Anais da Academia Brasileira de Ciências
ISSN: 0001-3765
aabc@abc.org.br
Academia Brasileira de Ciências
Brasil

Kiyohara, Pedro K.; Santos Souza, Helena; Coelho Vieira, Antonio C.; Santos de Souza, Pérsio
Structure, surface area and morphology of aluminas from thermal decomposition of Al(OH)(CH3COO)2 crystals
Anais da Academia Brasileira de Ciências, vol. 72, núm. 4, dez, 2000, pp. 471-495
Academia Brasileira de Ciências
Rio de Janeiro, Brasil

Structure, Surface Area and Morphology of Aluminas from thermal decomposition of $Al(OH)(CH_3COO)_2$ Crystals

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Manuscript received on August 27, 1998; accepted for publication on June 1, 2000; contributed by PÉRSIO DE SOUZA SANTOS*

ABSTRACT

Crystalline aluminium hydroxiacetate was prepared by reaction between aluminium powder (ALCOA 123) and aqueous solution of acetic acid at 96°C±1°C. The white powder of $Al(OH)(CH_3COO)_2$ is constituted by agglomerates of crystalline plates, having size about 10μm. The crystals were fired from 200°C to 1550°C, in oxidizing atmosphere and the products characterized by X-ray diffraction, scanning electron microscopy and surface area measurements by BET-nitrogen method. Transition aluminas are formed from heating at the following temperatures: gamma (300°C); delta (750°C); alpha (1050°C). The aluminas maintain the original morphology of the $Al(OH)Ac_2$ crystal agglomerates, up to 1050°C, when sintering and coalescence of the alpha-alumina crystals start and proceed up to 1550°C. High surface area aluminas are formed in the temperature range of 700°C to 1100°C; the maximum value of 198m^2/g is obtained at 900°C, with delta-alumina structure. The formation sequence of transition aluminas is similar to the sequence from well ordered boehmite, but with differences in the transition temperatures and in the development of high surface areas. It is suggested that the causes for these diversities between the two sequences from $Al(OH)\ Ac_2$ and boehmite are due to the different particle sizes, shapes and textures of the gamma-Al_2O_3 which acts as precursor for the sequence gamma- to alpha-Al_2O_3.

Key words: aluminium hydroxiacetate, boehmite, transition aluminas, active aluminas, aluminum hydroxides.

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INTRODUCTION

Crystalline aluminas are formed by the thermal dehydroxilation of the aluminium hydroxides between 300°C and 600°C (Dörre & Hübner 1984). They all start crystallization into alpha-alumina at 1100°C (Rankin & Merwin 1916), but some procedures can be made to lower that phase-transition temperature (Kumagai & Messing 1985, Jagota & Raj 1987, Yang et al. 1988).

Stumpf et al. (1950) showed that between the dehydroxilation of the hydroxide and the alpha-alumina crystallization a certain number of intermediate crystalline structures of alumina are formed, which are reproducible; each one has a different crystalline structure and is stable in a given temperature range (Russell & Cochran 1950, Ervin Jr 1952, Brown et al. 1953, Day & Hill 1953, de Boer et al. 1954, Stirland et al. 1958, Sato 1959, Francombe & Rooksby 1959, Wefers 1963, Lima-de-Faria 1963, Aldcroft & Bye 1967, Tanev & Vlaev 1993). The structure of each alumina and its temperature range of existence are determined by the structure of the starting or precursor hydroxide (Wefers & Misra 1987); 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 this latter is the phase formed in the industrial Bayer Process. These aluminas are called "Transition Aluminas" and are identified by Greek letters alpha; gamma; delta and others (Stumpf et al. 1950). Brindley (1963) reviewed the results of the simultaneous application of X-ray and electron diffractions and differential thermal analysis to characterize the products of the thermal recrystallization reactions of aluminum hydroxides and other metal hydroxide and hydroxisilicates. Beta-alumina is not a transition alumina; it is used as a ceramic solid electrolyte and has the composition $Na_2O.11Al_2O_3$ (Gitzen 1970).

The term "pseudoboehmite" literally means "false boehmite"; it differs in crystallite size and hydroxyl contents from the so called well-ordered crystalline boehmite; by pseudoboehmite is meant the poorly crystallized Al^{III} compound of composition $Al_2O_3.xH_2O$ ($2.0 > x > 1.0$) with interplanar spacings increased in the [020] direction to 6.7Å in comparison with 6.12Å for boehmite (Krivoruchko et al. 1978); the value $x = 1.0$ corresponds to well-ordered crystalline boehmite. It is also refered in literature by other names, which do not necessarily correspond to the same structure. Examples are: aluminium oxide hydrate, microcrystalline boehmite, gelatinous boehmite, gel alumina, amorphous alumina and bayerite sols (Oberlander 1984). Pseudoboehmite is one of the most prevalent precursor form of alumina for producing catalysts. Fibrillar pseudoboehmite is the name proposed by Bugosh (Bugosh et al. 1962) for the colloidal fibrous polymer of approximate AlOOH formula, formed from the addition reaction of linear polymerization between hydroxyls and with H_2O molecules formation (olation) in aqueous solutions in pH's range of 4,5 and 7,4 (Souza Santos et al. 1953); these fibrils are formed by ageing amorphous $Al(OH)_3$ gels in acid pH's at room up to boiling temperatures (Souza Santos & Souza Santos 1957, 1958, 1993, Souza Santos et al. 1990, 1997a, Neves et al. 1991). The several morphologies of the crystals of boehmite were reviewed by Souza Santos et al. (1998b).

The thermal transformation of the freshly (non aged) precipitated boehmite, named "gelatinous

boehmite" or "alumina gel", was studied by Lippens (1961) Souza Santos and Souza Santos (1992); Souza Santos et al. (1994, 1996a, b); Souza Santos and Toledo (1994); Campos and Souza Santos (1996) and Souza Santos (1998) characterizing the aluminas formed by the thermal dehydroxilation of colloidal crystals of fibrillar pseudoboemite and of hydrothermal lamellar boehmite crystals by electron microscopy, X-ray and electron diffractions and differential thermal analysis. Antunes et al. (1996); Antunes and Souza Santos (1998) and Antunes (1998) described the aluminas formed by the thermal dehydroxilation of nordstrandite and bayerite. The most recent review on the transition alumina series formation from aluminium hydroxide precursors was made by Wefers (1990).

Transition aluminas may also be formed by thermal decomposition of crystalline hydrated aluminium salts as sulphate; nitrate; ammonium aluminium sulfate; chloride and formate (Sato et al. 1978, Sato 1962, 1964, Johnson & Gallagher 1971, Drobot et al. 1971, Tsuchida et al. 1981, Kato et al. 1981, Ciminelli & Messing 1984, Tomasi & Souza Santos 1989, 1990, Xavier & Souza Santos 1995, Xavier 1997, Dweck et al. 1996).

Aluminium oxides, in their several forms, have a large use in the chemical process industry (Hart & Lense 1990), as a catalyst, a catalyst support (Oberlander 1984) or as an adsorbent (active aluminas) (ALCOA 1969, 1972), due to variety of surface properties or in the advanced and traditional ceramic industries (McZura et al. 1976, Xavier 1997), due to the remarkable thermal, mechanical and chemical properties of the alpha-alumina structure. According to Oberlander, there are 27 aluminum chemicals listed as "alumina" in the literature (Oberlander 1984, McZura et al. 1978), which show a wide range of physical and chemical properties. Synthetic commercial aluminas exhibit a variety of physical properties suitable for adsorbents and catalysts; examples are: specific surface area from 0,01m^2/g to 400m^2/g; volume of the pores from 0,1cm^3/g to 1,4cm^3/g and average pore size from 2nm or 20Å to 177μm; these aluminas are components of commercial products known as "active aluminas".

The term "active alumina" is used in three ways (Oberlander 1984): (a) in catalyst technology it typically means aluminas with high surface areas and considerable chemical activities; (b) as a term patented by ALCOA (ALCOA 1969, Goodboy & Downing 1990) refered to aluminas that exhibit an ability in adsorbing significant quantities of water from gases and liquids; (c) in advanced ceramics, active alumina is used as a contraction of the term "reactive alumina" (ALCOA 1972); the reactive aluminas are aluminas which, after pressed without the addition of sintering catalysts and fired at high temperatures (smaller than the 2050°C, melting point of alumina), they sinter into very hard low-porosity pieces having alpha-alumina structure.

Gibbsite is produced industrially in the Bayer Process as an intermediate for aluminium metal production (Misra 1986, Burke 1987); the Bayer alumina produced from the Bayer gibbsite is not adequate for some modern uses due to its high sodium, iron and silica contents; the removal of these elements (for instance, by thermal volatilization of the sodium borate formed by adding boric acids) is very expensive (McZura et al. 1976, Mistler & Shanefield 1978). So, new routes must be found for producing pure aluminum compounds as precursors for aluminas of controlled purity

(Ruthner & Krischner 1973, Nono & Casarini 1982, Tomasi & Souza Santos 1989, 1990, Kiyohara 1994, Kiyohara & Souza Santos 1997). A new route for producing very pure $Al(OH)(CH_3COO)_2$ crystals using aluminium powder produced in Brazil was recently developped by Xavier et al. (1998). No publications exist on the characterization of the structure, surface area and morphology of the aluminas formed by the thermal decomposition of any aluminium acetate; specially of the crystals of $Al(OH)Ac_2$ prepared by the method of Xavier et al. (1998). That compound, of high purity, may be a precursor of aluminas for use in advanced ceramics, adsorbents, catalysts and carriers.

The purpose of this paper is to characterize the alumina phases formed by the thermal transformation of crystals of aluminium hydroxiacetate, prepared from chemicals produced in Brazil.

MATERIALS AND METHODS

Preparation of Crystals of $Al(OH)Ac_2$

The crystalline powder of aluminium hydroxiacetate was prepared according Xavier et al. (1998) by reacting, at 96°C ±1°, aluminium powder ALCOA 123 with aqueous solution of acetic acid in the molar proportion of 1,0Al:2,5HAc:50H_2O. The white precipitate, after washing with distilled water, was dried at 60°C producing a fine free-flowing powder. It has a loss-on-ignition of 68,15%, in oxidizing atmosphere at 1100°C. Its X-ray powder diffraction (XRD) lines agree with the ICDD card no 13-0833 for the salt $Al(OH)(CH_3COO)_2$ or $Al(OH)Ac_2$ as synthetized by Maksimov et al. (1960) by a different route. The theoretical loss-on-ignition of that salt in presence of oxygen is 68,32%, according to equation (A):

$$2[Al(OH)(CH_3 \cdot COO)_2] + 8O_2 \rightarrow 8CO_2 + 7H_2O_{(g)} + Al_2O_3 \qquad \text{(A)}$$

Heating of the $Al(OH)Ac_2$ Crystals

Differential thermal analysis (DTA) of the crystalline powder was carried out in an equipment made by BP Engenharia, Campinas, SP, in presence of air. The differential thermal curve of the $Al(OH)Ac_2$ is shown in Figure 1. It shows an endothermic peak, starting at 300°C, with a maximum at 370°C; this peak corresponds to equation (A); the three small ones (one endothermic and two exotermic) are observed at 500°C, 840°C and 1050°C; from the XRD results, it can be concluded that these peaks are probably related to the gamma-delta and delta-alpha-aluminas. Taking 300°C as the initial temperature for the reaction (A), experiments for characterization of the phase changes after heating were started at 200°C. Approximately 3.0 grams of the powder of Al(OH)Ac were placed in a platinum crucible and heated in a programmed electric furnace made by EDG, São Carlos, SP, under oxidant conditions; the maximum temperature was kept during four hours in all experiments. After natural cooling, the heated powder was kept in a closed flask for XRD and electron optical charaterization and for measurement of surface area by the BET method using low-temperature adsorption of nitrogen. The maximum temperatures were increased by 100°C in each experiment or by 50°C, when necessary, from 200°C to 1550°C.

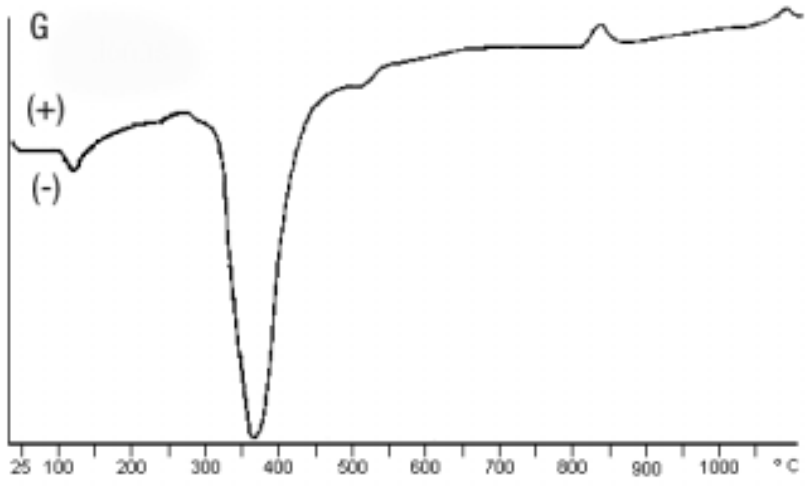

Fig. 1 – Differential thermal analysis curve in air of $Al(OH)Ac_2$ crystals.

METHODS

Three experimental methods were used for characterization of the phases formed by the thermal decomposition of the $Al(OH)Ac_2$ crystals: (a) X-ray powder diffraction (XRD) to identify the crystalline structure of the aluminas; (b) scanning electron microscopy (SEM) to visualize the morphology of the crystalline particles before and after heating; (c) the specific surface area measurements to follow the values developed in the particles along the heating up to 1550°C.

X-RAY DIFFRACTION

The equipment used was a Philips Diffratometer, X'Pert Model MPD (PW 3050/10), using copper K-alpha radiation operating at 40kV and 40mA. The scanning was made in the range of $2\theta(1°)$ and $2\theta(90°)$. The X-ray data were compared with those from Wefers and Misra (1987) and from the ICDD Files. Table I presents the identification of the crystalline phases as a function of the heating temperature of the powder.

SCANNING ELECTRON MICROSCOPY (SEM)

The equipment used was a scanning electron microscope JEOL model JSM 840A. The powder (original or heated crystals) was placed upon SEM stubs covered with double-face tape and covered with gold in an Edwards Sputter Coater model 150B. The images were registered under magnifications from $1200\times$ to $6000\times$.

SURFACE AREA

TABLE I

X-Ray diffraction data of the powders after heating at different temperatures.

Temperature											
250°C		300°C		700°C		750°C		1000°C		1050°C	
d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io	d(Å)	I/Io
7.02	45					8.41	22			3.48	67
6.25	100					4.49	7			2.55	95
4.56	33	2.22	79	2.8	46	2.74	6	2.72	19	2.38	43
3.89	20	1.98	59	1.96	32	2.39	41	2.42	50	2.09	100
3.49	3	1.40	100	1.40	100	2.26	20	2.28	31	1.74	40
3.37	26					1.98	71	1.98	67	1.60	75
3.02	10					1.40	100	1.40	100	1.60	37
2.95	9									1.41	28
										1.37	42
$Al(OH)Ac_2$		gamma		gamma		delta		delta		alpha	
13-0833*		10-425*				16-394*				10-173*	

(*)ICDD card numbers (1995)

The surface area of the powders was measured by using the BET low temperature nitrogen adsorption method (Brunauer et al. 1938). About 300mg of the dried powder were placed in the sample holder of the Micromeritics model ASAP 2010 BET adsorption apparatus. The previous drying was carried out at 200°C under vacuum in the pre-treatment unit of the equipment; six hours were the minimum time for the drying. The heating was interrupted when the chamber pressure lowered to 10^{-5}mm of mercury. In the adsorption measurements, ultra-pure (99.995%) nitrogen from Air Liquid was used. Table II and Figure 11 present the total external specific surface area function of temperature; the Table II also presents the external specific surface area after discounting the area of the micropores and the values of the constant C of the BET equation.

RESULTS

X-Ray Diffraction

The alumina phase formed at each heating temperature was identified by X-ray diffraction. Figures 2 and 3 show the XRD curves in the temperatures in which crystalline changes could be detected in the heated samples.

No significant change was observed in the XRD powder patterns of $Al(OH)Ac_2$ dried at 60°C and after heating up to 250°C, as shown in Figure 2. Heating at 300°C destroyed completely the Al-hydroxiacetate crystalline structure and a transition alumina, with, a less ordered structure than the hydroxiacetate, is formed; its X-ray diffraction curve has no sharp peaks as it is shown in the

TABLE II

Surface areas and values of C of the Aluminas formed from heating $Al(OH)Ac_2$ at several temperatures.

Temp. (°C)	Alumina Type	Total specific surface area(m^2/g)	External specific surface area(m^2/g)	Value of C
200	$Al(OH)Ac_2$	38	34	130
700	Gamma	92	78	158
900	Delta	202	198	111
1000	Delta	154	152	139
1100	Alpha	39.3	38.9	97
1500	Alpha	4.89	7.11	23
1550	Alpha	5.41	6.98	12

third XRD curve of Figure 2 and in the first curve of Figure 3 (curves 300C - C); in that third curve, the 1.98Å and 1.40Å lines, the two more intense and characteristic of gamma-Al_2O_3, can be identified plus a weaker line at 2.28Å, also related to that transition alumina. Heating the sample for 24 hours did not improve the sharpness of the XRD curve; just one new line of 1.22Å appeared; this line exists only in eta-Al_2O_3, which is formed by dehydroxilation of the so-called gelatinous boehmite (Wefers & Misra 1987). Therefore, the reflexions of the 300°C fired sample can be identified as of gamma-alumina. This temperature is lower than the 470°C/480°C temperature of the dehydroxilation of well ordered crystalline boehmite into gamma-Al_2O_3, as reported by Wefers and Misra (1987); the other crystalline aluminium hydroxides do not produce gamma-Al_2O_3 by direct thermal dehydroxilation.

The gamma-Al_2O_3 structure is formed by heating the hydroxiacetate from 300°C up to 700°C, as shown in the fourth XRD curve in Figure 2 and in the second curve in Figure 3 (curves 700C - D). Heating the hydroxiacetate at 750°C produces a more ordered structure with sharper and more intense lines as shown in the fifth XRD curve in Figure 2 and in the third curve in Figure 3 (curves 750C - E): they correspond to the pattern of delta-alumina. The gamma-Al_2O_3 structure from heating well-ordered boehmite crystals is stable up to 780°C (Wefers & Misra 1987). From 700°C to 1000°C, delta-alumina is the transition alumina produced as shown by the sixth XRD curve in Figure 2 (curve 1000C - F); no theta-Al_2O_3 is detected.

According to Wefers and Misra (1987), the delta structure is stable up to 930°C when well ordered boehmite is the precursor. Theta-alumina is formed between 930°C and 1000°C from delta-alumina, when well-ordered boehmite is the precursor and is kept stable up to 1050°C (Wefers & Misra 1987).

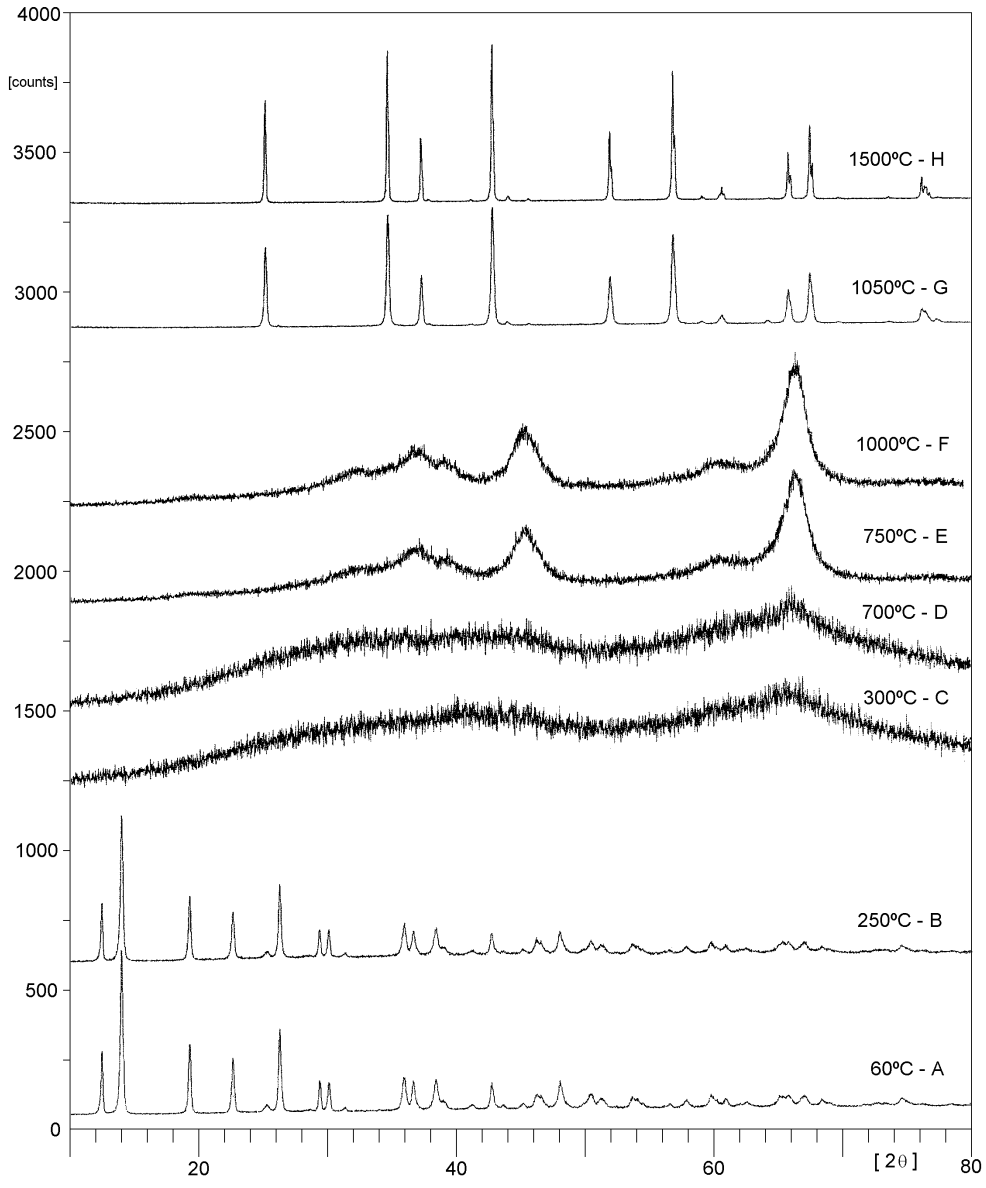

Fig. 2 – X-ray diffraction curves of crystals of $Al(OH)Ac_2$ at the temperatures of formation of the transition aluminas.

Alpha-alumina is the phase present from heating the hydroxiacetate crystals from 1050°C up to 1550°C: it is the seventh and eigth XRD curves in Figure 3 (curves 1050C - G and 1500C - H); there is no temperature difference in alpha-Al_2O_3 formation when well-ordered boehmite crystals

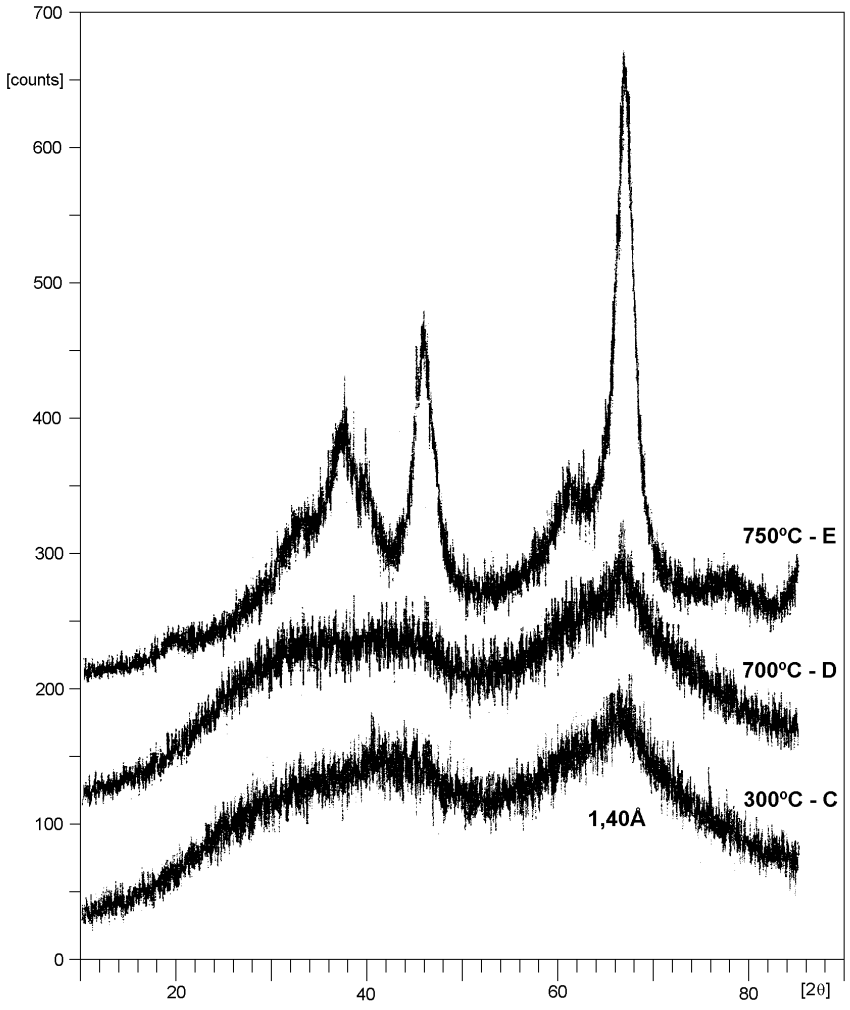

Fig. 3 – Some XRD curves of Figure 2 at lower temperatures.

are the precursor.

These results show that the pyrolysis of the Al-hydroxiacetate crystals in air produces crystalline transition aluminas in a similar sequence to the thermal dehydroxilation of well-ordered crystalline boehmite, as described by Wefers and Misra (1987), but with some differences: for instance, the lower values of the temperatures in which the phase transformation occurs; other differences will be described below.

Scanning Electron Microscopy

According to equation (A) the weight loss as gases at 370°C of the crystals of $Al(OH)Ac_2$ is four times greater than the loss at 470°C of boehmite crystals when gamma-alumina is formed; so it could be expected that the hot gases would burst and destroy the crystalline structure of $Al(OH)Ac_2$, leaving a non-crystalline or amorphous alumina; surprisingly, the XRD results have shown that the same gamma-alumina is formed as in boehmite. The same behavior was expected for the morphology of the original particles: the loss of 68,15% of gases would break the crystals into much smaller particles of alumina, with high surface areas. Again that expectation failed since the scanning electron microscopy has shown that the particle shape of the pseudomorphs heated up to 1050°C was the same as the original crystals of $Al(OH)Ac_2$. Due to these facts, a careful documentation of the particle shape in function of the temperature was made in order to show that the transformation of $Al(OH)Ac_2$ to gamma-Al_2O_3 to delta-Al_2O_3 to alpha-Al_2O_3 transformations occur without any changes in morphology.

Figure 4 shows a micrograph of the free-flowing powder of $Al(OH)Ac_2$; the first observation is that the powder is constituted by micrometer sized particles, well separated from each other; having diameters in the 10 to 20μm range and with no tendency to form aggregates (Rouquerol et al. 1994) of the particles, even on drying. This property of not forming aggregates is probably directly related to the free-flowing characteristics of the dry powder.

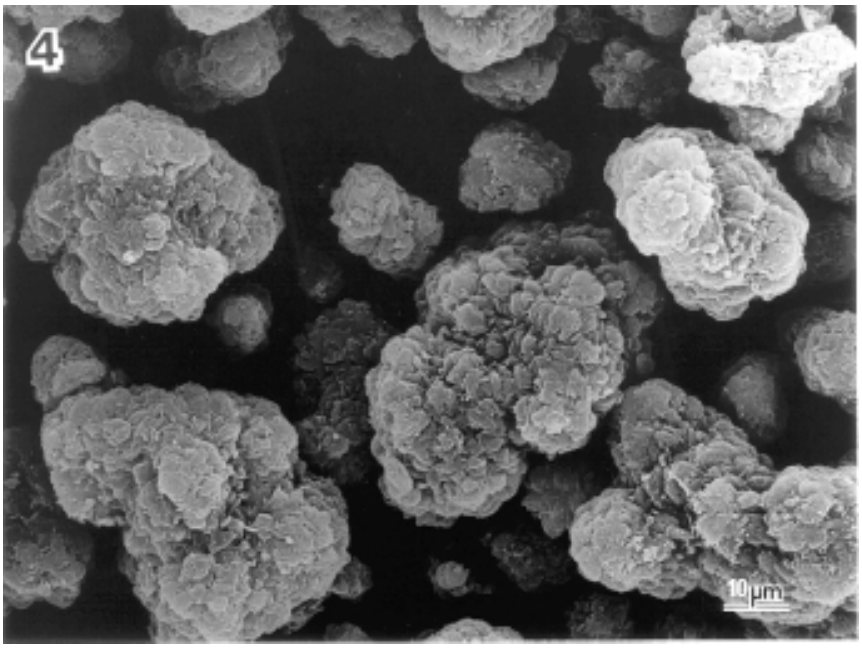

Fig. 4 – Scanning electron micrograph (SEM) of several crystalline particles (agglomerates) from a free-flowing powder of $Al(OH)Ac_2$ (low magnification).

A second observed feature is the peculiar morphology of each particle, shown in higher mag-

nification in Figure 5. Each particle is an agglomerate of crystals, most of them platy, with sharp edges. This peculiar shape can be compared to that of a lettuce. These crystalline particles or agglomerates are constituted by the aluminium hydroxiacetate $Al(OH)Ac_2$ and have about the same size as the original aluminium powder ALCOA 123 particles; so, it is tempting to suggest that each crystalline particle of $Al(OH)Ac_2$ was formed by the reaction of aqueous HAc with each single aluminum powder particle.

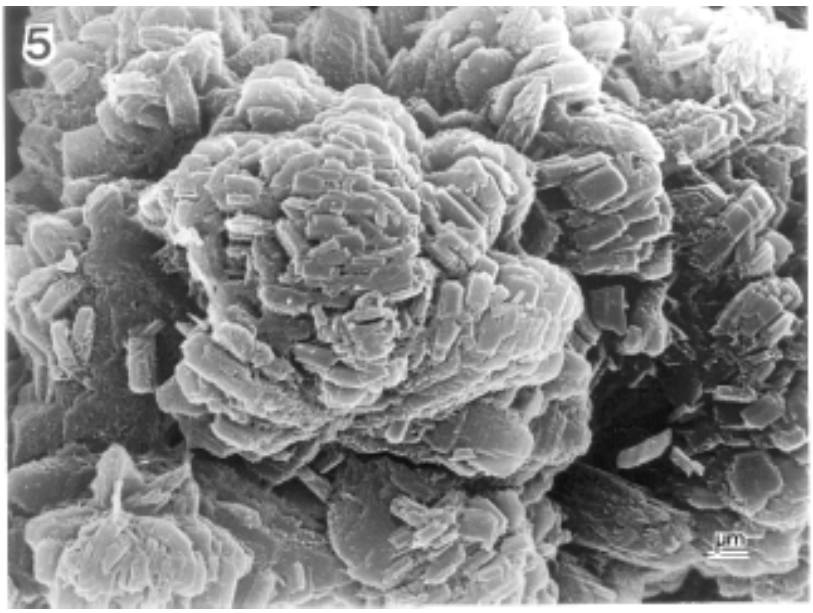

Fig. 5 – SEM of one particle of Figure 4 at higher magnification.

XRD and DTA results show that the $Al(OH)Ac_2$ crystalline structure is maintained up to 250°C, but it is destroyed at 300°C; the endothermic peak of DTA, at 370°C is related to the equation (A); the weight loss, according to equation (A), is 68% due to the evolution of the gases $CO_2 + H_2O$: it is a large value and therefore it could be expected that severe changes would occur in morphology of the original particles of crystalline $Al(OH)Ac_2$ of Figures 4 and 5, after being fired at the temperature of 300°C.

Figure 6 shows the original powder after being fired at 300°C and has the same magnification of the original crystals shown in Figure 5: by comparing Figure 6 (300°C) and Figure 5 (original) and remembering that the samples have different XRD powder patterns, it is surprising to observe that there is no significant difference neither in the shape or in the size of the platy crystals, nor in the morphology of the agglomerate; perhaps the only difference is the small number of very small particles irregularly distributed on the surface of the agglomerate. The same behavior as 300°C was noted in samples heated at 250°C.

What is surprising in the fact noted at 300°C is that the heated powder, after a 68% loss-

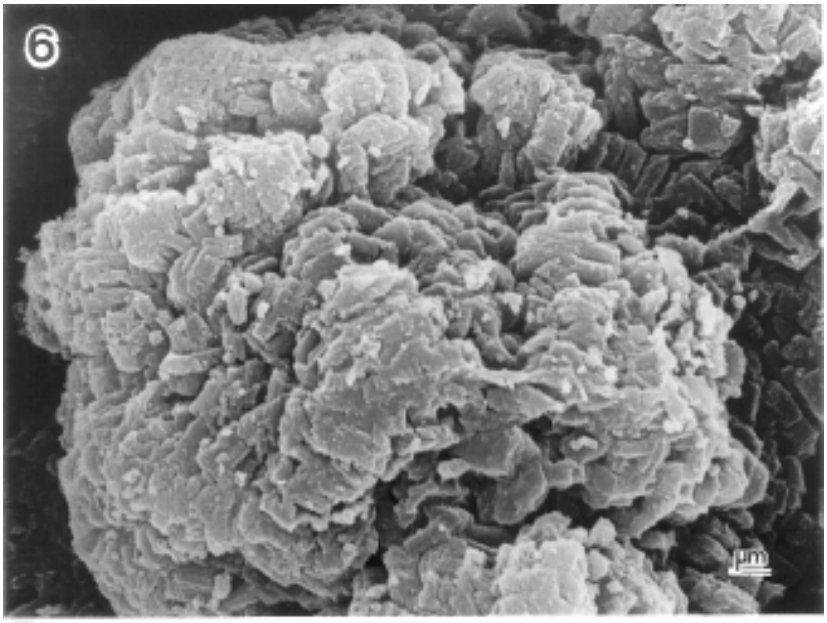

Fig. 6 – SEM of an agglomerate after being heated at 300°C.

of-weight of gases (obviously effecting some internal pressure) and having changed from a well ordered crystalline structure to the defect structure of gamma-Al_2O_3, the external shape of the agglomerates of platy crystals of gamma-Al_2O_3 has not changed from the original shape of the $Al(OH)Ac_2$ agglomerates of Figure 5 (original).

The crystalline structure of gamma-alumina is kept in the range of 300°C−700°C. Figure 7 is a micrograph of the powder after being heated at 700°C: by comparing with Figure 6, no significant change in morphology is observed in the agglomerate of platy crystals. The only difference is the larger number of small particles on the surface of the agglomerate of Figure 7; the nature of the small particles could not be identified by XRD. They should be separated and characterized by selected area electron diffraction, if they are crystalline; if the separation is successfull, they will be object of further studies.

The XRD patterns of the powders fired at 700°C and 750°C show that the crystalline structure of the transition aluminas change from gamma to delta. In spite of the change in crystalline structures of the agglomerate pseudomorphs, again no significant change in the original lettuce general aspect is observed. By scanning electron microscopy, the small particles on the surface of the agglomerate continue to exist.

The crystalline structure of delta-alumina is maintained in the range of 750°C−1000°C. Again, no significant difference is observed, except by the much smaller number of small particles on the surface of the pseudomorph, as compared to samples heated at 750°C.

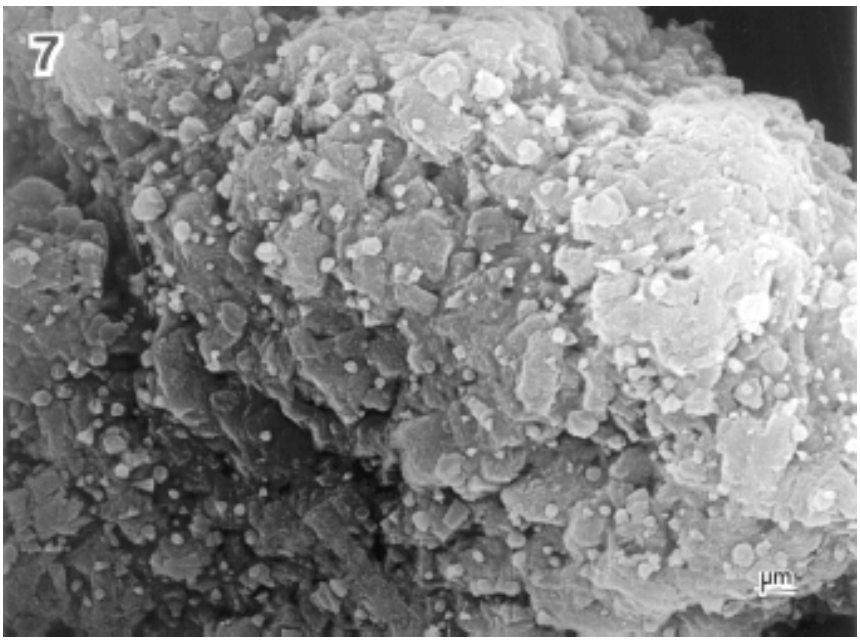

Fig. 7 – SEM of an agglomerate after being heated at 700°C.

The XRD patterns of the powders heated at 1000°C and 1050°C show that the crystalline structure of the transition alumina changes from delta to alpha and no theta is detected as an intermediate. Figure 8 is a micrograph of the powder after being heated at 1050°C. Again, in spite of the change in the crystalline structure of the agglomerate pseudomorphs, no significant change in the general lettuce aspect is observed. However, the small particles on the surface of the pseudomorphs are not observed anymore.

By increasing the heating temperatures of the powders in the range of 1050°C−1550°C, no change in the alpha-alumina XRD powder pattern was observed. However, significant changes occurred inside each agglomerate or pseudomorph due to morphological changes in the platy crystals: they sintered, coalesced, lost the sharp edges and became thicker with round profiles: examples are in Figures 9 and 10, both at the same magnification of Figures 5 to 8.

Figure 9 shows the powder heated at 1300°C; the alpha-alumina platy crystals are in the way of losing their sharp edges and begin to coalesce; as a result, the agglomerate pseudomorphs acquires a corroded aspect on the surface. That coalescence may produce a rough surface texture on the surface of the sintered alumina agglomerate, which could be useful for immobilizing and growth of the yeast *Saccharomyces cerevisae*; the surface texture would be rather called channeled (Souza Santos et al. 1996b, 1998a) than porous, either meso or macro.

Figure 10 shows the powder heated at 1500°C; the platy crystals of alpha-alumina have already coalesced and sintered in an appreciable degree; however, the pseudomorphs still have a peculiar

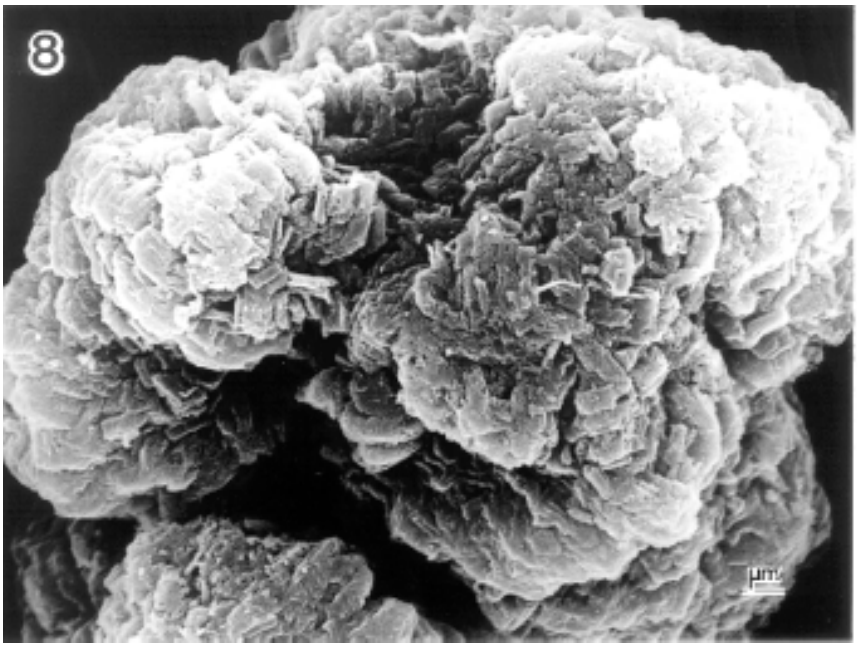

Fig. 8 – SEM of an agglomerate after being heated at 1050°C.

appearance which is now more similar to some types of coral or brain surfaces; some platelets with the typical hexagonal profile of alpha-alumina platelets can be observed. Longer times of heating, as well as temperatures higher than 1550°C, certainly will improve the external hexagonal shape of the alpha-alumina platelets; however, in this research, for comparative reasons, the time used for heating at the maximum temperature was the same in all experiments.

Surface Area

Equation (B) is an example of the typical equation for the preparation of an "active solid" according to Gregg (1951) and to Gregg and Sing (1967):

$$\text{Solid } X \rightarrow \text{Solid } Y(\text{active}) + G(\text{gas}) \qquad \text{(B)}$$

Gregg (1951, p. 63) used the term "activity of a solid" to denote chemical and physico-chemical reactivity; he wrote (1951, p. 64) that an increase in activity is usually traceable to an increase in the surface area of the powder. According to Gregg (1958), the minimum specific surface area of an "active solid" is arbitrarily $1m^2/g$; that value is also the minimum value which is usually measured by BET method (Sing 1976). On the other side, according to Oberlander (Oberlander 1984 p 80), a value greater than $100m^2/g$ is the arbitrary threshold number used to identify high surface area aluminas; he presents data of commercial aluminas from the dehydroxilation of pseudoboehmite (Oberlander 1984 p 81, Table IV), with specific surface areas ranging from 250 to $300m^2/g$.

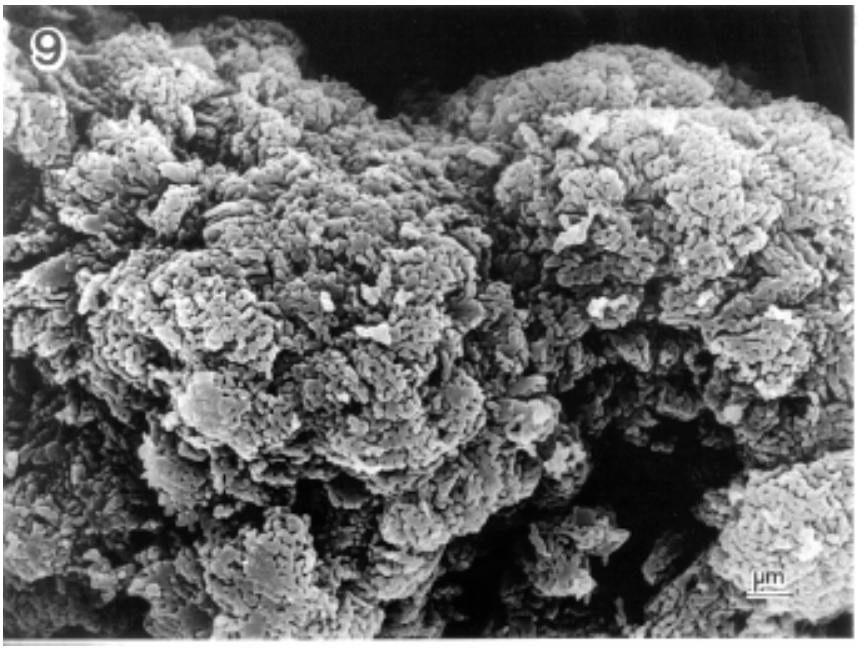

Fig. 9 – SEM of two agglomerates of alpha-alumina after being heated at 1300°C.

Since transition aluminas are formed from the pyrolysis of aluminium hydroxiacetate crystals following Equation (A), the next step is to measure their surface area by the BET -nitrogen method, to verify if low-or-high surface area aluminas were produced; the results are shown in Table II and in Figure 11; also, in the Table II are listed the heating temperatures of the hydroxiacetate crystals; the alumina structures of the heated samples and their total and external specific surface areas. The Table also shows the values for the constant C of the BET equation. In reporting the surface area data, as well as the use of the terms agglomerate, aggregate and specific surface area, the IUPAC recomendations were followed (Sing et al. 1985, Rouquerol et al. 1994).

Figure 12, by Wefers and Bell (1972), is presented to illustrate the development of a gamma-alumina of high-surface area from Bayer gibbsite crystals by thermal transformation, passing by boehmite as an intermediate; that Figure is frequently reproduced for that purpose (Wefers & Misra 1987 p 49, Goodboy & Downing 1990 p 93, Carbone 1990 p 99).

The data from Table II show that the thermal decomposition of the $Al(OH)Ac_2$ into gamma-Al_2O_3 increases the external specific surface area of the original lettuce-shaped crystals from 34 to $78 m^2/g$.

At 900°C, delta-Al_2O_3 is the transition alumina present and a large increase to a maximum specific surface area of $198 m^2/g$ is observed; increasing the temperature to 1000°C, the delta structure is maintained, but a sharp decrease in the external specific surface area to $152 m^2/g$ occurs.

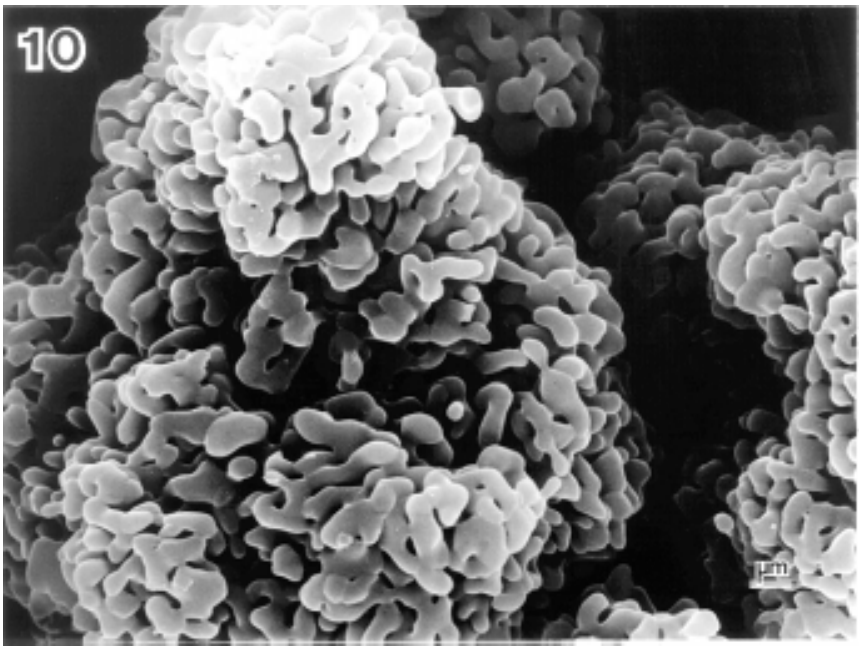

Fig. 10 – SEM of several agglomerates of alpha-alumina after being heated at 1500°C.

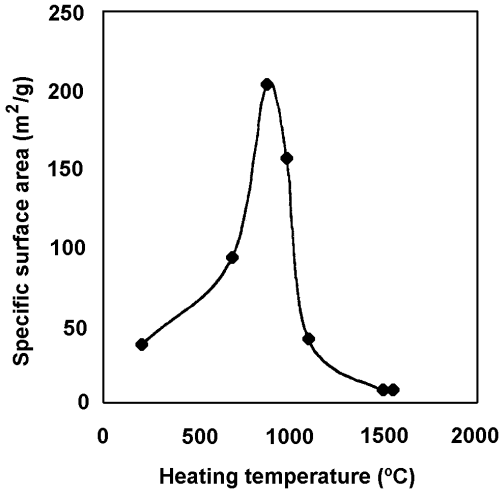

Fig. 11 – Specific surface area (m^2/g) of the aluminas from heating aluminium hydroxiacetate crystals in the range of 200°C and 1500°C.

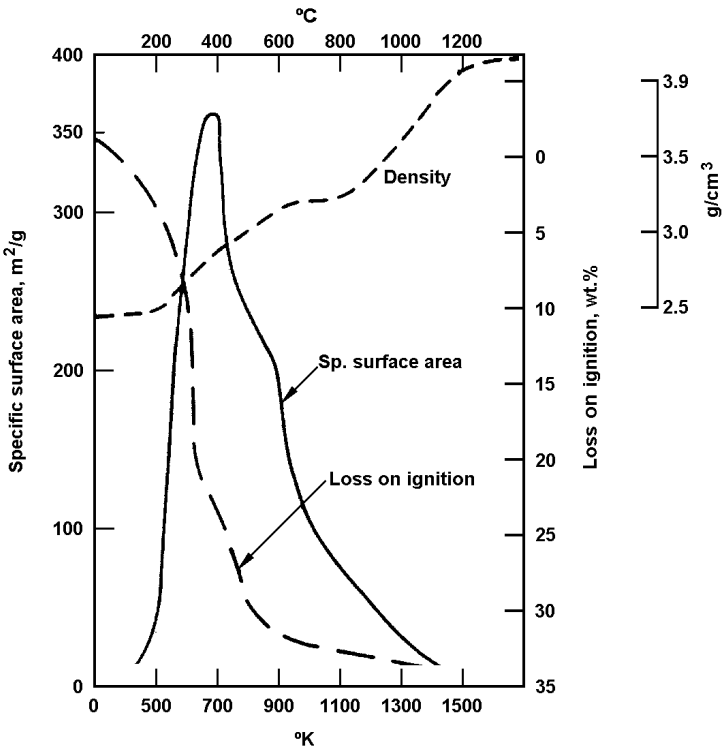

Fig. 12 – Specific surface area (m^2/g) of the transition aluminas from heating Bayer gibbsite crystals (adapted from Figure 22 from Wefers & Bell 1972).

At 1100°C, the alpha-Al_2O_3 structure is observed, presenting a sharper specific surface area decrease to $39m^2/g$. At higher temperatures (1500°C and 1550°C) the surface areas decrease to $7m^2/g$.

The *C* constant from the BET equation is exponentially related to the heat of adsorption of the first layer of N_2 adsorbed molecules; it should have a value larger than 50, so that the BET equation could be used; that is true for the C values measured for the gamma, delta and alpha aluminas; but it fails when alpha is recrystallized at 1500°C, indicating a change in the surface structure. After delta-alpha transition, the constant *C* becomes smaller than 100, what makes it difficult to obtain a reliable value for the constant n_m of the BET equation, necessary for the calculation of the BET – nitrogen surface area (Rouquerol et al. 1994).

Another difference from boehmite can be seen in Figure 12: heating changes gibbsite into boehmite which produces gamma-alumina with a maximum value of specific surface area, of about $370m^2/g$ at 400°C. The $Al(OH)Ac_2$ crystals produce a maximum value of specific surface area near $200m^2/g$, with delta-alumina structure, but at 900°C; so, delta-alumina of high surface area

is formed at high temperature, which is useful for delta-alumina catalyst carriers to be used in applications where temperatures are too high for gamma-alumina to exist (Oberlander 1984 p 68). The gamma-alumina, formed at 700°C from Al(OH)Ac_2, has a specific surface-area smaller than $100 m^2/g$; therefore, it is not a high-surface area alumina. The two surface area curves, from Al(OH)Ac_2 and gibbsite, have a similar shape, but differ in the temperature range values in which the maximum values of specific surface areas occur, as well as in the values of these maxima.

DISCUSSION

Wefers and Misra (1987 p 47) present the following sequence for transition aluminas from well-ordered crystalline boehmite in function of the temperature up to 1550°C:

$$|\text{Boehmite}|(470^\circ C)\gamma - Al_2O_3|(780^\circ C)\delta - Al_2O_3|(930^\circ C)\theta - Al_2O_3|(1050^\circ C)\alpha - Al_2O_3|$$
$$(1550^\circ C)(\alpha - Al_2O_3) - \text{melts at } 2050^\circ C$$

In this work, we propose the following sequence of transition aluminas, formed from Al(OH)Ac_2 by thermal treatment, as characterized by XRD:

$$|Al(OH)Ac_2|(300^\circ C)\gamma - Al_2O_3 - |(750^\circ C)\delta - Al_2O_3 - |(1050^\circ C)\alpha - Al_2O_3|(1550^\circ C)\alpha - Al_2O_3.$$

Comparing both formation sequences of transition aluminas in function of temperature, it can be concluded that the Al(OH)Ac_2 one is similar to that from well-ordered boehmite, with some differences: (a) no theta-Al_2O_3 could be detected; (b) the gamma and delta aluminas are formed at lower temperatures than boehmite.

This similarity is surprising due to two facts: (a) the higher weight loss of Al(OH)Ac_2, of 68,15%, with hot gases leaving the pseudomorph at 370°C but still not destroying it, in comparison with the smaller 15% weight loss of boehmite at 470°C; (b) both substances have orthorhombic unit cells, with different sizes, boehmite with 8 AlOOH per unit cell (Wefers & Misra 1987) and Al(OH)Ac_2 with 16 molecules per unit cell (Maksimov et al. 1960). A possible explanation for this similarity may be the formation mechanism of the gases and their diffusion out the pseudomorphs, which can be the same, thus leaving behind the same crystalline structure, in the present case gamma-alumina. However, the thin bohemite micro crystals present a change in the internal morphology, when transformed into gamma-alumina; the new morphology can only be observed by transmission electron microscopy (Souza Santos 1998).

The Al(OH)Ac_2 crystals change to gamma and afterwards to delta and then to alpha-Al_2O_3, but all the pseudomorphs do not present, up to temperatures as high as 1100°C, any significant external morphology change either in the agglomerates or in the individual platy crystals, in spite of the the high weight loss of gases occuring at 370°C. That property of losing gases at high temperatures without any change of crystal shape is frequent in the thermal dehydroxilation of layer lattice metal hydroxides and clay minerals; at the same time, it leads to topotactical relationships with the new crystalline phase (Brindley 1963, Souza Santos & Yada 1988) even when the value of the

loss-on-ignition is as high as 34,6% as in the aluminum trihydroxide gibbsite; the water vapour diffuses between 1:1 or 2:1 layers of the crystal, leaving the pseudomorph without any change of shape. However, that mechanism does not occur in all crystals with layer lattices; for instance, vermiculite exfoliates and gypsum – $CaSO_4 \cdot 2H_2O$ – explodes when water vapour is leaving the crystals. So, a better knowledge about the internal organization of the platy crystals of $Al(OH)Ac_2$ is necessary in order that an interpretation could be offered for the maintenance of external shape of the agglomerates up to 1050°C.

Two problems exist in relation to surface areas:

1^{rst}. Which is the mechanism that happens for increasing the surface area by heating, until a maximum value at 900°**C?** The production of gases, according to equation (A), ends in the gamma phase, therefore before the delta phase where the maximum occurs. There is no agglomerates explosion to produce comminution of the original platy crystals and the aggregation of the self ground ones; the scanning electron microscopy has shown no changes in, because morphology from 300°C to 900°C. A possible explanation is the formation of a system of alumina granules inside the pseudomorph after the thermal dehydroxilation; the transformations that affect the values of the surface area of the alumina would occur inside and between the granules, but without interaction between the pseudomorphs. The granular structures formed by dehydroxilation in the gibbsite/chi-alumina and kaolinite/metakaolin transformations are clearly observable in thin microcrystals by transmission electron microscopy (Souza Santos et al. 1997b, 1998c).

2nd. In the delta-alpha transition, there is a sharp decrease in the specific surface area. **Which is the mechanism for that transformation in order to decrease the high specific surface area developed at** 900°**C?** A possible interpretation may be found from the knowledge of the internal organization of the platy crystals of $Al(OH)Ac_2$ and of the gamma, delta and alpha - Al_2O_3 crystals obtained by TEM. However, special embedding procedures must be developed in order to obtain ultrathin sections (250Å thick) of the platy crystals, to allow the observation of the internal organization by TEM, because they are too thick for direct examination.

A further question may be asked: Why the theta phase is absent in the sequence delta/alpha from $Al(OH)Ac_2$? A tentative explanation is the following: (a) the crystalline structure of theta is more ordered than delta's and is closer to that of alpha-alumina (Wefers & Misra 1987 p 53); (b) the temperature range of existence of theta is shorter in comparison with the other aluminas of the sequence; (c) *assuming* that the rate of transformation of delta/theta from $Al(OH)Ac_2$ is smaller than in boehmite crystals, due to the high weight loss in the former, then it could happen that the amount of the change delta/theta is very small at the rate of heating used; in consequence, as the temperature of 1000°C is reached, the delta phase remains unchanged; however, at 1050°C, changes directly to alpha with an exothermic effect; that effect could be the cause for the surface sintering of particles, the sharp decrease in specific surface area and the closing of the open microporosity and appears in the DTA curve.

CONCLUSIONS

l[st]) The powder of $Al(OH)(CH_3COO)_2$ crystals is constituted by micrometric size particles; they are agglomerates of platy crystals of sharp edges and present an aspect similar to lettuces.

2[nd]) Heating the crystals from 300°C up in air, they change to two transition aluminas: at 1050°C they recrystallize into alpha-alumina.

3[rd]) The sequence of thermal transformation of the $Al(OH)Ac_2$ crystals is:

$$Al(OH)Ac_2 - |(300°C)\gamma - Al_2O_3 - |(750°C)\delta - Al_2O_3 - |(1050°C)\alpha - Al_2O_3 - (1550°C)\alpha - Al_2O_3$$

4[th]) That sequence is similar to that from well ordered crystalline boehmite. However, there are some differences: (a) the temperatures of formation of gamma and delta-aluminas are lower for the $Al(OH)Ac_2$ crystals. (b) No theta-Al_2O_3 is detected between the delta and alpha-aluminas. (c) The maximum specific surface area alumina from boehmite is formed at 400°C and from $Al(OH)Ac_2$ crystals is at 900°C, with the value of $198 m^2/g$. (d) The values of the maxima for the surface areas are different, being higher for the aluminas from boehmite. (e) The alumina with maximum specific surface area from boehmite has gamma-alumina structure; from $Al(OH)Ac_2$ it has delta-alumina structure, which is very suitable for high temperatures alumina catalyst carriers.

5[th]) The difference in the weight losses by dehydroxilation between Al (OH) Ac_2 and boehmite produces significative diversities in the particle sizes, shapes and textures of the pseudomorphic crystals of gamma-Al_2O_3 formed from each one. These diversities in the gamma-Al_2O_3 crystals from each precursor, Al_2O_3 or boehmite, are responsible for the differences observed at higher temperatures in the transformation sequence gamma to alpha-Al_2O_3.

ACKNOWLEDGEMENTS

This paper is part from the Projeto Temático FAPESP no. 1995/0544-0.

REFERENCES

ALCOA. 1969. Activated and Catalytic Aluminas, Aluminum Company of America, Pittsburgh, p. 1-12.

ALCOA. 1972. Reactive Aluminas, Alcoa Laboratories, Pittsburgh, p. 1-18.

ALDCROFT D & BYE GC. 1967. Crystallization processes in aluminium gels: the formation and thermal decomposition of nordstrandite. *Science of Ceramics* **3:** 75-94.

ANTUNES MLP. 1998. Estudo da formação e caracterização de hidróxido de alumínio por métodos óptico-eletrônicos. Tese de Doutoramento. Instituto de Física da Universidade de São Paulo. Dezembro de 1998.

ANTUNES MLP & SOUZA SANTOS H. 1998. Nordstrandita: Um estudo de transformação de fase – *Cerâmica* **44:** 28.

ANTUNES MLP, SOUZA SANTOS H & SOUZA SANTOS P. 1996. Preparação do trihidróxido de alumínio nordstrandita em microcristais em forma de estrelas. *Anais* 12° *CBECIMAT* 96, Águas de Lindóia, SP, p. 71-74.

BRINDLEY GW. 1963. Crystallographic aspects of some decomposition and recrystallization reactions. In: BRINDLEY, G.W., ed., *Progress in Ceramic Science*, Oxford, Pergamon Press, Vol. 3, p. 3-55.

BROWN JF, CLARK D & ELLIOT WW. 1953. The thermal decompostion of the alumina trihydrate gibbsite. *J Chem Soc January* **13:** 84-88.

BRUNAUER S, EMMETT PH & TELLER E. 1938. Adsorption of gases in multimolecular layers. *J Amer Chem Soc* **60:** 309-319.

BUGOSH J, BROWN RL, MCWHORTER JR, SEARS GW & SIPPEL RJ. 1962. A novel fine alumina powder, fibrillar boehmite – *Ind Eng Chem Product R & D* **1:** 157-161.

BURKE AR. 1987. Production of Aluminum and Alumina, Wiley, Chichester, p. 11-44.

CAMPOS TW & SOUZA SANTOS H. 1996. Caracterização de uma nova fase (alumina delta) nas transformações térmicas da boemita. *Cerâmica* **42:** 20-22.

CARBONE TJ. 1990. Production, Processes, Properties and Applications for Calcined and High-Purity Aluminas, in *Hart LD & Lenz*, p. 99-108.

CIMINELLI RR & MESSING GL. 1984. Transformações químicas e estruturais no sistema de nitrato de alumínio. *Cerâmica* **30:** 131-136.

DAY MKB & HILL VJ. 1953. The thermal transformations of the aluminas and their hydrates. *J Phys Chem* **57:** 946-950.

DE BOER JH, FORTVIN JMH & STEGGERDA JJ. 1954. The dehydration of alumina hydrates. *Proceed. Kominkl. Nederl. Van Wettenschappen* – Amsterdam **57B**(3): 170-180.

DÖRRE E & HÜBNER H. 1984. *Alumina: Processing, Properties and Applications*, Berlin, *Springer-Verlag*, p. 12.

DROBOT NM, IONE KG & BUYANOVA NE. 1971. Kinetics of the crystallizaiton and properties of aluminum oxide formed in the heat treatment of certain aluminum salts and hydroxides. *Kinetika i Kataliz* **11:** 1537-1544. (translated by Consultants Bureau).

DWECK J, XAVIER C, SOUZA SANTOS P & SHANEFIELD DJ. 1996. A study of alpha-alumina obtained from monobasic aluminum formate and organic additives. *Brazilian J Chem Eng* **13:** 21-28.

ERVIN JR G. 1952. Structural interpretation of diaspore/corundum and boehmite/gamma-Al_2O_3 transitions. *Acta Crystal* **5**(1): 103-108.

FRANCOMBE MH & ROOKSBY HP. 1959. Structure transformations effected by the dehydration of diaspore, goethite and delta ferric oxide. *Clay Min Bull* **4**(21): 1-14.

GITZEN WH. 1970. Alumina as a Ceramic Material, Columbus, Ohio, *American Ceramic Society*, p. 4.

GOODBOY KP & DOWNING JC. 1990. Production, Processes, Properties and Applications of Activated and Catalytic Aluminas. In: HART LD & LENSE E., p. 93-108.

GREGG SJ. 1951. The Surface Chemistry of Solids, New York, *Reinhold* p. 65.

GREGG SJ. 1958. Active Solids in REES, A.L.G., Ed., Surface Phenomena in Chemistry and Biology, *Pergamon Press* London p. 195.

GREGG SJ & SING KSW. 1967. Adsorption, Surface Area and Porosity, *London Academic Press* p. 4.

HART LD & LENSE E. 1990. *Alumina Chemicals: Science and Technology Handbook*, Nesterville, Ohio, *American Ceramic Society* p. 193.

JAGOTA S & RAJ R. 1987. Sapphire whiskers from boehmite gel seeded with alpha-alumina. *J Crystal Growth* **85:** 527-534.

JOHNSON JR DW & GALLAGHER PK. 1971. Kinetics of the decompositon of freeze dried aluminum sulfate and ammonium aluminum sulfate. *J Amer Ceram Soc* **54:** 461-465.

KATO E, DAIMON K & NAMBU M. 1981. Decomposition of two aluminum sulfates and characterization of the resultant aluminas. *J Amer Ceram Soc* **64:** 436-443.

KIYOHARA PK. 1994. Caracterização da estrutura de membranas de AlOOH auto-suportadas formadas a partir de sóis de pseudoboemita fibrilar com diversas idades de envelhecimento térmico. São Paulo, 73p. (Tese de Livre-Docência; Departamento de Engenharia Química, Escola Politécnica da Universidade de São Paulo).

KIYOHARA PK & SOUZA SANTOS P. 1997. Characterization of the aluminas formed by pyrolisis between 200°C and 1500°C. In: *First International Latin-American Conference on Powder Technology*, Águas de Lindóia, São Paulo, Proceedings, Associação Brasileira de Cerâmica, SP, p. 11.

KRIVORUCHKO OP, BUYANOV RA, FEDOROV MA & PLYASOVA LM. 1978. Mechanism of formation of bayerite and pseudoboehmite. *Russian J Inorg Chem* **23:** 988-991.

KUMAGAI M & MESSING G. 1985. Controlled transformation and sintering of a boehmite sol/gel by alpha-alumina seeding. *J Amer Cer* **68:** 500-505.

LIMA-DE-FARIA J. 1963. Dehydration of goethite and diaspore. *Zeit Krist* **119:** 176-206.

LIPPENS BC. 1961. Structure and Texture of Aluminas. Delft 179p. (Ph.D. Thesis, Technische Hogeschool te Delft).

MAKSIMOV VN, SEMENENKO KN, NAUMOVA TN & NOVOSELOVA AV. 1960. The aluminium acetates, *Russian J Inorganic Chem* **5:** 267-270.

MCZURA G, FRANCIS TL & ROESEL RE. 1976. Special aluminas for ceramics and other industrial applications. *Interceram* n° 3 p. 206-212.

MCZURA G, GOODBOY KP & KOENIG JT. 1978. Aluminum Oxide. In: Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Vol. 2, p. 218-244, New York.

MISRA C. 1986. Industrial Alumina Chemicals ACS, Monograph 184; *Amer Chem Soc*, Washington, p. 8-53.

MISTLER RE & SHANEFIELD DJ. 1978. Washing ceramic powders to remove sodium salts. *Amer Ceram Soc Bull* **57:** 689-???

NEVES RF, SOUZA SANTOS H & SOUZA SANTOS P. 1991. Desenvolvimento em escala de laboratório de um método reprodutível para obtenção de géis de hidróxido de alumínio (pseudoboemita de morfologia fibrilar). *Cerâmica* **37**(247): 1-6.

NONO MCA & CASARINI JC. 1982. Redução carbotérmica de óxidos cerâmicos em aluminas nacionais. *Cerâmica* **28:** 41-48.

OBERLANDER RK. 1984. Aluminas for Catalysts: Their Preparation and Properties. In: LEACH, B.E., *Applied Industrial Catalysis, Vol. 3*, Chapter 4, Academic Press, Orlando, p. 63-112.

RANKIN GA & MERWIN HE. 1916. Ternary system CaO-Al_2O_3-MgO. *J Am Ceram Soc* **38:** 568-588.

ROUQUEROL J, AVNIR D, FAIRBRIDGE CW, EVERETT DH, HAYNES JH, PERNICONE N, RAMSAY JDF, SING KSW & UNGER KK. 1994. Recommendations for the characterization of porous solids, *Pure & Appl Chem* **68:** 1739-1758.

RUSSELL AS & COCHRAN CN. 1950. Surface areas of heated alumina hydrates. *Ind Eng Chem* **42:** 1336-1340.

RUTHNER MJ & KRISCHNER H. 1973. Production of alkali-free alumina: 3^{em} Congrès ICSOBA, Nice, p. 547-555.

SATO T. 1959. The dehydration of alumina trihydrate. *J Appl Chem* June 9, 331-339.

SATO T. 1962. Thermal transformation of alumina trihydrate, bayerite. *J Appl Chem* December 12, 553-556.

SATO T. 1964. Thermal transformation of alumina trihydrate, hydrargillite. *J Appl Chem* July 14, 303-308.

SATO T, OSAWA F & IKOMA S. 1978. Thermal decompostion of aluminum salts: hydrates of the chloride, nitrate and sulphate and of ammonium alum. *J Appl Chem Biotechnol* **28:** 811-822.

SING KSW. 1976. Surface Characterization: Physical. In PARFITT, G.D. & SING, K.S.W., Ed., Characterization of Powder Surfaces, Academic Press, London, p. 12.

SING KSW, EVERETT DH, HAUL RAW, MOSCOU L, PEROTTI RA, ROUQUEROL J & SIEMIENIEWSKA T. 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure & Appl Chem* **57:** 603-619.

SOUZA SANTOS H. 1998. Formation of aluminas from boehmite crystals. Electron optical studies. *Acta Microscopica* **7:** 1-11.

SOUZA SANTOS H & YADA K. 1988. Thermal transformation of talc as studied by electron-optical methods. *Clays and Clay Minerals* **36:** 289-297.

SOUZA SANTOS H & SOUZA SANTOS P. 1992. Pseudomorphic formation of aluminas from fibrillar pseudoboehmite. *Materials Letters* **13:** 175-179.

SOUZA SANTOS H & TOLEDO SP. 1994. Aluminas formadas a partir da boemita ripiforme: Contribuição da microscopia eletrônica de varredura. *Cerâmica* **40:** 69-73.

SOUZA SANTOS H, KIYOHARA PK & SOUZA SANTOS P. 1994. Pseudomorphic transformations of euhedral crystals of beta-AlOOH into aluminas. *Ceramics International* **20:** 175-181.

SOUZA SANTOS H, CAMPOS TW, SOUZA SANTOS P & KIYOHARA PK. 1997b. Phase sequences in an high alumina clay. *Acta Microscopica* **6A**: 82-83.

SOUZA SANTOS H, SOUZA SANTOS P, KIYOHARA PK & CAMPOS TW. 1998c. Characterization of synthetic gibbsite microcrystals. *Acta Microscopica* **7A:** 61-64.

SOUZA SANTOS P & SOUZA SANTOS H. 1957. Preparation of colloidal aluminum oxide hydrate with anisometric particles. *Naturwissenchaften* **44:** 113-114.

SOUZA SANTOS P & SOUZA SANTOS H. 1958. The fine structure of Schmidt's aluminum hydroxide gel. *Experientia* **14:** 318-321.

SOUZA SANTOS P & SOUZA SANTOS H. 1993. Preparation of aqueous sols containing well shaped boehmite crystals. *Colloid Polymer Sci* **271:** 197-200.

SOUZA SANTOS P, VALLEJO-FREIRE A & SOUZA SANTOS H. 1953. Electron microscope studies on the aging of amorphous colloidal aluminum hydroxide. *Kolloid Z.* **133:** 101-107.

SOUZA SANTOS P, SOUZA SANTOS H & NEVES RF. 1990. Sobre o envelhecimento em meio aquoso de precipitados de hidróxidos de alumínio tendo dimensões coloidais. *Cerâmica* **36**(245): 120-126.

SOUZA SANTOS P, KIYOHARA PK & SOUZA SANTOS H. 1996a. Thermal transformation of synthetic euhedral and fibrillar crystals of boehmite into aluminas. *Materials Res Bull* **31:** 799-807.

SOUZA SANTOS P, KIYOHARA PK, SOUZA SANTOS H & LIMA UA. 1996b. Desenvolvimento de esferas e membranas porosas de hidróxido de alumínio e alumina para imobilização e crescimento de levedura de cerveja. In: 12° *Congresso Brasileiro de Engenharia e Ciência dos Materiais,* Águas de Lindóia, São Paulo, Anais 1, p. 21-23.

SOUZA SANTOS P, SOUZA SANTOS H & KIYOHARA PK. 1997a. Characterization of the aluminum hydroxide formed by homogeneous precipitation from some aluminum salts and precipitants. *Anais Ass Bras Quim* **46:** 16-20.

SOUZA SANTOS P, LIMA UA, SOUZA SANTOS H & KIYOHARA PK. 1998a. Preparation of channeled alumina and aluminum hydroxide beads and membranes for yeast cell immobilization. *An Acad Bras Ci* **70:** 23-34.

SOUZA SANTOS P, KIYOHARA PK & SOUZA SANTOS H. 1998b. Morphology of the crystals of monohydroxide of aluminium boehmite; study by electron microscopy. *Bol Téc PETROBRÁS* **41:** 45-63.

STIRLAND DJ, THOMAS AG & MOORE NC. 1958. Observations on thermal transformations in alumina. *Trans Bri. Ceram Soc* **57:** 69-84.

STUMPF HC, RUSSEL AS, NEWSOME JW & TUCKER CM. 1950. Thermal transformations of aluminas and alumina hydrates. *Ind Eng Chem* **42:** 1398-1403.

TANEV PT & VLAEV LT. 1993. Effect of grain size on the synthesis of active alumina from gibbsite by flash calcination and rehydration. *Catalysis Letters* **19:** 351-360.

TOMASI R & SOUZA SANTOS P. 1989. Estudo experimental da pirólise de cristais de cloreto de alumínio hexahidratado. *Cerâmica* **35:** 8-12.

TOMASI R & SOUZA SANTOS P. 1990. Cristalização da alumina na pirólise de cloreto de alumínio hexahidratado. *Cerâmica* **36:** 41-44.

TSUCHIDA T, SAKATA A, FURUICHI R & ISHII T. 1981. Reactivity of amorphous aluminas prepared by the thermal decomposition of aluminum chloride and nitrate. *Thermochim. Acta* **43:** 91-102.

WEFERS K. 1963. Uber die thermische unwandlung des diaspors. *Erzmetall* **15:** 339-343.

WEFERS K. 1990. Nomenclature, Preparation and Properties of Aluminum Oxides, Oxide, Hydroxides and Trihydroxides. In: HART LD & LENSE E. p. 13-22.

WEFERS K & BELL GM. 1972. Oxides and Hydroxides of Aluminum, ALCOA Research Laboratories, Technical Paper n° 19, Pittsburg, p. 40.

WEFERS K & MISRA C. 1987. Oxides and Hydroxides of Aluminum, Pittsburgh, Alcoa Laboratories p. 18.

XAVIER C. 1997. Estudo Comparativo de Algumas Aluminas Comerciais no Desenvolvimento de um Compósito Cerâmica/Metal Resistente a Impactos Balísticos. Tese de Livre-Docência, Departamento de Engenharia Química, Escola Politécnica da Universidade de São Paulo, São Paulo, SP.

XAVIER C & SOUZA SANTOS P. 1995. Síntese de alumina-alfa a partir de formato de alumínio e alumínio em pó como precursores. *Materiais 95*, Aveiro, Sociedade Portuguesa de Materiais, Vol. 1, p. 399-406.

XAVIER C, KIYOHARA PK, SOUZA SANTOS H & SOUZA SANTOS P. 1998. Preparation of crystalline aluminium hydroxiformate and acetate using aluminium powder. *An Acad Bras Ci* **70:** 411-422.

YANG X, PIERRE AC & UHLMANN DR. 1988. TEM study of boehmite gels and their transformation to alpha-alumina. *J Non-Crystal Sol* **100:** 371-377.