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Tuning Al₂O₃ 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 tuning the crystallinity of the obtained alumina by a simple modification of the fluid nature. Using CO₂/Ethanol or H₂O/Ethanol, respectively amorphous or boehmite alumina can be successfully obtained. The sintering paths of the two types of powders differ greatly. It has been correlated to their grain morphology and crystalline state. It is shown that the alumina elaborated in CO₂/Ethanol shows a significant decrease of the γ -Al₂O₃→ α -Al₂O₃ transition temperature resulting in a lower densification temperature.

Keywords: Al₂O₃ (D), Sintering (A), Powders-chemical preparation (A), Supercritical fluids

1. Introduction

Alumina is 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 -Al₂O₃ phase.¹ This stable corundum structure is obtained at high temperature and is used in a wide range of ceramic and refractory applications.² A key interest for cost reduction is to soften the sintering conditions required to obtain interesting alumina-based ceramics. Global sintering processes involve different oxide-hydroxides of aluminium as starting materials, which lead first to various metastable alumina through dehydration/dehydroxylation mechanisms.³ Then, phase transitions involving eventually microstructural rearrangements lead to corundum formation.⁴ Once corundum crystallized, the final material densification occurs.

Improvement of corundum densification is expected by lowering the transition temperature. Many strategies have thus been probed. Legros *et al* have summarized in a recent review paper the main efficient processes used during the sintering stages.⁵ Seeds of alpha alumina and other doping agents have been commonly introduced into transition alumina before sintering in order to enhance kinetics of transition.^{6,7} Although the transition temperature actually decreased, it is difficult to obtain monolithic pieces by this first route. In the case of the use of doping elements like Y, Zr, Mg, formation of parasite phases is hardly avoided.⁸ Another strategy is to use pressure sintering but it requires heavy equipments which do not allow an efficient control of the sample geometry.^{4,9}

Besides, some research groups focussed their work on optimising the synthesis routes of starting alumina powders. Several wet chemical methods lead to diverse oxide/hydroxides of aluminium, crystallized or not. Using sol-gel method, Sharma *et al.* have obtained gels with different crystallinities according to pH conditions. As a result,

the transition temperature was lowered from 1170 to 930°C.¹¹ However, this route required long reaction times. A recent report by Hernandez *et al.* showed the influence of synthesis route for obtaining dense TiO₂-doped alumina ceramics.¹² Using co-precipitation, γ -alumina was also synthesized and the resulting ceramics, obtained after calcinations at 1125°C, were made of θ -alumina. Pechini and sol-gel processes lead to amorphous alumina as starting alumina powder. Transformation in α -alumina is fully achieved after a similar thermal treatment. These two examples highlight the role of crystallinity as a key factor for the sintering process.

As an alternative synthesis method, supercritical fluid route is a versatile method allowing the control of powder properties (size, morphology, crystallinity...).^{13,14} For example, Araï *et al.* have obtained boehmite with different particle size and shape.¹⁵ Danchevskaya *et al.* have obtained directly α -Al₂O₃.¹⁶ These works were both performed in supercritical water. Here, we propose to optimise the reaction media in order to tune the alumina crystallinity. Our objective is to investigate the influence of the powder crystallinity on the microstructure of the final ceramic. 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 were used to prepare α -alumina (Fig. 1). In both cases, the metal precursor used was aluminium acetylacetonate (99%, Aldrich). The chemical transformation of Al(C₅H₇O₂)₃ in water/ethanol results in the formation of boehmite, as already observed in supercritical water¹⁵ whereas the thermal decomposition of

$\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ in supercritical CO_2 /ethanol leads to the formation of amorphous alumina.¹⁷

The experimental set-up is described in Fig. 2. The precursor and liquid solvents are added into the high pressure and high temperature stirred vessel reactor (volume of 60 cm^3). The reactor is closed, filled with carbon dioxide in the case of CO_2 /ethanol and reaches the operating conditions indicated in Fig.1. In these experimental conditions, the CO_2 /ethanol mixture is supercritical ($P_c(\text{mixture}) = 14.5 \text{ MPa}$, $T_c(\text{mixture}) = 92^\circ\text{C}$)¹⁸ whereas the water/ethanol mixture is subcritical ($P_c(\text{mixture}) = 11 \text{ MPa}$, $T_c(\text{mixture}) = 315^\circ\text{C}$)¹⁹.

The last step of the process differs for the two systems. For water/ethanol, the as-synthesized powder is collected in the initial mixture after vessel cooling. It is then filtered. For CO_2 /ethanol, pure supercritical CO_2 flows through the reactor to remove ethanol and organic residues from aluminium precursor. The powder is then dry and can be recovered without any additional filtering step.

The two different powders were then cold pressed and sintered in order to obtain ceramics. The heating schedule was made of two steps : 680°C during 1h and 1200°C during 4 hours, with a heating rate of 300°C/h ,

2.2. Characterization methods

Transmission electron microscopy (TEM) imaging was performed using a Philips Tecnai 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 ceramics microstructure was observed using a scanning electron microscope (SEM) JEOL JSM 6360A. A thin platinum 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 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 ($\lambda=1.5418\text{\AA}$). It was equipped with a high temperature room (Anton Paar HTK16).

3. Results and discussion

3.1. XRD analysis

The X-ray patterns of the powders obtained by the two routes are shown in Fig. 3. The powder formed in the water/ethanol medium is a well-crystallized boehmite phase ($\text{AlO}(\text{OH})$) whereas CO_2 /ethanol solvent leads to an amorphous powder.

The structural evolution of the powder with temperature has been highlighted thanks to temperature X-ray diffractions (Fig. 4).

Boehmite from water/ethanol system transforms into α -alumina via three transition alumina: δ , γ and θ . The mixture of δ -and γ - alumina, observed at 500°C, is transformed

into a mixture of γ - and θ - alumina, as shown by the diffractogram recorded at 1080°C in (Fig. 4(a)).

Amorphous powder obtained in the CO₂/ethanol system is also transformed in α -alumina but with only one intermediate phase observed at 850°C which is the γ -alumina phase (Fig. 4b).

Both boehmite and amorphous powders are transformed into α -alumina via the same γ -alumina intermediate. The transformation into α -alumina is complete at 1080°C when the initial powder is amorphous whereas θ -alumina still remains with α -alumina up to 1215°C for the boehmite powder.

3.2. TMA/TGA analysis

Dimensional and mass changes of pellets during the heating steps have been used to determine the sintering paths (Fig. 5). Both techniques have been correlated to X-ray diffraction results. In fact, the thermal behaviour of the two powders differs greatly depending on their crystalline state.

The pellet made of boehmite (synthesized in water/ethanol medium) follows a two-step process. Further to dehydration/dehydroxylation phenomena that take place under 500°C, a part of boehmite transforms into δ -alumina and γ -alumina. Dehydration and dehydroxylation mechanisms, already reported in the literature³, are pointed out by the TGA measurement, which shows a 15% weight loss at 470°C. The second shrinkage occurs between 800°C to 1200°C. It is due to the network contraction that corresponds to the evolution of the δ and γ -alumina powders towards a mixture of θ - and γ -alumina. It finally transforms into α -alumina above 1150°C as shown by X-ray analysis.

The pellet of amorphous alumina, obtained in the CO₂/ethanol supercritical medium, undergoes, at low temperature, two first shrinkages due to the departure of organic residues of the aluminium precursor. Weight losses observed in TGA measurement for the same temperature range confirm this hypothesis. Then, still in agreement with XRD analyses, an important peak close to 800°C confirms the crystallization of amorphous alumina into γ -alumina. A last shrinkage indicates that γ -alumina already transforms into α -alumina since 1000°C and that the transition is complete at 1080°C.

In Fig. 6, an enlargement of the shrinkage rate curve in the temperature range of the γ -Al₂O₃→ α -Al₂O₃ transition allows to compare the onset of this transition according to the fluid nature. The transition of the powder synthesized in water/ethanol actually starts at 1150°C whereas the transition of the powder obtained from CO₂/ethanol starts at 1000°C.

3.3. Powder morphology and microstructure

Fig. 7 shows the final microstructures of the ceramics obtained after sintering of the two powders at 1200°C. Boehmite, obtained in water/ethanol, leads to a porous ceramic with a vermicular microstructure composed of submicrometers grains. The amorphous powder synthesized in supercritical CO₂/ethanol gives a ceramic made of large and dense grains.

3.4. Sintering paths

Thanks to thermal and X-ray diffraction characterizations, a sintering path is proposed in Fig. 8, which explains the different behaviours according to the crystallinity of the starting powders.

In the case of boehmite, the initial powder is made of very small crystallites (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 the densification of such loose packing powder requires very high temperatures and also rearrangements during sintering stages.¹⁹ In fact, the densification of this boehmite sample is limited by the loose packing but also by the coexistence of different transition alumina (Fig. 8(a)). Boehmite transforms first into γ and δ which transforms itself into θ above 800°C. First, this transformation delays the γ -Al₂O₃ → α -Al₂O₃ transition to higher temperature (1150°C). In that temperature range sintering already takes place which makes the material more rigid and necessarily limits intergranular rearrangement. Second, the occurrence of residual θ grains can impede the rearrangement stage required to reach a good densification as it is commonly observed during the densification of two-phase composite materials.²⁰ As a result, boehmite sintering leads to a porous ceramic with a vermicular microstructure.

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 (nearly 50% in weight observed in TGA). In the early stage of sintering, a first interparticle rearrangement is associated with organics elimination (peak close to 400°C on TMA). The α crystallisation follows very closely the γ one

(800°C) and occurs at lower temperature (1000°C) than usually observed¹⁰. In this temperature range, the ceramic is sufficiently “soft” to allow intergranular movements. A second grains rearrangement could accompany the $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation. This transformation is already finished at 1080°C; as the densification is then high, grain growth is favoured until 1200°C (Fig. 8(b)).

The amorphous character of the powder elaborated in CO₂/ethanol allows decreasing the temperature of the $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ transition of about 150°C and it leads to a denser ceramic than the one made of powder crystallized in water/ethanol (boehmite).

4. Conclusions

Supercritical fluids route allows controlling the elaboration of two types of α -alumina precursors by a simple modification of reaction medium. Boehmite in water/ethanol and amorphous alumina in CO₂/ethanol are thus obtained. The influence of the starting powder crystallinity on the sintering properties has then been studied. Sintering paths have been proposed for each starting alumina. Both powders lead to the thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ phase through the same transition alumina: $\gamma\text{-Al}_2\text{O}_3$. The alumina elaborated in CO₂/ethanol shows interesting sintering properties and in particular it presents a significant improvement in the lowering of the temperature of the $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ transition (150°C).

Acknowledgements

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Figure Captions

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).

Fig. 2. High pressure, high temperature stirred reactor for material synthesis in supercritical fluids. P and T are pressure and temperature controllers, respectively.

Fig. 3. X-ray patterns of the powders according to the fluid nature used for the powder synthesis.

Fig. 4. Structural evolution with temperature of powders synthesized in (a) water/ethanol (\square boehmite, \circ γ -alumina, \bullet δ -alumina, \bullet θ -alumina and * α -alumina) and (b) CO₂/ethanol. (\circ γ -alumina, * α -alumina).

Fig. 5. TMA (shrinkage rate) and TGA for powders obtained in a) water/ethanol b) CO₂/ethanol. TGA ordinate axis is on the left side of the figure. The derivative of the shrinkage ordinate axis is on the right side of the figure.

Fig. 6. Shrinkage rate in the temperature range of the $\gamma \rightarrow \alpha$ transition for the two powders.

Fig. 7. SEM micrographs of alumina ceramics sintered during 4h at 1200°C.

Fig. 8. Proposed sintering paths for (a) boehmite obtained in water/ethanol and (b) amorphous alumina synthesised in CO₂/ethanol.¹⁹

H₂O/Ethanol medium CO₂/Ethanol medium

50/50 in mass
(pc mixture = 14.5 MPa,
Tc mixture = 92°C)

80/20 in mass
(pc mixture = 11 MPa,
Tc mixture = 315°C)

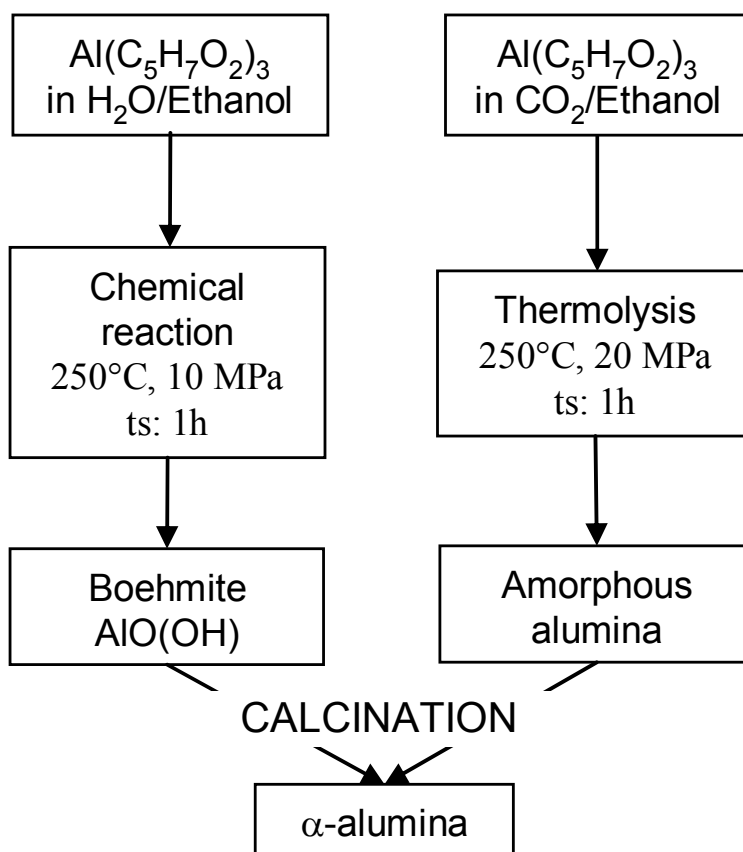


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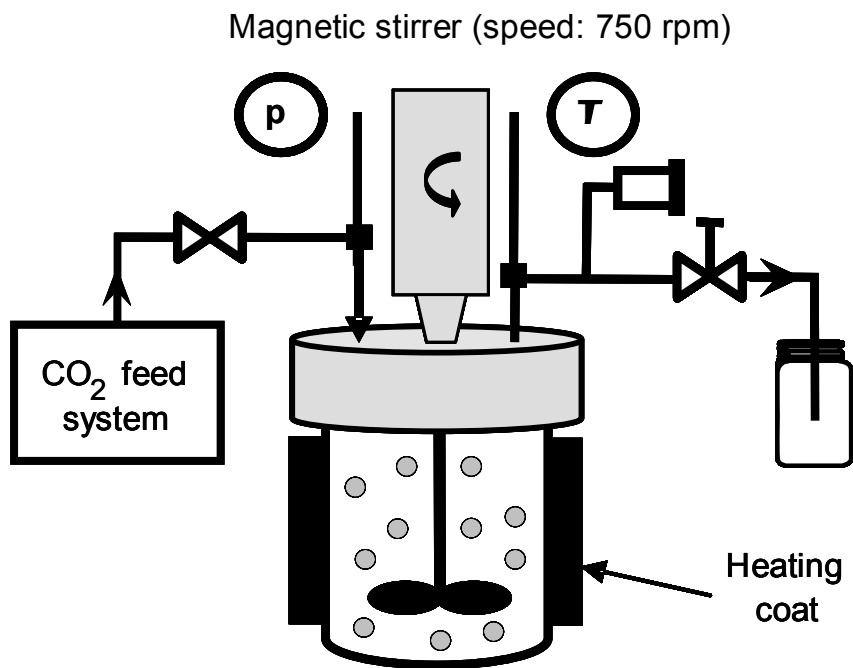


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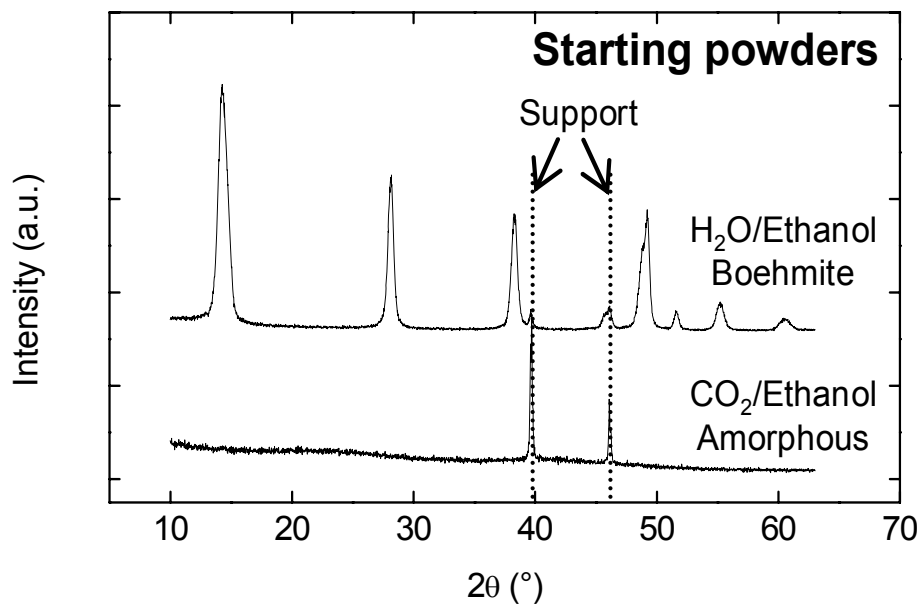


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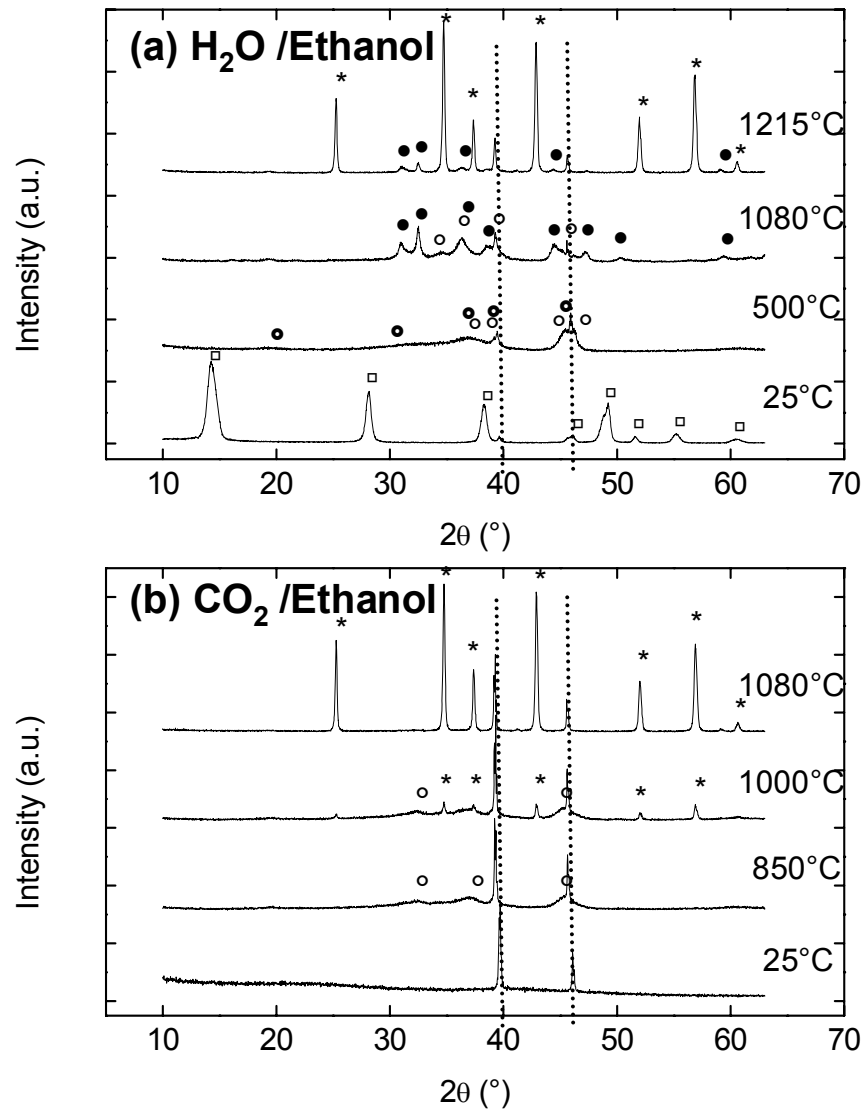


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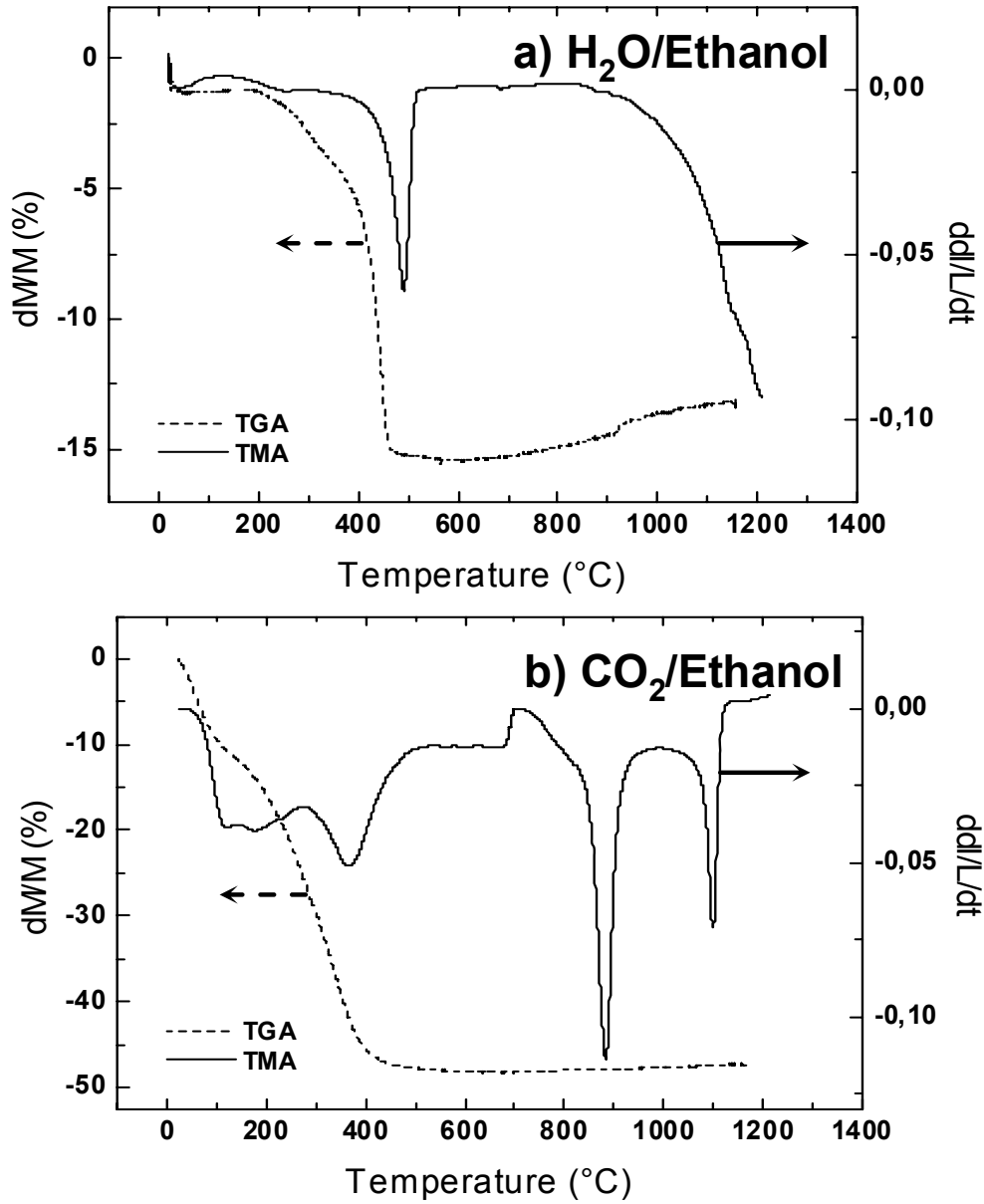


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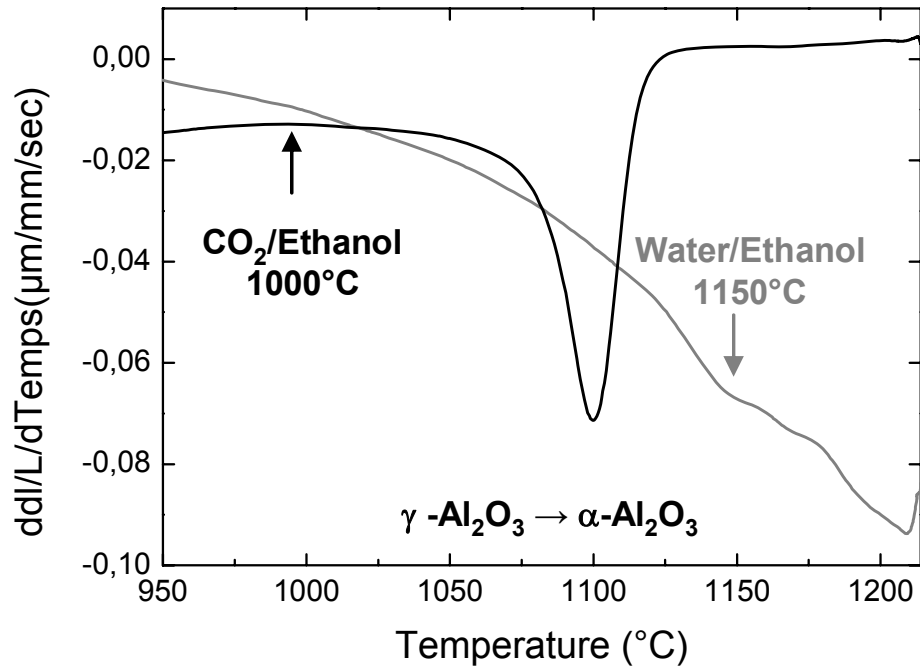


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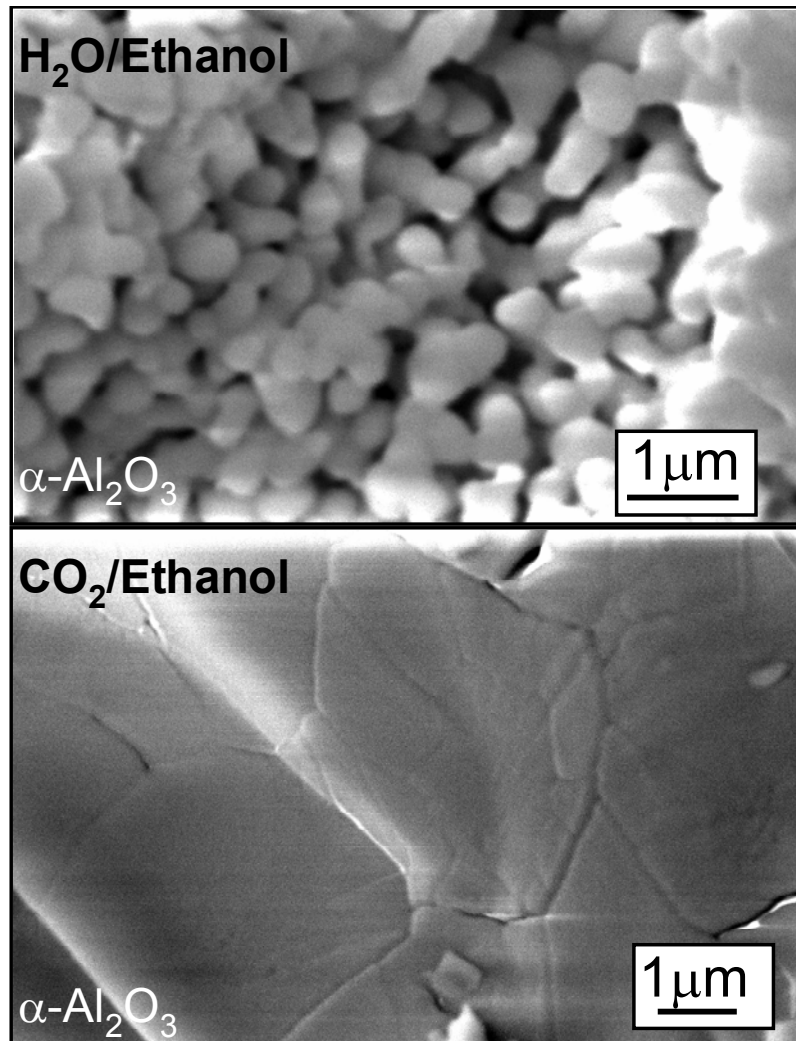


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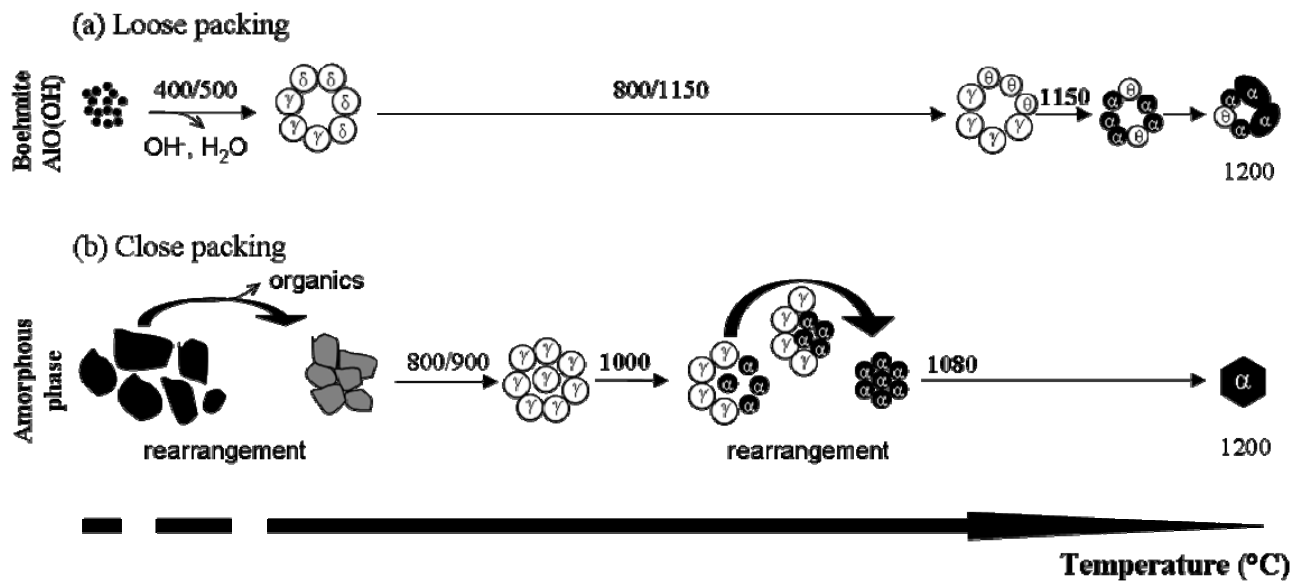


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