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Tuning Al_2O_3 crystallinity under supercritical fluid conditions: Effect on sintering

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Abstract

Supercritical fluids have been used to prepare alumina powders. This versatile technique allows the tuning of the crystallinity of the obtained powders by a simple modification of the fluid's nature. Amorphous or boehmite alumina could be successfully synthesised using either CO_2/Ethanol or H_2O/Ethanol, respectively. The two powders present very different sintering paths, which have been correlated to the grain morphology and crystalline state of the powders. We have established that the alumina elaborated in CO_2/ethanol exhibited a significant decrease of the γ-Al_2O_3 → α-Al_2O_3 transition temperature resulting in a lower densification temperature.

Keywords: Al_2O_3; Sintering; Powders-chemical preparation; Supercritical fluids

1. Introduction

Alumina is one of the most widely used oxide ceramic material. It can be obtained in many metastable states (γ, δ, θ, κ, ε, η, χ) which lead upon thermal treatment to the thermodynamically stable α-Al_2O_3 phase.[1] Whatever the starting powders, the sintering temperatures required to obtain full densification remain usually quite high, above 1400 °C. In a general way, different oxide-hydroxides of aluminium used as starting materials lead, first, to various metastable alumina through dehydration/dehydroxylation mechanisms.[2] Then, phase transitions possibly involving microstructural rearrangements lead to corundum formation.[3] Once corundum crystallized, the final material densification occurs.

Previous works have shown that improvement of corundum densification is expected by lowering the transition temperature required to obtain corundum. Indeed, this relation has already been highlighted in many studies, some of which develop efficient materials chemistry strategies.[3–10] These strategies can be divided into two distinct categories.

One approach consists in adding second phases during the sintering stages which also allows retaining nanograins in the final ceramics. Bowen and Carry have summarized the most commonly used processes in a recent review.[3] Seeds of alpha alumina and other doping agents are commonly introduced into transition alumina before sintering in order to enhance kinetics of the transition. The seeds of alumina mixed with starting alumina, mostly boehmite gel, act as low energy sites for heterogeneous nucleation, resulting in a decrease of the activation energy barrier required to obtain α-alumina.[4,5] The transition temperature is thus reduced and the final microstructure refined. However, the applications are limited by the difficulty of obtaining monolithic pieces using this route.[6–8] Besides, doping elements have generally low solubility limits in α-alumina.[9] Then, formation of parasite phases is hard to avoid: elements segregate at the grain boundaries and precipitate when the grain boundaries are saturated. Consequently, the grain boundaries diffusion properties are modified i.e., either increased with Mg or Ti addition or decreased with Y or Zr addition. Conversely to Mg, Ti also increases grain boundary mobility. As a consequence, the ceramic densification is improved, however, without the ability to obtain a significant lowering of the transition temperature.[3,9]

A second strategy consists in modifying starting alumina properties by adjusting the chemical synthesis parameters. It is not possible here to review all the studies describing the

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chemical routes used to obtain the diverse oxides/hydroxides of alumina; however, an interesting point can be noticed in the literature concerning the relation between alumina syntheses and sintering. The question arose from two recent studies[10,11] as to whether the control of starting alumina crystallinity allows to decrease the temperature of the transition towards α-alumina and consequently to improve its densification? First, using sol–gel method, Sharma et al. have obtained gels with differing crystallinities depending on pH conditions. After calcinations at 450 °C, a gel obtained at high pH leads to boehmite, whereas one at low pH leads to an amorphous powder. As a result, the transition temperature towards α-Al_2O_3 was lowered from 1170 to 930 °C when starting from the amorphous powder.[10] Unfortunately, the microstructure of final ceramics has not been studied but the results concerning the temperature of transition are encouraging even if the reaction times required by this route appeared quite long. Second, a recent report by Hernandez and Bautista showed the influence of the synthesis route for obtaining dense TiO_2-doped alumina ceramics.[11] On one hand, using co-precipitation, γ-alumina was synthesized and the resulting ceramics, obtained after calcinations at 1125 °C, were composed of θ-alumina. On the other hand, Pechini and sol–gel processes lead to amorphous alumina as starting alumina powder. As a consequence, transformation to α-alumina was achieved after a similar thermal treatment. In addition, aluminium with lower crystallinity transforms towards α-alumina at a lower temperature. However, Hernandez used three different routes and as well as Ti, which, as mentioned earlier, has an important influence on alumina sintering. These two examples highlight the role of crystallinity as a key factor for the sintering process.

As an alternative synthesis method, the supercritical fluid route is a versatile method and allows for control over the powder properties (size, morphology, crystallinity ...) in short reaction times.[12,13] For example, Arai and coworkers have obtained boehmite with different particle size and shape.[14] Danchevskaya and coworkers have obtained α-Al_2O_3 directly.[15] None of these works, however, describe the sintering properties of the as-obtained alumina. Moreover, they were both performed exclusively in supercritical water. Here, we propose to adjust the reaction media in order to tune the alumina crystallinity. Thus, to answer the initial question, we report on a global study: (i) the synthesis of alumina powder with controlled crystallinity (from amorphous to crystalline form) using the supercritical form method, (ii) the influence of the alumina powder microstructure and transition temperature. Such an approach is based on the understanding of the phase transition mechanism during sintering.

2. Experimental procedure

2.1. Sample preparation

Two different routes are used to prepare α-alumina (Fig. 1). In both cases, the metal precursor used was aluminium acetylacetonate (99%, Aldrich). The chemical transformation of $Al(C_5H_7O_2)_3$ in water–ethanol mixture resulted in the formation of boehmite, as already observed in supercritical water,[14] whereas the thermal decomposition of $Al(C_5H_7O_2)_3$ in supercritical CO_2–ethanol mixture led to the formation of amorphous alumina.[16]

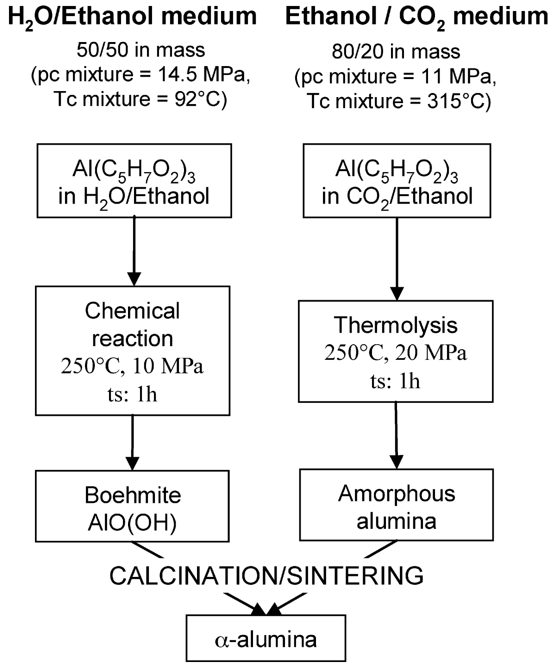

Fig. 1. Flow diagrams for the two routes used to produce α-alumina in sub- and supercritical fluid media ts: residence time, pc: critical pressure, Tc: critical temperature.

The precursor (1.5×10^{-2} mol) and liquid solvents were added into the high pressure and high temperature stirred vessel reactor (volume of 60 cm^3). The reactor was closed, back filled with carbon dioxide in the case of CO_2–ethanol and brought to the operating conditions indicated in Fig. 1. Under these experimental conditions, the CO_2–ethanol mixture is supercritical i.e., p_c(mixture) = 14.5 MPa, T_c(mixture) = 92 °C,[16] whereas the water–ethanol mixture is subcritical i.e., p_c(mixture) = 11 MPa, T_c(mixture) = 315 °C.[17]

The last step of the process differs for the two systems. In the case of the water–ethanol, the as-synthesized powder is collected in the initial mixture after vessel cooling, and filtered. In the case of the CO_2–ethanol, pure supercritical CO_2 is passed through the reaction vessel to remove ethanol and organic residues from the aluminium precursor. The powder is then dried and can be recovered without any additional filtering.

The two different powders are then cold-pressed (100 MPa) and sintered to obtain ceramics (ϕ = 5 mm, thickness = 1 mm). The heating schedule consisted in two steps: 680 °C for 1 h and 1200 °C for 4 h, with a heating rate of 300 °C/h.

2.2. Characterization methods

Transmission electron microscopy (TEM) imaging was performed using a Philips Tecnai 20 FEM, F-20 equipped with a Megaview II camera. The specimen for the TEM was prepared by depositing a few droplets of a dilute nanoparticles suspension in ethanol onto a carbon-coated copper grid, followed by drying under ambient conditions.

The ceramic microstructure was observed using a JEOL JSM 6360A scanning electron microscope (SEM). A thin gold coating was deposited on the fracture surface prior to observation.

Thermal behaviour of powders was investigated by thermal gravimetric analysis (TGA), dilatometry (TMA) and X-ray diffractometry (XRD).

Thermal gravimetric analysis was performed using a SETARAM microbalance mtb 10-8.

NETZSCH 402 ED differential dilatometer was used to record the length change of samples with a heating rate of 5 °C/min.

Phase analysis was conducted using a panalytical X'Pert MPD diffractometer with Bragg Brentano geometry and CuK_α radiation ($\lambda = 1.5418$ Å). It was equipped with a high temperature chamber (Anton Paar HTK16).

3. Results

3.1. Powder characterisation

The X-ray patterns of the powders obtained by the two routes are shown in Fig. 2. The powder formed in the water/ethanol medium was a well-crystallized boehmite phase (AlO(OH)) whereas CO_2/ethanol solvent led to an amorphous powder. These powders also differed largely in terms of grain size and morphology. AlO(OH) was made of acicular and nanometric grains (∼100 nm length) while the amorphous powder presented a very large distribution size and facetted grains (Fig. 3).

The structural evolution of the powder with respect to the temperature was determined using temperature X-ray diffractions (Fig. 4).

Boehmite from the water–ethanol system transformed into α-alumina via three transition alumina: δ, γ and θ. The mixture of δ- and γ-alumina, observed at 500 °C, was transformed into a mixture of γ- and θ-alumina, as shown by the diffractogram recorded at 1080 °C (Fig. 4(a)).

The amorphous powder obtained in the CO_2/ethanol system was also transformed into α-alumina but with only one intermediate phase observed at 850 °C: the γ-alumina phase (Fig. 4b).

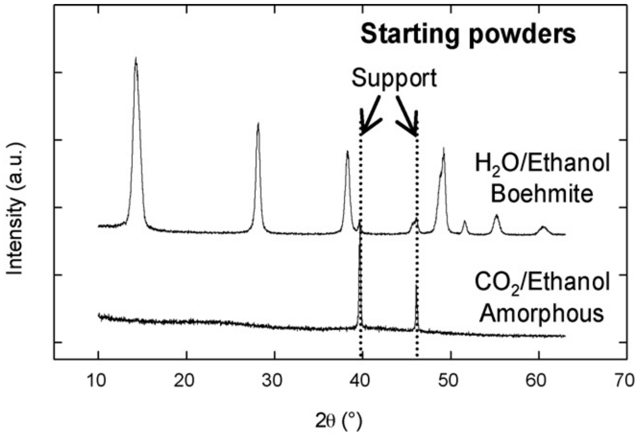

Fig. 2. X-ray patterns of the powders according to the fluid nature used for the powder synthesis.

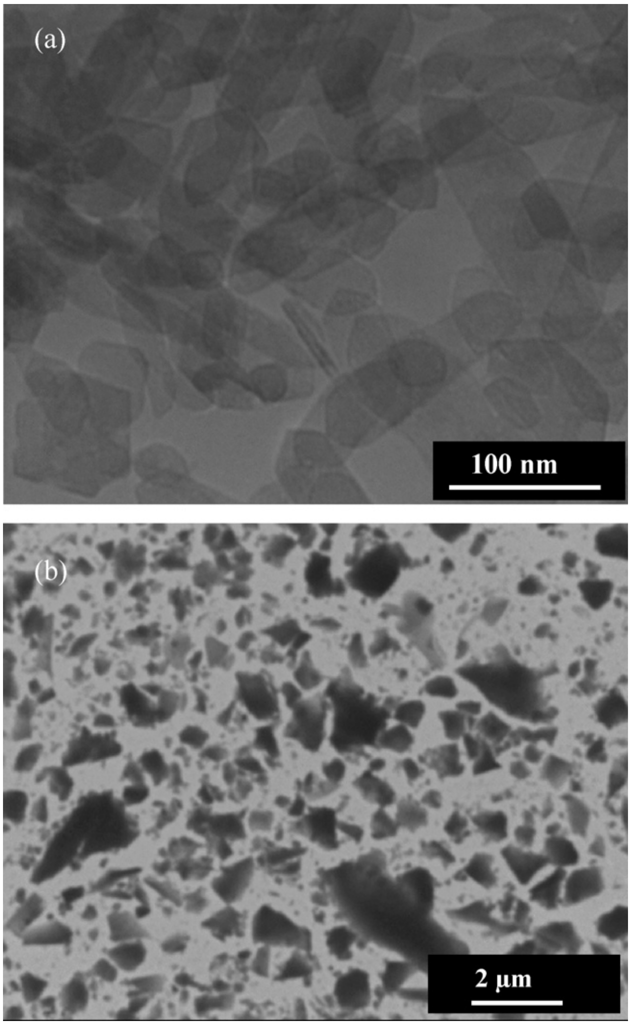

Fig. 3. TEM micrographs of starting alumina obtained in (a) water/ethanol and (b) CO_2/ethanol.

Both boehmite and amorphous powders were transformed into α-alumina via the same γ-alumina intermediate. The transformation into α-alumina was complete at 1080 °C in the first case whereas θ-alumina was still present with the α-alumina up to as high as 1215 °C for the boehmite powder.

3.2. TMA/TGA analysis

The pellet obtained from the powder synthesized in the water–ethanol medium followed a two-step process (Fig. 5a). Dehydration and dehydroxylation mechanisms, already reported in the literature[3], were pointed out by the TGA measurement, which showed a 15% weight loss at 470 °C. Following dehydration and dehydroxylation, a first shrinkage could be associated to the first phase transition that was observed in that temperature range, corresponding to the boehmite → δ, γ alumina as illustrates on Fig. 4a. The second shrinkage occurs between 800 and 1200 °C and is still not finished at 1200 °C. This shrinkage does not directly correspond to the last phase transition. Fig. 6 actually shows an enlargement of the shrinkage rate curve in the temperature range of the $\gamma\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3$ phase transition,

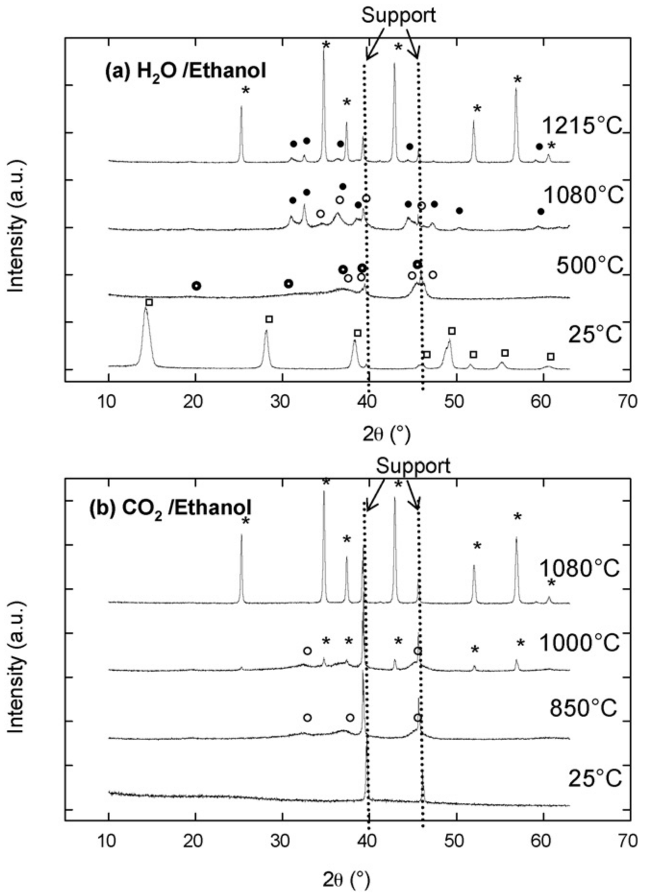

Fig. 4. Structural evolution with temperature of powders synthesized in (a) water/ethanol; (□) boehmite, (◯) γ-alumina, (◉) δ-alumina, (●) θ-alumina and (*) α-alumina, and (b) CO_2/ethanol; (◯) γ-alumina, (*) α-alumina.

observed by XRD. It started at 1150 °C in the middle of the densification phenomenon.

The pellet obtained from the powder produced in the CO_2–ethanol supercritical medium, underwent, at low temperature, two first shrinkages which occurred simultaneously with large weight losses (Fig. 5b). Therefore these shrinkages can be attributed to the release of organic residues present in the aluminium precursor. A small accident can be noted on the sintering curve around 680 °C. It corresponds to the 1 h holding time step performed at that temperature during the sintering schedule. Above 700 °C, two shrinkage phenomena were observed: the first one took place between 850 and 900 °C and the second one between 1050 and 1150 °C. This is highlighted on the derivative of the shrinkage curve which shows a first peak around 880 °C and a second one at 1100 °C. The last one occurred clearly after the γ → α phase transition that took place at ∼1000 °C for that powder (Fig. 6).

4. Discussion

The thermal behaviour of the two powders differed greatly depending on their crystalline state. The γ → α phase transition of the powder synthesized in water/ethanol actually started at 1150 °C, whereas the transition of the powder obtained from CO_2/ethanol began at 1000 °C. Therefore, a scheme illustrating the sintering path relative to each powder is proposed in Fig. 7.

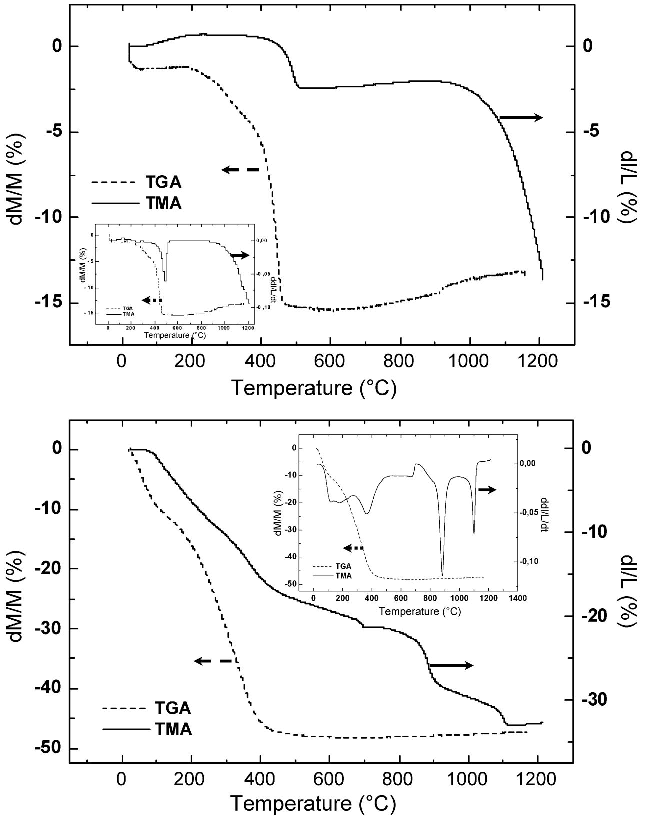

Fig. 5. TMA (shrinkage rate) and TGA for powders obtained in (a) water/ethanol (b) CO_2/ethanol. TGA ordinate axis is on the left side of the figure. The shrinkage ordinate axis is on the right side of the figure. In the insert, the derivative substitutes for its corresponding shrinkage curve.

In the case of boehmite, the initial powder is made of very small crystallites i.e., nm size range as determined by TEM. Such a powder is very difficult to compact and leads to a porous green sample. It has been shown that full densification of such loose packing powder requires large rearrangements during sintering, and very high temperatures.[18] In fact, the densification of this

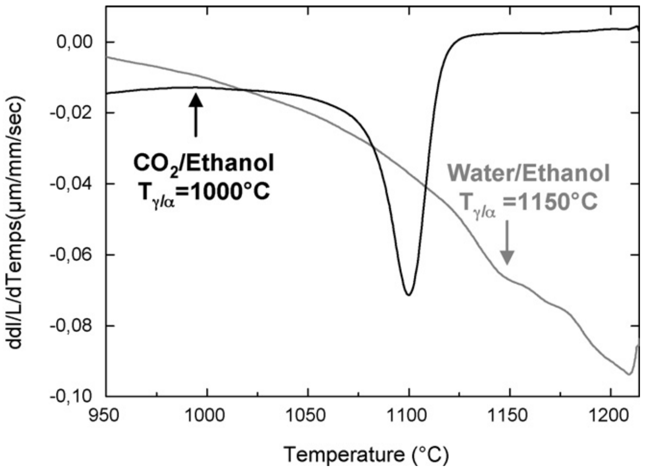

Fig. 6. Shrinkage rate in the temperature range of the γ → α transition for the two powders.

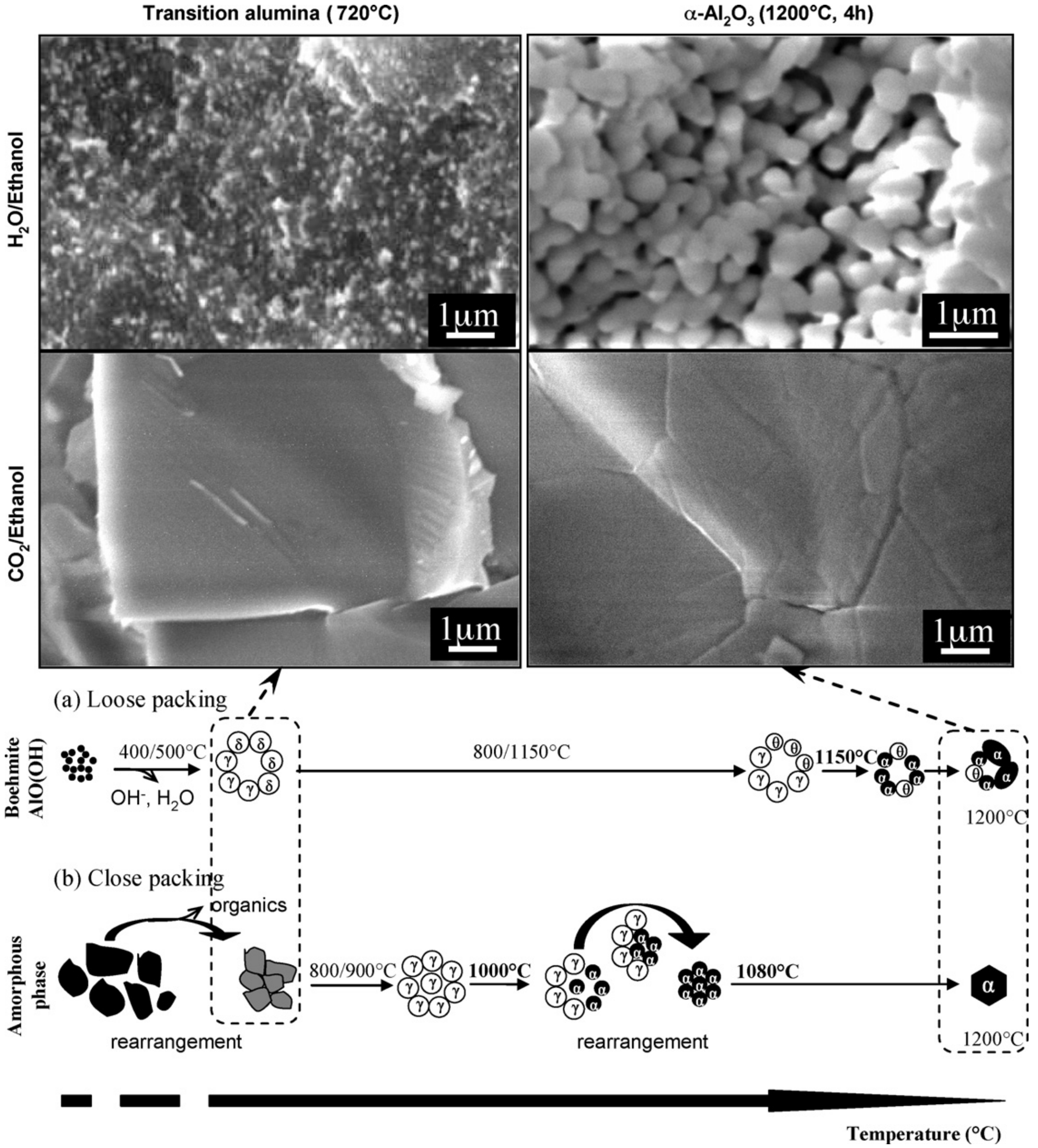

Fig. 7. Proposed sintering paths for (a) boehmite obtained in water/ethanol and (b) amorphous alumina synthesised in CO_2/ethanol[18] based on the SEM micrographs of the alumina pellets heated at 720 °C and of the final ceramics sintered at 1200 °C during 4 h.

boehmite sample was indeed limited by the loose packing but also by the presence of different transition alumina (Fig. 7(a)). Boehmite transformed first into a γ and δ mixture, and δ which transformed in turn, above 800 °C, into θ. Firstly, this transformation delays the γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ transition to a higher temperature (1150 °C). In that temperature range, sintering has already taken place, which makes the material more rigid and thus limits intergranular rearrangement. Secondly, the occurrence of residual θ grains can impede the rearrangement stage required to reach a good densification as is commonly observed during the densification of two-phase composite materials.[18] As a result, boehmite sintering led to a porous ceramic with a vermicular microstructure composed of submicrometer grains. (Fig. 7)

In the case of amorphous alumina, the starting powder contains larger grains (μm size range as determined by TEM) and a more important organic part due to the precursor decomposition i.e., nearly 50% by weight observed in TGA. In the early stage of sintering, a first interparticle rearrangement is likely associated with organics elimination i.e., see the peak close to 400 °C on TMA. The α crystallisation followed very closely the γ crystallisation (800 °C) and occurred at lower temperature (1000 °C) than usually observed.[10] In this temperature range, the ceramic is not completely densified which allows intergranular movements. A second grain rearrangement could then accompany the γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ transformation. This transformation was already finished at 1080 °C when the last shrinkage took place (corresponding to α densification). For that sample, the densification was important and grain growth was then favoured up to 1200 °C (Fig. 7). The amorphous powder synthesised in supercritical CO_2/ethanol results in a ceramic comprised of large and dense grains.

5. Conclusions

Supercritical fluids route allows for control over the preparation of two types of α-alumina precursors by a simple modification of reaction medium. Boehmite in water/ethanol and amorphous alumina in CO_2/ethanol were thus obtained. The influence of the starting powder crystallinity on the sintering properties has been studied, and sintering paths have been proposed for each starting alumina. Both powders led to the thermodynamically stable α-Al_2O_3 phase through the same transition alumina: γ-Al_2O_3. The amorphous character of the powder elaborated in CO_2/ethanol lowered the temperature of the γ-Al_2O_3 → α-Al_2O_3 transition by about 150 °C and it led to a denser ceramic than the one made of powder crystallized in water/ethanol (boehmite).

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