The formation of the hexagonal crystals of α -Al₂O₃ may be accelerated by the addition of 0.1% AlF₃.

Stumpf *et al.*⁶ (from ALCOA’S Research Laboratories, now Technical Center, Pittsburgh, USA), showed that,

between the temperatures of dehydroxilation of the aluminum hydroxides and the alpha-alumina first crystallization, a number of well characterized and reproducible intermediate crystalline alumina structures are formed; each one has a stable different crystalline structure at a given temperature range, with just one exception which is “amorphous”.

The type or structure of each alumina and its temperature range of existence are determined by the structure of the starting or precursor hydroxide; they are different for gibbsite, bayerite, nordstrandite, boehmite or diaspore*. Extensive literature exists on the dehydroxilation of the crystalline hydroxides, in special on gibbsite, because it is the phase formed in the industrial Bayer Process. These seven aluminas are called “Transition Aluminas” and received Greek letters to identify them: gamma; delta; theta; kappa; chi; eta and rho. Figure 1 is adapted from the most recent review⁷ of the thermal transformation sequence:



From Fig. 1, may be concluded that all Transition Aluminas may be produced from gibbsite; that fact is one reason more for the industrial importance of the Bayer gibbsite. All Transition Aluminas are synthetic.

The five crystalline hydroxides can be synthetic or natural; from either origin, the Transition Aluminas are formed under firing. These same Transition Aluminas may also be formed by pyrolysis of crystalline hydrates of aluminum salts as sulphate; nitrate; ammonium alum; chloride; formate; and hydroxiacetate. Other methods for preparing Transition Aluminas are reviewed by Wefers and Misra⁷.

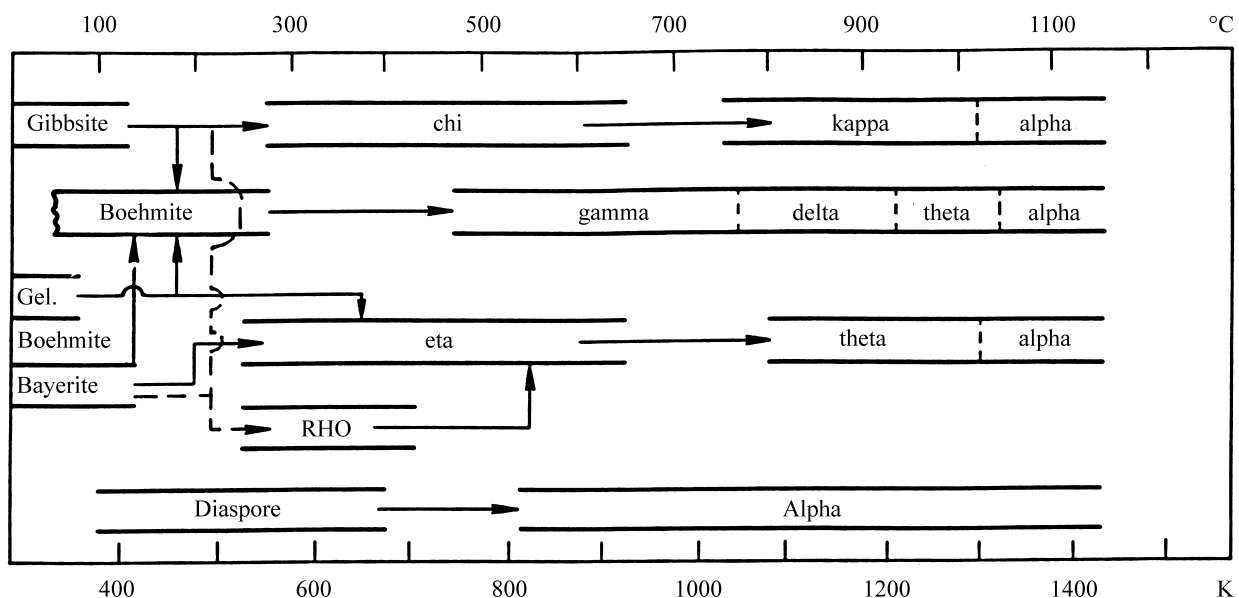


Figure 1. Thermal transformation sequence of the aluminum hydroxides (adapted from Ref. 7).

* In order to be coherent, the crystalline Al-hydroxides should have standard names for their structures; in fact they have, but nordstrandite has none⁷; so, it became common practice to use the mineral name to designate the hydroxides, natural or synthetic.

In spite of its Greek letter, α - Al_2O_3 is not a transition alumina, but is the last crystalline material formed by the effect of increasing temperatures on the transition aluminas. Also, β - Al_2O_3 is not a transition alumina; it has the composition $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ and has use as a ceramic electrolyte; today, a whole family of beta-aluminas exists, containing groups I and II cations and with several molar ratios, generally between 5 and 9.

It is interesting to point out that alumina plasma sprayed onto a cooled substrate is known to solidify in the form of one or more metastable or transition aluminas; the most frequent is γ - Al_2O_3 , which by annealing reverts to α -through δ - Al_2O_3 .

The Transition Aluminas cannot be considered true polymorphs of α - Al_2O_3 . The low temperature ones in particular may contain some residual OH anions. Moreover, as pointed above, the sequence of transformation is not reversible, that is, neither α - Al_2O_3 nor any of the high temperature aluminas can be converted to one of the Transition Aluminas that occur at a lower temperature. Therefore, according to Wefers and Misra⁷ they may be classified as thermodynamically unstable, although reproducible, states of structural reordering of the α - Al_2O_3 structure. Some authors⁹ prefer to call them "metastable alumina polymorphs".

So, Fig. 1 is a schematic diagram that only indicates general temperature ranges in which the Transition Aluminas occur, but should not be considered a "phase diagram". It is common that more than one form may be present simultaneously within a crystal of a decomposed hydroxide or oxide.

Stumpt *et al*⁶ have observed that the same Transition Aluminas are encountered after short and long heating periods: the observed effect of long holding at the same temperature is merely to lower the transformation temperatures of the Transition Aluminas⁸.

The Transition Aluminas have uses in ceramics, particularly as adsorbents, catalysts, coatings and soft abrasives.

According to Gitzen¹⁰, also from ALCOA, other investigators have, since 1950, discovered new transition alumina phases or disagreed with the published X-ray patterns or even with the existence of the seven listed phases. The aluminum oxide films formed on aluminum by electrolytic oxidation (anodization) and fired at 800 °C have γ - Al_2O_3 structure. Direct thermal oxidation of aluminum metal foils produces a new "epsilon-alumina"; as it does not come from an Al-hydroxide precursor, it is not considered a transition alumina.

Table 1 shows the X-Ray Powder Data of the Transition Aluminas and of α - Al_2O_3 and Fig. 2 shows their X-Ray Powder Diffraction Curves.

As pointed before, all the seven Transition Aluminas are naturally micrometer sized particles, because their pre-

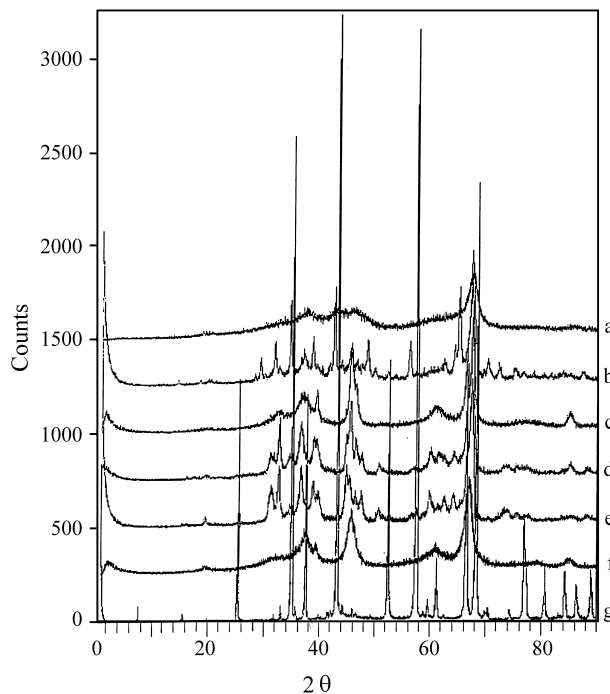


Figure 2. X-ray diffraction powder curves of: (a) chi- Al_2O_3 ; (b) kappa- Al_2O_3 ; (c) gamma- Al_2O_3 ; (d) delta- Al_2O_3 ; (e) theta- Al_2O_3 ; (f) eta- Al_2O_3 ; (g) α - Al_2O_3 .

cursors were fine grained synthetic aluminum hydroxides particles; Rooksby¹¹; Bye and Simpkin¹² improved the crystallinity of gamma-, delta-, theta- and kappa-aluminas by the effect of addition of Mo, V, Cr and Fe, with various temperature and time treatments.

Very small amount of published information exists on the particle shapes obtained by transmission electron microscopy of the transition aluminas, the majority being supplied by ALCOA'S investigators. Transition aluminas crystals with the structures of gamma-, delta- and theta- Al_2O_3 crystals were studied using high resolution electron microscopy (HREM) by Iijima¹³, by Morrissey *et al.*¹⁴ and more recently, by Levin and Brandon⁹; Morrissey *et al.*¹⁴ wrote: "Although the existence of the transition aluminas, specifically gamma-, delta- and theta-aluminas have been recognized for many years, their structure is still not well understood. Lack of structural information is due in part to the growth characteristics of these forms of alumina. Large single crystals of these materials cannot be made...". The phase transformation during calcination of the aluminum hydroxides was firstly studied employing SAED by Lipens and De Boer¹⁵. The growth of α - Al_2O_3 by CVD was studied by Sears and De Vries¹⁶. The morphologies of particles and agglomerates of several commercial aluminas and aluminum hydroxides were described using scanning electron microscopy by Castro *et al.*¹⁷ and by Passaro and Souza Santos¹⁸.

1.4. Aim

The purpose of this paper is to describe the particle morphologies as observed by transmission and scanning electron microscopy of six standard transition aluminas samples supplied by ALCOA.

2. Experimental

2.1. Samples

The six Transition Alumina samples (white powders) were kindly supplied by Dr. Karl Wefers, Head of the Surface Technology Group of the ALCOA Technical Center, Pittsburgh; they belong to the Center collection of chemical standards⁶. They were previously used for reference in X-ray studies to characterize the aluminas formed in the thermal transformation of synthetic crystals of aluminum hexachloride, hydroxiacetate, fibrillar pseudoboehmite and euhedral boehmite¹⁹.

No rho-alumina was supplied, because it is so unstable, that it must be kept permanently under high vacuum. Rho-alumina is formed by the rapid heating in vacuum of gibbsite to 575-700 K (302-427 °C); it is non-crystalline (amorphous to X-rays), very reactive due to its high free energy resulting from lattice disorder and large surface area; in contact with water vapour, gibbsite or boehmite are formed. Rho-Al₂O₃ is used as an intermediate for the production of a type of activated aluminas (with gamma-Al₂O₃ structure) and surface areas between 250 and 375 m²/g; also Claus catalysts for sulfur production and some hydrogenation catalyst supports use an activated alumina which is a mixture of chi-, rho- and eta-aluminas, with surface areas between 275 and 375 m²/g²⁰.

As reference, sintered particles of α -Al₂O₃ formed at 1200 °C from pseudoboehmite¹⁹ and at 1500 °C from microcrystals of synthetic gibbsite, are also presented.

2.2. X-ray diffraction (XRD)

The XRD curves were obtained in a Philips Diffractometer model X-Pert, operating with copper K-alpha radiation, at 40 kV and 40 mA; the scanning was conducted between 1° (2 θ) and 90° (2 θ). Figure 2(a) - (g) shows the XRD powder patterns of the six standard Transition Aluminas and of the α -Al₂O₃ samples.

2.3. Electron Optical Examination

Each powder was ultrasonified for 20 min and dry prepared for transmission electron microscopy (TEM), and selected area electron diffraction (SAED), on carbon covered grids; for the scanning electron microscopy (SEM) they were directly placed on the stubs (double face taped) and gold covered in an high vacuum sputtering unit. The preparations were examined in a Philips CM200 transmis-

sion electron microscope at 200 kV and in a JEOL JSM 840A scanning electron microscope.

3. Results and Discussion

3.1. chi-Al₂O₃

From Fig. 1, it can be concluded that gibbsite is the only aluminum hydroxide that produces chi-alumina crystals by thermal dehydroxilation.

Several authors^{7,10,21} noted that the dehydration of gibbsite crystals (Bayer agglomerates) is pseudomorphic, that is, the external shape of the crystals is retained and there is an orientation relationship of the crystal axes of the new phase to those of the original crystal; it seems that the pseudomorphosis goes up to corundum crystallization. As the dehydroxilation leads to a loss of 33% of weight (water vapour), there is an increase in density from 2.42 to 3.98 g/cm³; as a consequence, a large internal microporosity is developed in the chi-Al₂O₃ crystals. The basic crystal habit of gibbsite, natural or synthetic, is pseudohexagonal tabular (hexagonal plates), of micrometric size; these crystals are named "tabular gibbsite"⁷.

Figure 3A is a TEM of chi-Al₂O₃ crystals; they are hexagonal plates, most probably pseudomorphic after gibbsite crystals; they present a fine granular texture due to the thin platelets microporosity. X-ray powder pattern lines fully agrees with the ICDD card n° 04-0880 for chi-Al₂O₃; the X-ray diffraction curve is shown in Fig. 2(a); its SAED pattern confirms the chi-Al₂O₃ structure of the platelets (Fig. 3B).

Figure 3C is a scanning electron micrograph of the chi-Al₂O₃ powder showing that the platelets exist as small agglomerates of the platy crystals.

3.2. kappa-Al₂O₃

From Fig. 1, it can be seen that kappa-Al₂O₃ is only formed from heating chi-Al₂O₃ and that it transforms above 1000 °C into alpha-alumina or corundum; from what is written on gibbsite, it should be expected that the transformed chi-kappa crystals should be pseudomorphic; in other words, chi- and kappa-Al₂O₃ crystals would have very close shapes.

Figure 4A is a TEM of a kappa-Al₂O₃ crystal: it has an irregular outline, different from those of Fig. 3A of chi-Al₂O₃; however, it shows a development in the internal porosity: many large voids, appearing as holes, have been formed, probably from the coalescence of several micropores.

Figure 2(b) shows the XRD pattern of kappa-Al₂O₃ which indicates a higher degree of order than in the chi's; it coincides with the ICDD card n. 04-0878 of kappa-Al₂O₃; its SAED pattern (Fig. 4B) obviously has much more spots and confirms the kappa structure.

Figure 4C is an scanning electron micrograph of the powder of kappa- Al_2O_3 ; the particles are agglomerates of stacks or booklets of plates of different sizes and very irregular profile; however, in some points of the Fig. 4C,

stacks of hexagonal plates are seen, all of them clearly showing 120° angles.

Therefore, it is clear that the chi and kappa- Al_2O_3 came from gibbsite crystals, but not from the same type of crystal.

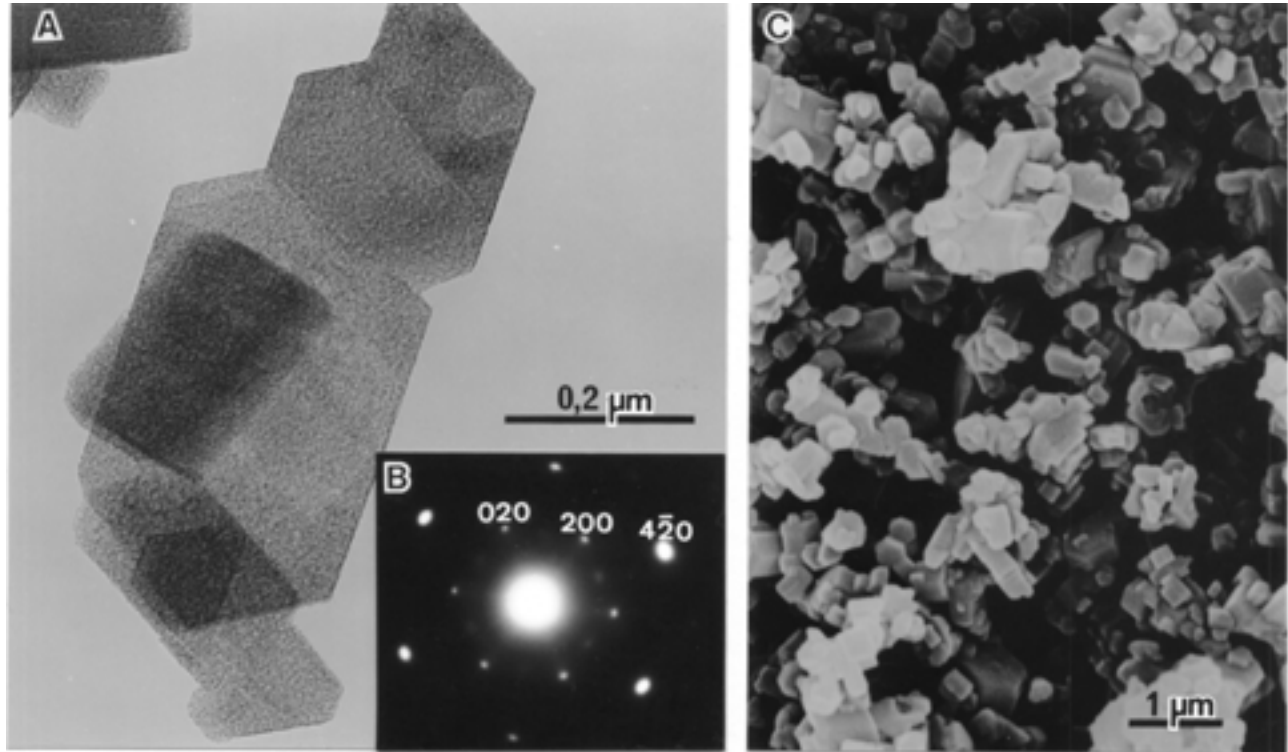


Figure 3. chi- Al_2O_3 (A) - transmission electron micrograph; (B) - selected area electron diffraction pattern; (C) scanning electron micrograph.

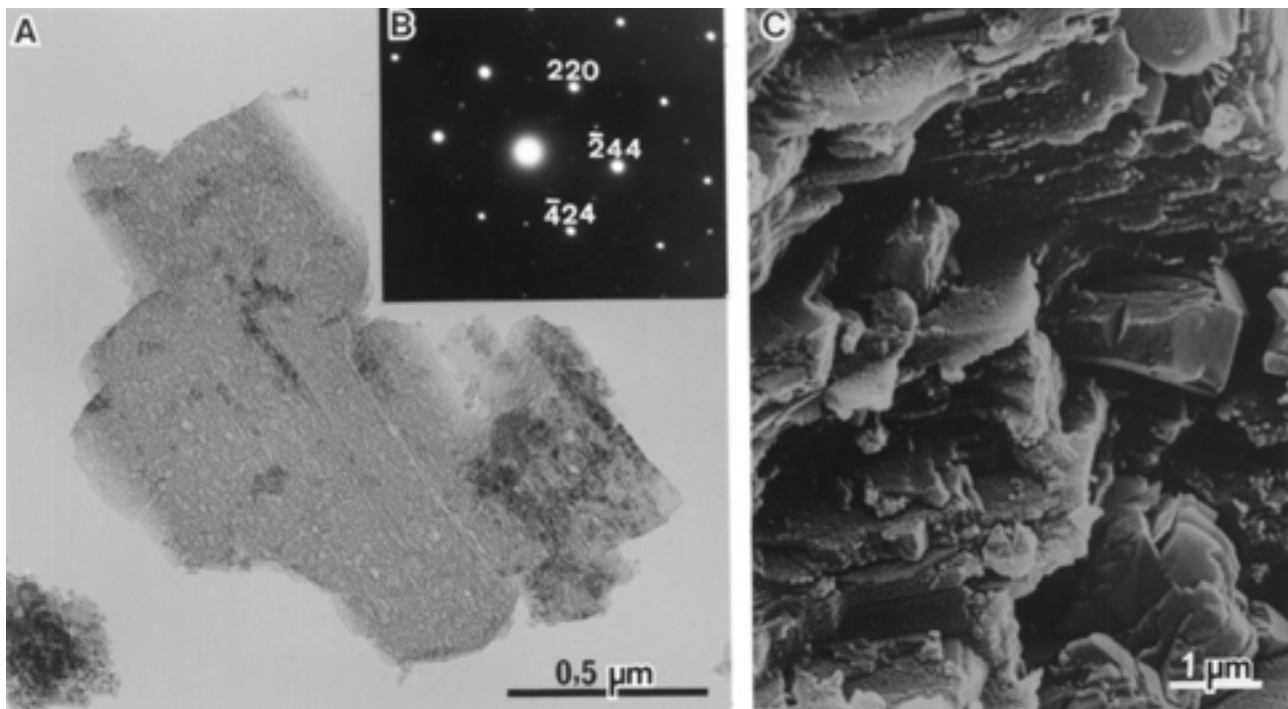


Figure 4. kappa- Al_2O_3 (A) - transmission electron micrograph; (B) - selected area electron diffraction pattern; (C) scanning electron micrograph.

An hypothesis is that chi- comes from the Hydral series which is constituted by hexagonal plates and kappa from ground Bayer gibbsite, which is constituted by agglomerates composed by tabular and prismatic crystals.

3.3. γ -Al₂O₃

From Fig. 1, it can be seen that the monohydroxide boehmite is the only one to produce γ -Al₂O₃ by dehydroxilation (pseudoboehmite also can do). However, boehmite can be produced by two different routes: (a) hydrothermal synthesis at 180-250 °C from aluminum trihydroxides or from pseudoboehmite; (b) thermal dehydroxilation in air, at 300 °C, of coarse (100 μ m) gibbsite crystals.

Route (a) produces either regular hexagonal plates or euhedral laths of hexagonal profile; route (b) produces pseudomorphs of the original gibbsite crystals, Bayer or tabular; therefore, both routes would produce platy crystals with hexagonal shape or showing clearly some 120° angles. Gitzen, from ALCOA, wrote (Ref. 10, p.14) the following referring to a special route for synthesis of boehmite crystals: "Boehmite forms well-crystallized rhombs (lozanges) from alkaline solutions, but generally as thin curve-edged plates, often as coarse as 5 microns, when formed in water. This process has been investigated to some extent as a potential source of alumina for ceramic purposes. It will probably receive more attention in the future". Wefers and Misra (Ref. 7, Fig. 4.15) presented a TEM of gamma-alumina from well formed boehmite crystals: the alumina is a pseudomorph after the hexagonal plate; the dehydroxilation

develops a system of lamellar pores which are oriented parallel to the (100) direction of the boehmite crystal. Curiously, in the same figure there are two lozanges with parallel striations, which have the same direction of the lozange short diameter; the lozange has 80° and 105° angles. Therefore, that gamma-alumina was produced from the boehmite rhombs described by Wefers and Misra. The synthetic boehmite crystals named CERA hydrate produced by the British Aluminum Co. have the rhomb shape²².

Figure 5A is a TEM from crystals of the sample of γ -Al₂O₃: curiously it is a platy crystal with sharp edges, a pair forming a 80° angle and other a 105°.

Figures 2(c) and 5B are, respectively, the XRD powder pattern and the SAED pattern of the sample; they agree with the ICDD card n. 10-0425 from gamma-Al₂O₃. The crystals have a porous texture, which forms parallel striations at right angles with the 80° bissectrix. Figure 5C is a scanning electron micrograph of the γ -Al₂O₃ sample: it clearly shows that the losanges are pseudomorphs from boehmite rhombs. So, this gamma-Al₂O₃ is a very special sample, because γ -Al₂O₃ is a widely used industrial product in catalysts and adsorbents and is produced from other precursors with different crystal shapes⁸.

3.4. δ -Al₂O₃

From Fig. 1, it can be seen that delta-Al₂O₃ is produced only from γ -Al₂O₃; references^{19,23,24} indicate that the transformation is pseudomorphic either from hexagonal laths of

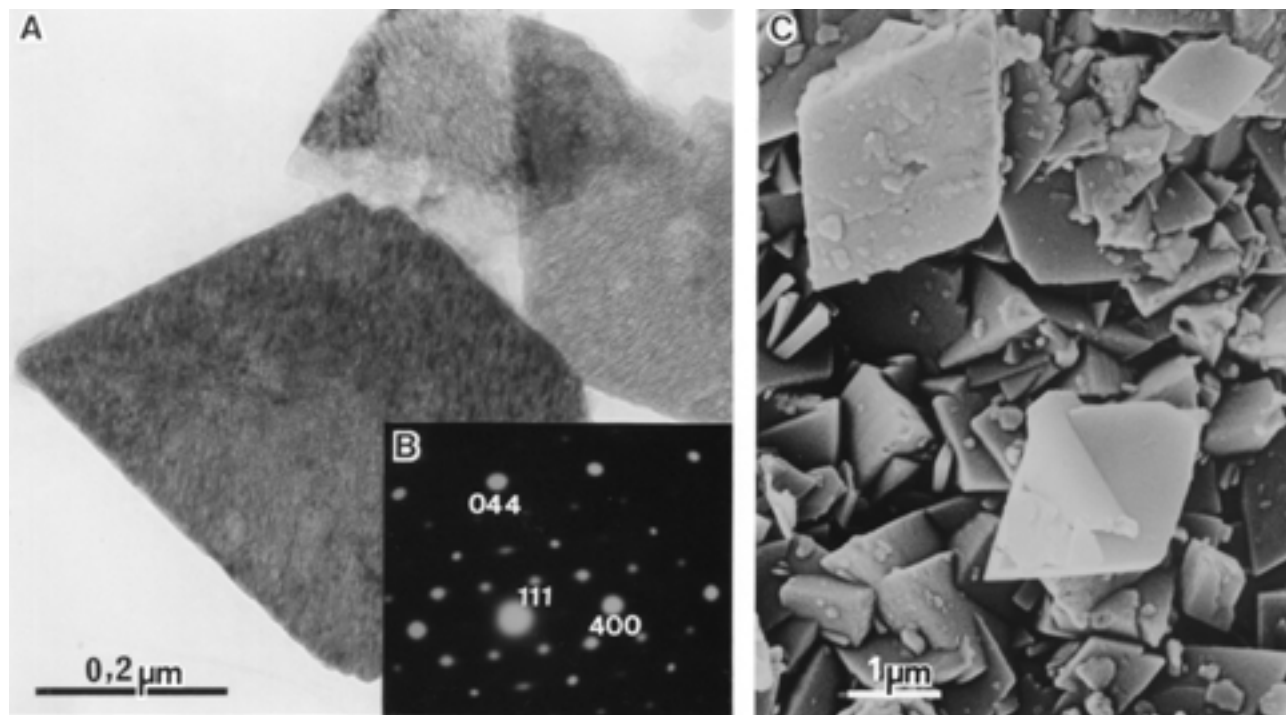


Figure 5. γ -Al₂O₃ (A) - transmission electron micrograph; (B) - selected area electron diffraction pattern; (C) scanning electron micrograph.

boehmite or from fibrillar pseudoboehmite as precursors of γ - Al_2O_3 .

Figures 6A and 6C are TEM and SEM micrographs from crystals of the sample of δ - Al_2O_3 ; it is very clear that they are pseudomorphs after the crystals of γ - Al_2O_3 of Figs. 5A and 5C; the texture of the pseudomorph of δ - Al_2O_3 still maintain the parallel striations, but between them several pores or holes can be observed, similarly to kappa- Al_2O_3 (Figure 4A).

Figures 2(d) and 6B are, respectively, the XRD powder pattern and the SAED pattern of the sample; they agree with the card n. 04-0877 from delta- Al_2O_3 .

Some images of the rhomb in Fig. 6C suggest the hypothesis that they are intermediates in the crystallization of euhedral hexagonal plates of boehmite in the hydrothermal synthesis: the disappearance of the two 80° angles would produce two new parallel sides and an hexagonal plate would be formed in the end of the process, if enough time was given for the crystal to be completed.

3.5. theta- Al_2O_3

From Fig. 1, it can be seen that theta- Al_2O_3 may be produced from two routes: (a) from delta- Al_2O_3 ; (b) from eta- Al_2O_3 .

Figures 2(e) and 7B are, respectively, the XRD powder pattern and the SAED of the sample; they agree respectively with the ICDD cards n. 35-0121 and 23-1009. Figures 7A and 7C are TEM and SEM micrographs of the sample of θ - Al_2O_3 . The first observation is that the crystals

are clearly not pseudomorphs from delta-alumina, because platy crystals with 80° angles are absent. The particles have irregular outlines and are agglomerates of small round particles, presenting a parallel orientation of strings of particles observed in the thinner particles. In the scanning micrographs, the particles appear to be packets of layers.

The morphology of theta- Al_2O_3 sample is confusing: (i) it is not a rhomb pseudomorph; (ii) its irregular shape suggest to be ground particles, but not from delta- Al_2O_3 pseudomorphs (absence of plates, some with 80°); (iii) it could be a pseudomorph after eta- Al_2O_3 formed, not from delta- Al_2O_3 ; that is the most probable hypothesis.

3.6. eta- Al_2O_3

From Fig. 1, it can be seen that eta- Al_2O_3 may be produced from two routes: (i) from bayerite; (ii) from gelatinous boehmite. No information exists on pseudomorphism from these crystals. Bayerite micro-crystals may be produced with two different morphologies: (I) as hourglass shaped somatoids, by crystallization of non-crystalline $\text{Al}(\text{OH})_3$ in water where no chemical was dissolved; (II) by controlled neutralization of aqueous sodium aluminate solution by CO_2 at 30 - 35°C , producing round agglomerates of polyhedral crystals. Gelatinous boehmite is a synonymous of pseudoboehmite; it is constituted by a linear polymer of the $-(\text{Al}100\text{H})-$ group; by TEM appears as microfibrils, which length is dependent of the degree of polymerization. Long fibrils first produce pseudomorphic gamma- Al_2O_3 by thermal dehydroxilation²³.

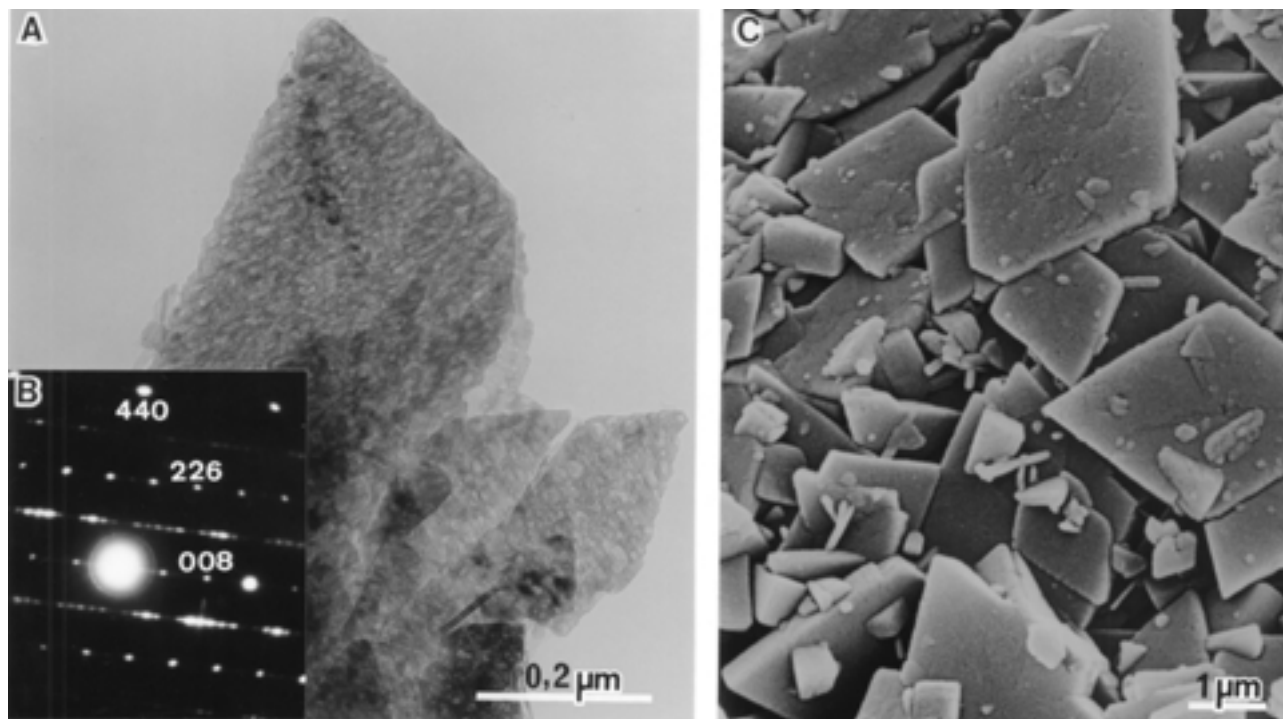


Figure 6. delta- Al_2O_3 (A) - transmission electron micrograph; (B) - selected area electron diffraction pattern; (C) scanning electron micrograph.

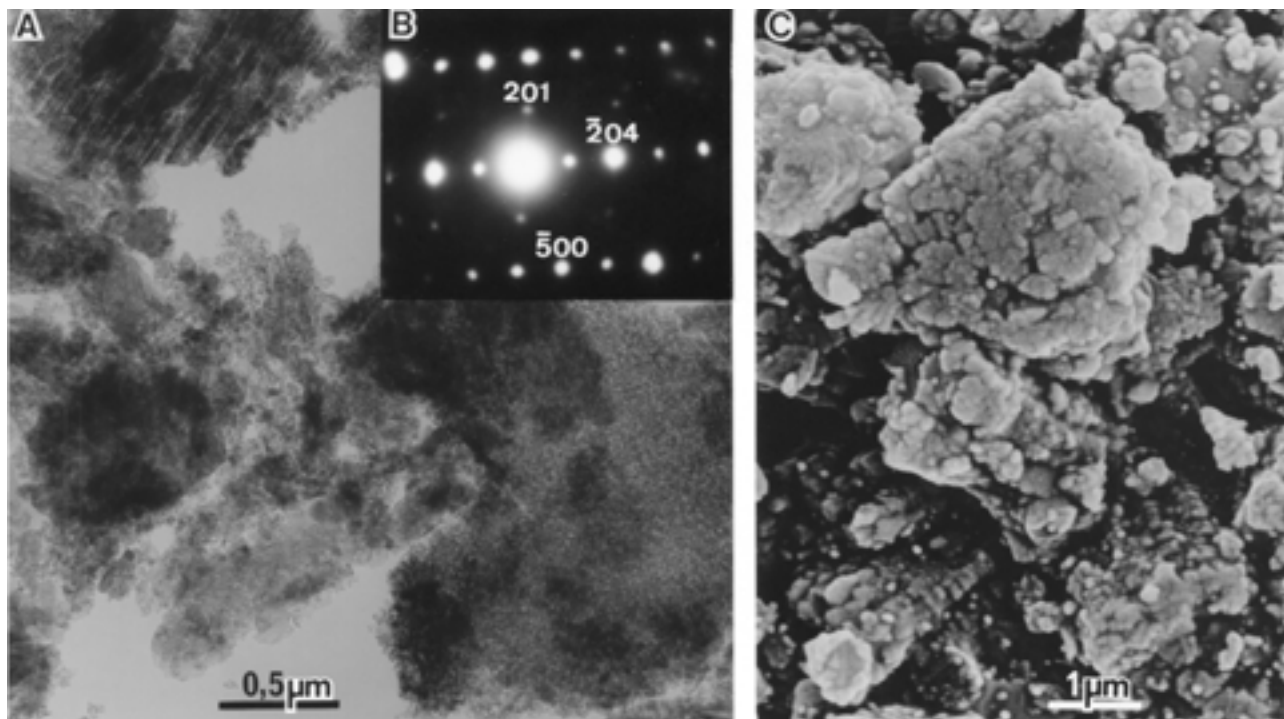


Figure 7. theta- Al_2O_3 (A) - transmission electron micrograph; (B) - selected area electron diffraction pattern; (C) scanning electron micrograph.

Figures 2(f) and 8B are, respectively, the XRD powder pattern and SAED pattern of the sample; they agree with the ICDD card n. 0-0875. Figures 8A and 8C are TEM and SEM micrographs of the η - Al_2O_3 sample: the particles have irregular shape and are agglomerates of smaller round particles; these particles present, when observed by TEM, a fine internal granulation and porosity.

Either by TEM or SEM, there is no evidence of somatoid or fibrillar pseudomorphs presence; on the other hand, Fig. 8C is very similar to the bayerite particles prepared by the CO_2 method whose micrographs are presented by Misra⁸. Therefore, there is a strong possibility that the η - Al_2O_3 come from bayerite agglomerates prepared by CO_2 precipitation for Na AlO_2 solution.

3.7. Sintered alpha- Al_2O_3

As pointed before, alpha-alumina is not a Transition Alumina, but it is the end-structure formed above 1000 °C when kappa and theta- Al_2O_3 are heated or is formed at 500 °C when diasporite is dehydroxilated; these powdery forms produce alpha- Al_2O_3 also as a fine powder. Its XRD pattern is shown in Fig. 2(g) - ICDD card n. 43 - 1484. The particle shape of the α - Al_2O_3 vary with the nature of the precursors; Fig. 9 is a TEM from an alpha- Al_2O_3 from a fibrillar pseudoboehmite powder fired at 1200 °C to illustrate the morphology: some of the particles of theta- Al_2O_3 have changed into alpha and have started to coalesce in larger particles producing the sintering of the powder, but some pseudomorphs of theta- Al_2O_3 still remain unchanged. Its

heating up to 1500 °C does not produce the well formed hexagonal platelets of α - Al_2O_3 , shown in Fig. 10 from MEV, of ALCOA' 2011 alpha-alumina.

Concluding, no data could be obtained from the electron optical observations which could indicate the exact heating temperature used at ALCOA's laboratories to prepare the studied samples of transition aluminas; so, no detailed preparation route could be described.

4. Conclusions

The electron microscope examination of the six standard Transition Alumina powders allowed the following specific conclusions to be drawn on their morphology and about the precursors of their microcrystals:

4 (a). chi- Al_2O_3 crystals are pseudomorphs from pseudo-hexagonal plates of gibbsite (tabular gibbsite).

4 (b). kappa- Al_2O_3 crystals are platy irregular crystals formed from chi- Al_2O_3 and from gibbsite, as former precursors, probably being pseudomorphs after them.

4 (c). gamma- Al_2O_3 crystals are pseudomorphs from rhombs or lozange platy crystals of boehmite as former precursors.

4 (d). delta- Al_2O_3 crystals are pseudomorphs from rhombs of gamma- Al_2O_3 and from boehmite as former precursors.

4 (e). theta- Al_2O_3 crystals are agglomerates of round particles that are not pseudomorphs from delta- Al_2O_3 rhombs.

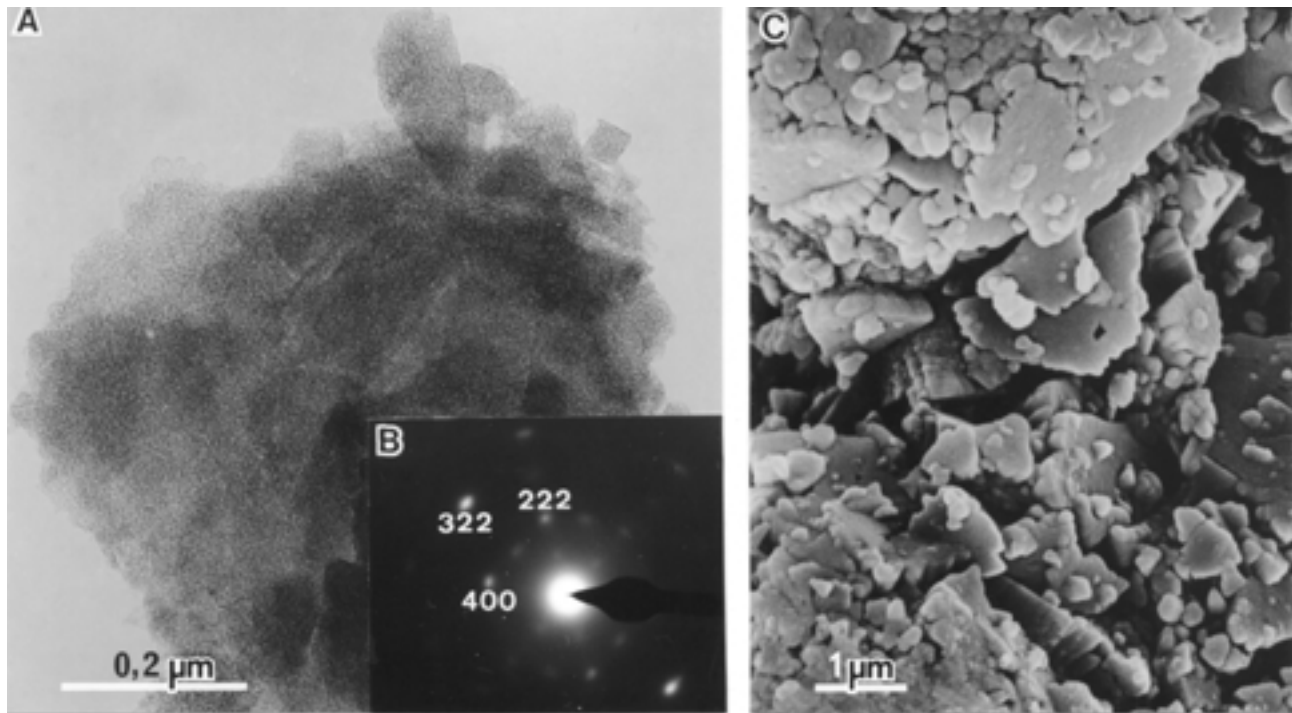


Figure 8. eta- Al_2O_3 (A) - Transmission electron micrograph; (B) - selected area electron diffraction pattern; (C) scanning electron micrograph.

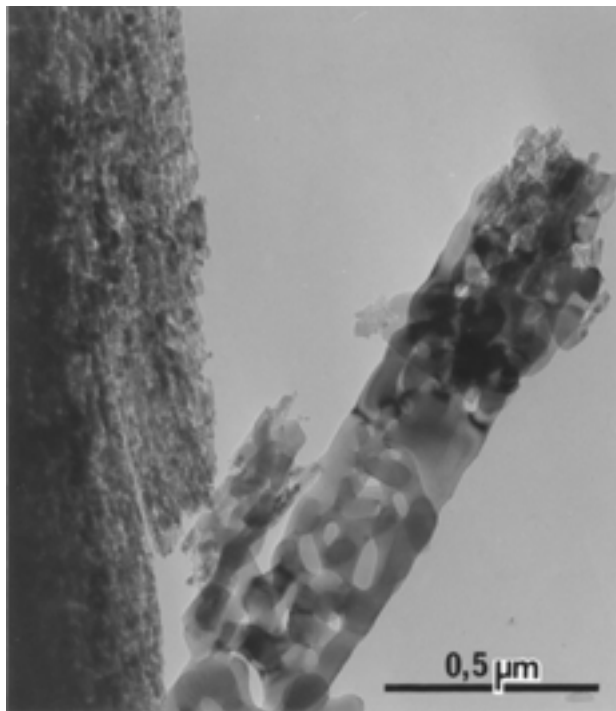


Figure 9. Transmission electron micrograph of alpha- Al_2O_3 from fibrillar pseudoboehmite fired at 1200 °C.

4 (f). eta- Al_2O_3 are agglomerates of small round particles, probably from CO_2 -precipitated bayerite crystals (not somatoids).

4 (g). All the six Transition Aluminas microcrystals present internal porous textures which are different among

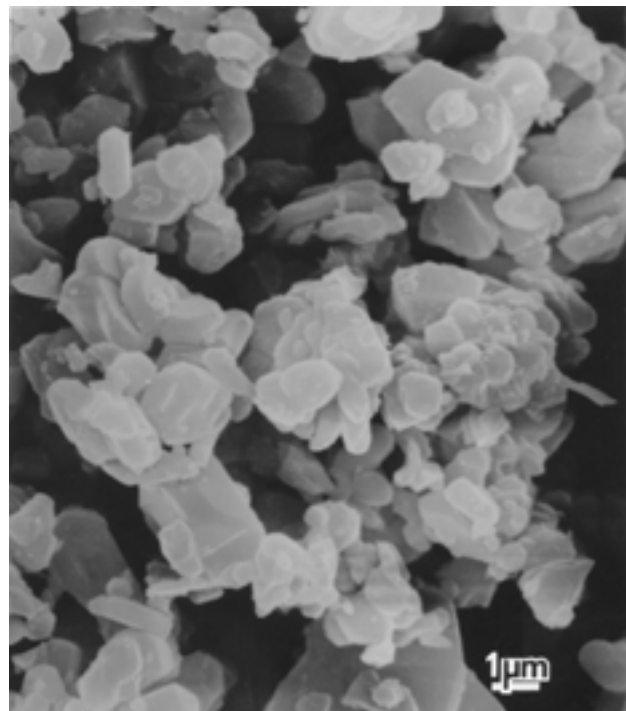


Figure 10. Scanning electron micrograph of ALCOA 2011 $\alpha\text{-Al}_2\text{O}_3$.

the several forms, depending from the precursor and the temperatures of formation.

4 (h). alpha- Al_2O_3 crystals at 1100 °C are pseudomorphs from the Alumina precursor; at 1200 °C, pseudomorphs and round shaped sintered crystals of alpha- Al_2O_3 may

coexist; at 1500 °C only the sintered crystals exist as coalesced round plates, some with 120° angles, because perfect hexagonal platelets are only formed by addition of small percentages of AlF₃.

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