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Tuning Al_2O_3 crystallinity under supercritical fluid conditions: Effect on sintering

C. Bousquet, C. Elissalde, C. Aymonier, M. Maglione, F. Cansell, J.M. Heintz *

Institut de Chimie de la Matière Condensée de Bordeaux ICMCB-CNRS and ENSCPB, Université Bordeaux I,
87 Av. Dr A. Schweitzer, 33608 PESSAC Cedex, France

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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-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ 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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* Corresponding author. Tel.: +33 5 40 00 62 57.
E-mail address: heintz@icmcb-bordeaux.cnrs.fr (J.M. Heintz).

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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]

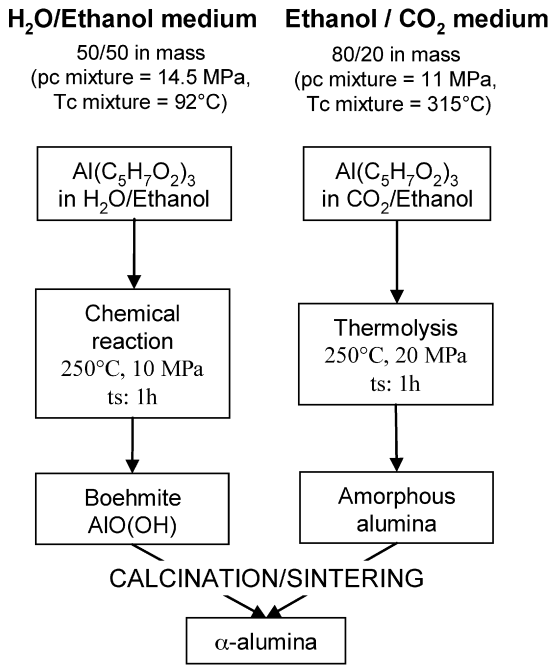

Fig. 1. Flow diagrams for the two routes used to produce α-alumina in sub- and supercritical fluid media ts: residence time, pc: critical pressure, Tc: critical temperature.

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.