

# Densification ability of combustion-derived $\text{Al}_2\text{O}_3$ powders

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## Abstract

Nanocrystalline  $\text{Al}_2\text{O}_3$  powders containing different amounts of MgO (0.1–5.0 mol%) or added boehmite ( $\text{AlOOH}$ ) have been synthesized by combustion synthesis from aluminium nitrate and magnesium nitrate, using urea or sucrose as fuels. The as synthesized alumina powders were deagglomerated, compacted by dry pressing and sintered at 1625 °C for 2 h. For comparison purposes, a commercial high purity  $\alpha$ - $\text{Al}_2\text{O}_3$  powder (ACC) was also processed following the same route. The sintered materials were characterized for bulk density (BD), apparent porosity (AP), and water absorption (WA) capacity, microstructure using SEM, and XRD phase composition. In comparison to boehmite, the MgO had a considerable effect on the densification behaviour of combustion-synthesized powder.

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## 1. Introduction

Alumina is one of the most important oxide ceramics with a wide range of uses, including high-temperature applications and microelectronics. Now a days, the nanocrystalline materials are receiving a great deal of attention with a belief that their mechanical properties are greatly affected by the presence of extremely fine crystallites with typical sizes of the order of 100 nm or less [1,2]. Over the last few decades, a great variety of techniques such as, hydrothermal synthesis, plasma spray decomposition of oxides, sol–gel method, freeze drying of sulphate solutions, controlled hydrolysis of metal alkoxides, decomposition of organo-metallic compounds in supercritical fluids, aerosol methods, etc., have been developed to prepare nanocrystalline alumina powders [3–5]. Many of these techniques are able to produce nanometer-sized particles which are either amorphous or in  $\gamma$ -phase. Though these materials found important catalyst related applications, they loose their nanocrystalline nature upon heat treatment due to  $\gamma$ - to  $\alpha$ -phase transformation accompanied by a rapid grain growth. This grain growth process destroys the beneficial properties of the starting

nanocrystalline alumina powders. Literature reports [6–8] have suggested that for obtaining dense nanocrystalline alumina products, either the transformation of  $\gamma$ - to  $\alpha$ -phase has to be arrested or nanocrystalline  $\alpha$ - $\text{Al}_2\text{O}_3$  powders have to be used. In a recent work, Kumagai and Messing [6] densified alumina ceramics to full extent while keeping grain size  $<0.5\ \mu\text{m}$  by using boehmite sol–gels seeded with  $<2.0\ \text{wt.}\%$   $\alpha$ -alumina powder in a boehmite hydrosol at pH 3. However, the technique used seems to be very expensive and lengthy. Recently, Bhaduri et al. [7,8] suggested that combustion synthesized (i.e., auto-ignition processed) nanocrystalline  $\alpha$ - $\text{Al}_2\text{O}_3$  powders could undergo full densification as there is no grain growth process due to  $\gamma$ - to  $\alpha$ -phase transformation. In fact, this auto-ignition process along with the self-propagating high temperature synthesis, SHS, has emerged as safe, simple, and most economic process, which yields high purity powders with excellent homogeneity and fine particle sizes in the case of composite materials [9–11]. Furthermore, as this process does not require washing, filtration, drying, calcination steps, and any acid or base to hydrolyze the corresponding salts, a lot of energy and time can be saved.

Though Bhaduri et al. [7,8] succeeded in retaining grain size of  $\alpha$ - $\text{Al}_2\text{O}_3$  materials within the sub micrometer size range, the extent of densification achieved in consolidated powders obtained by the auto ignition process was only about 90%. It has been reported that the powders obtained by this route suffer from

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low surface area hence poor reactivity and undesired powder morphology due to the high temperatures achieved during the combustion synthesis [12,13]. Different types of high molecular weight organic fuels have been successfully employed to synthesize materials with high specific surface areas. The use of these fuels requires an additional calcination step to obtain fully crystalline materials, which adds up to the processing cost [10,14]. The only fuel which facilitated the formation of fully crystalline materials on direct synthesis is urea owing to generation of a high adiabatic temperature [15,16]. By adding certain materials to the reaction mixture, the adiabatic temperature generated during reaction can be reduced to some extent so that the powders obtained are exposed to lower temperatures, hence, retaining superior properties [9]. However, such studies have not been conducted so far on materials obtained by the solution auto-ignition synthesis routes.

## 2. Experimental procedure

A systematic investigation was undertaken to study the effect of boehmite (0.1–5 mol%) as an inert material and magnesia (0.1–5 mol%) as a sintering aid on the densification behaviour of solution combustion synthesized (auto-ignition)  $\text{Al}_2\text{O}_3$  powder. Urea and sucrose were used as fuels. The combustion synthesized powders were processed and consolidated by dry pressing along with a commercial high purity  $\alpha$ - $\text{Al}_2\text{O}_3$  powder and sintered at 1625 °C for 2 h. The sintered materials were thoroughly characterized for XRD phase composition, microstructure, bulk density (BD), apparent porosity (AP), and water absorption (WA) capacity in order to understand the influences of fuel type, MgO sintering additive and boehmite as inert material on the densification behaviour of solution combustion synthesized  $\text{Al}_2\text{O}_3$  powders.

### 2.1. Material synthesis and processing

Analytical grade aluminium nitrate, magnesium nitrate, urea (all from Loba-Chemie, India) and sucrose were used as raw materials in the combustion synthesis route. A commercially available high purity  $\alpha$ - $\text{Al}_2\text{O}_3$  powder (HP grade, ACC India Limited, India) was also used in this study. Henceforth, this powder is termed as ACC powder. This powder contains >200 ppm MgO, <600 ppm  $\text{Na}_2\text{O}$ , <150 ppm CaO, <225 ppm  $\text{SiO}_2$  and <200 ppm  $\text{Fe}_2\text{O}_3$  as impurities; the average particle size is 0.6  $\mu\text{m}$  and consists corundum phase as claimed by the supplier.

In a typical combustion synthesis experiment involving urea as fuel, aqueous solutions containing the required amounts of urea, aluminium nitrate, and 0.1–5 mol% magnesium nitrate, or dispersed boehmite (Disperal, Condea, Brunsbüttel, Germany) to yield 200 g of each  $\text{Al}_2\text{O}_3$  powder were first prepared and put in a Pyrex dish. The acidity of the solution/suspension was adjusted to pH 1 by adding diluted nitric acid. The entire solution/suspension was then heated to 250 °C for 2 h. After complete dehydration, the Pyrex dish was transferred to an electric muffle furnace, the temperature of which was previously set at 500 °C, and held for 5 min at this temperature

to promote the ignition. After the combustion reaction, the resulting foamy material was cooled to room temperature and milled as described below. A similar procedure was adopted in the case of sucrose combustion synthesis, but only a single concentration of MgO (5 mol%) was attempted. The required amount of sucrose was slowly dissolved in an aqueous solution of aluminium nitrate and magnesium nitrate kept at pH 1, by adding diluted nitric acid, and at about 70 °C for 30 min under continuous stirring [12]. After complete dehydration of the solution at 250 °C for 2 h, the sucrose decomposition started, resulting in dense white fumes leaving behind a charred black precursor mass. This charred mass was crushed into fine powder using an agate mortar and pestle, transferred into a mullite tray and heated treated in an electric furnace under air atmosphere at a rate of 3 °C/min up to 600 °C, with 5 h holding time at this temperature. The charred mass was thus converted into voluminous, very fine, and pure white  $\text{Al}_2\text{O}_3$  powder [14]. This powder is hereafter termed as SCA5.

Differently synthesized  $\text{Al}_2\text{O}_3$  powders (UCA5 and SCA5) and a commercial  $\text{Al}_2\text{O}_3$  powder (ACC) were milled separately for 1 h under identical conditions in a planetary ball mill (Fritsch Pulverisette 5, Fritsch GmbH, Germany) consisting of an alumina vessel and 12-mm diameter balls, the charge to balls ratio being 1:3. The resulting fine powders were granulated using PVA solution (5 wt.%) and the as obtained granules were then dry pressed (200 MPa) in the form of pellets (30 mm diameter and 10 mm height). The pressed pellets were then sintered at 1625 °C for 2 h in an electric furnace [17].

### 2.2. Material characterization

A Gemini Micromeritics analyzer (Micromeritics Instrument Corporation, Norcross, USA) was used for Brunauer–Emmett–Teller (BET) surface area measurements. The BET surface area was measured by nitrogen physisorption at liquid nitrogen temperature (−196 °C) by considering 0.162 nm<sup>2</sup> as the area of cross section of  $\text{N}_2$  molecule. Prior to measurements, the samples were evacuated (up to  $1 \times 10^{-3}$  Torr (0.1333 Pa)) at 180 °C for 2 h. Particle sizes of all the powders were measured using a particle size analyzer (Granulometer G 920, Cilas, France). Phase analysis of the samples was carried out by X-ray diffraction (Bruker's D8 advance system, Bruker's AXS, GmbH, Germany) using  $\text{Cu K}\alpha$  radiation. The crystallite size of  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\gamma$ - $\text{Al}_2\text{O}_3$  powders was estimated with the help of Debye–Scherrer equation ( $\langle L \rangle_{hkl} = K\lambda/\beta_{hkl} \cos \theta$ ; where  $K$  is a constant taken as 1 and  $\beta$  is the integral breadth that depends on the half height width of the particular  $hkl$  plane;  $\lambda = 1.5406 \text{ \AA}$ , the wavelength of the  $\text{Cu K}\alpha$  source; and  $\theta$  is the Bragg's angle) using the XRD data of the corundum (1 0 4) and  $\gamma$ - $\text{Al}_2\text{O}_3$  (4 4 0) reflections, respectively [18]. The BD, AP and WA capacity of the sintered materials were measured by the Archimedes principle using a Mettler balance and attachment (AG 245, Mettler Toledo, Switzerland). The microstructure of dense alumina grains was examined by SEM (JSM-5410, JEOL, Japan) with an energy dispersive analysis with X-rays (Sigma 3.42 Quaser, Kevex, USA) for qualitative and quantitative microanalysis after mounted on araldite platform,

polished and chemically etched (phosphoric acid at  $185 \pm 5^\circ\text{C}$  for 4 min), and gold coated for conductivity.

### 3. Results and discussion

High temperatures might be achieved in the combustion process due to the exothermicity of the redox reactions occurring between the decomposition products of metal nitrates (oxidizers) and urea/carbohydrazide/sucrose (fuels). Stoichiometric compositions of the metal nitrates and urea (or sucrose) were calculated using the total oxidizing and reducing valences of the components which serve as numerical coefficients for stoichiometric balance so that the equivalent ratio is unity and the energy released by the combustion is maximum. According to the concepts used in propellant chemistry, the element Al has reducing valence of +3 and oxygen has an oxidizing valence of  $-2$ , and the valence of nitrogen is zero. Thus, the oxidizing and the reducing valences of aluminium nitrate, magnesium nitrate, urea and sucrose become  $-15$ ,  $-10$ ,  $+6$ , and  $+48$ , respectively [12,13,16,19].

Direct use of propellant chemistry criterion, with the metal precursor (aluminium nitrate) to determine the urea needed to balance the total oxidizing and reducing valences in the mixture, leads to:  $2(-15) + n(+6) = 0$ . Therefore, the stoichiometric composition of the aluminium nitrate and urea redox mixture that releases the maximum energy for the reaction requires  $n = 2.5$  moles of urea per mole of aluminium nitrate. The exothermicity is  $[-382.487 \text{ kcal/mol } (\Delta H^\circ, 25^\circ\text{C})]$  and this significant amount of generated heat confers to the reaction self-sustaining features. According to the same criteria, the amount of sucrose that is required for the synthesis of alumina from aluminium nitrate is 0.3125 moles per mole of aluminium nitrate. It has been reported that characteristics such as porosity fraction, surface area and fineness of the combustion-synthesized powder are depend on the amount of the gases that escape during combustion. Therefore, the use of 6–8 moles of sucrose in the combustion process to prepare single-phase crystalline  $\alpha\text{-Al}_2\text{O}_3$  powder with a surface area of  $>190 \text{ m}^2/\text{g}$  has been reported before [14]. However, the stoichiometric ratios between fuels and oxidizers were selected in the present work in order to compare the influence of fuel type on powders' characteristics. Accordingly, the following combustion reactions will take place:  $(2\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}_{(\text{s})} + 5\text{NH}_2\text{CONH}_{2(\text{s})} \Rightarrow \text{Al}_2\text{O}_{3(\text{s})} + 5\text{CO}_{2(\text{g})} + 8\text{N}_{2(\text{g})} + 28\text{H}_2\text{O}_{(\text{g})})$ , and  $(2\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}_{(\text{s})} + 0.625 \text{C}_{12}\text{H}_{22}\text{O}_{11(\text{s})} \Rightarrow \text{Al}_2\text{O}_{3(\text{s})} + 3\text{N}_{2(\text{g})} + 4.284\text{CO}_{2(\text{g})} + 21.927\text{H}_2\text{O}_{(\text{g})} + 3.216\text{O}_{2(\text{g})})$  when using urea or sucrose as fuels, respectively.

X-ray diffraction patterns of the commercial alumina ACC, and of the combustion synthesized powders UCA5 and SCA5, along with the standard ICDD files of corundum (C),  $\text{MgAl}_2\text{O}_4$  spinel (S) and  $\gamma\text{-Al}_2\text{O}_3$  ( $\gamma$ ) are presented in Fig. 1. It can be seen that the XRD lines of ACC, match with those of standard corundum phase. In the case of UCA5 powder, in addition to the main corundum peaks, some minor peaks corresponding to  $\text{MgAl}_2\text{O}_4$  spinel phase and  $\gamma\text{-Al}_2\text{O}_3$  were also identified. The formation of  $\text{MgAl}_2\text{O}_4$  spinel phase is quite expected as the

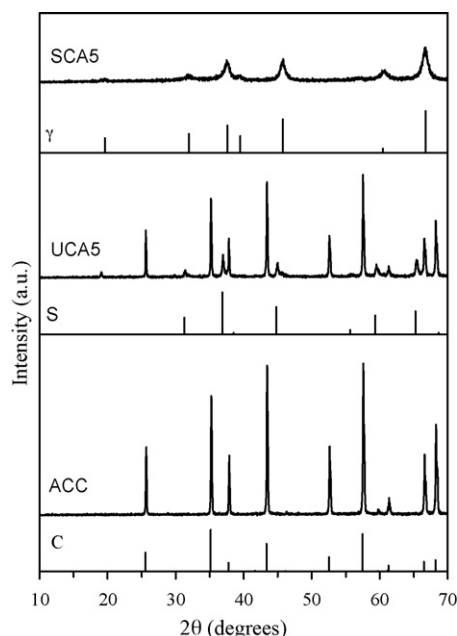


Fig. 1. X-ray diffraction patterns of purchased (ACC) and synthesized  $\text{Al}_2\text{O}_3$  powders (UCA5, SCA5, see Table 1). The diffraction lines of the standard ICDD cards of corundum (C, 00-046-2626),  $\text{MgAl}_2\text{O}_4$  spinel (S, 00-021-1152) and  $\gamma$ -alumina ( $\gamma$ , 00-029-0063) are also presented.

precursor mixture contains 5 mol%  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and the exothermicity of the combustion reaction in the case of urea is high enough to promote the formation of this phase [12,13]. The corundum or  $\text{MgAl}_2\text{O}_4$  peaks were not observed in the case of SCA5 powder due to the lower temperatures developed during combustion synthesis. As a matter of fact, only relatively broad and low intensity peaks of  $\gamma\text{-Al}_2\text{O}_3$  could be detected in this case. Das et al. [14], observed the formation of crystalline corundum upon using 6–8 moles of sucrose as a fuel to synthesize alumina by this process, although the degree of crystallinity obtained under these conditions was lower in comparison to that of urea synthesized UCA5 powder in the present work. This information indirectly confirms the much higher adiabatic temperature generated upon combustion synthesis when urea is used as fuel in comparison to that generated with sucrose. This is the reason for the absence of any XRD peaks due to corundum or  $\text{MgAl}_2\text{O}_4$  spinel phases in the SCA5 powder.

The BET specific surface areas (SSA) of ACC, UCA5 and SCA5 powders are presented in Table 1. The SCA5 powder exhibits a SSA of  $51.2 \text{ m}^2/\text{g}$ , whereas the ACC and UCA5 exhibit only  $8.0$  and  $4.3 \text{ m}^2/\text{g}$ , respectively. A SSA of  $\approx 190 \text{ m}^2/\text{g}$  was already reported for sucrose combustion synthesized powder when using 6–8 moles sucrose as a fuel [14]. The significant lower amount of sucrose (0.3125 moles per mole of aluminium nitrate) used in the present work will originate a smaller amount of gases during combustion, explaining the lower value of SSA of the SCA5 powder. Sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , molecular weight:  $342.30 \text{ g}$ ) is a larger molecule compared with urea ( $\text{N}_2\text{H}_4\text{CO}$ , molecular weight:  $60.06 \text{ g}$ ). The high molecular weight fuel separates the hydrolyzed metal ions (e.g.,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  in the present case) at a greater distance thereby

Table 1

The properties of various alumina powders and their corresponding consolidates sintered at 1625 °C for 2 h<sup>a</sup>

Material	Code <sup>b</sup>	BET SSA (m <sup>2</sup> /g)	Crystallite size (nm)	Average particle size (μm)	Major XRD phase	Green density (g/cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )	Relative density <sup>c</sup> (%)	Apparent porosity (%)	Water absorption (%)
Commercial alumina	ACC	51.2	86	1.07	Corundum	2.05	3.77	94.96	1.23	0.327
Urea was used as fuel	UCA5	8.0	98	7.22	Corundum	2.38	3.46	87.77	1.71	0.494
Sucrose was used as fuel	SCA5 <sup>d</sup>	4.3	16	5.66	γ-Al <sub>2</sub> O <sub>3</sub>	1.79	3.48	88.28	1.40	0.402

<sup>a</sup> All the properties were measured as mentioned in Section 2.<sup>b</sup> UCA5 and SCA5 contain 5 mol% MgO as a sintering additive.<sup>c</sup> In the case of UCA5 and SCA5, the theoretical density (3.942 g/cm<sup>3</sup>) was calculated by using the rule of mixtures (92.8 wt.% Al<sub>2</sub>O<sub>3</sub> with 3.97 g/cm<sup>3</sup> + 7.2 wt.% MgAl<sub>2</sub>O<sub>4</sub> with 3.58 g/cm<sup>3</sup>). The theoretical density of alumina (3.97 g/cm<sup>3</sup>) was considered for the ACC powder.<sup>d</sup> This powder was heat treated at 600 °C for 5 h in the open-air atmosphere.

decreasing the interaction between ions so that the particles formed are smaller, hence, with higher SSA and present a lower degree of agglomeration. This could be the probable reason for the higher specific surface area of the SCA5 powder in comparison to UCA5 powder.

Morphological observations of the ACC, UCA5 and SCA5 powders by SEM revealed some important features. The ACC powder consisted of fine primary particles forming agglomerates with a size of  $\approx 5 \mu\text{m}$ , whereas the UCA5 powder exhibited relatively coarse (diameters in the range of 10–30  $\mu\text{m}$ ) and faceted particles forming some hard agglomerates. The SCA5 powder presented relatively uniform flaky or equiaxed shape particles in the range of 1–4  $\mu\text{m}$ , but connected to each other forming agglomerates. The particle/agglomerate size distributions presented in Fig. 2 shows that the ACC powder has a much narrower size distribution (SD) than SCA5 and UCA5 powders. Combining the information obtained from SEM and particle size analysis, it is possible to conclude that what is being measured by the particle size analyzer in the combustion synthesized powders is mostly the size of agglomerates. On the other hand, the high BET surface area of SCA5 powder is hardly predicted by its SD, as can be understood from its porous and almost amorphous nature (Fig. 1).

The BET SSA and the average size (AS) data of the ground urea combustion synthesized alumina powders containing varying amounts (0.1–5 mol%) of either MgO or AlOOH are presented in Fig. 3. It can be seen that the MgO-doped powders

tend to exhibit higher AS values along the whole MgO concentration range and lower SSA values for MgO < 1 mol% in comparison to powders with added AlOOH. The evolution of the SSA of these last powders shows an abrupt increase with the addition of 0.5 mol% AlOOH reaching a maximum  $> 14 \text{ m}^2/\text{g}$ , followed by an almost symmetric decrease for further additions in such a way that for AlOOH > 1 mol% the values of SSA are always lower than those of MgO-doped powders. The presence of AlOOH in the combustion reaction mixture makes the adiabatic temperature to decrease due to the energy consumption in the conversion of AlOOH into Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O at temperatures of about 1100 °C. Therefore, the SSA of the powders with added AlOOH should increase as they are exposed to relatively lower temperatures. However, this effect is not seen when the concentration of AlOOH is beyond 1 mol% (Fig. 3). The reason for this anomalous behaviour is yet to be analyzed. Nevertheless, the SSA of the UCA5 was lower than that of the SCA5 powder.

The values of BD, AP and WA capacity of compacts made of urea combustion synthesized MgO-doped and AlOOH-added alumina powders after sintering at 1625 °C for 2 h are presented in Fig. 4. Enhanced densification occurred upon doping with small amounts (0.1–1 mol%) of MgO, with BD increasing from  $\sim 2.9$  to  $\sim 3.5 \text{ g/cm}^3$ , accompanied by drastic decreases of AP and WA capacity values. However, no appreciable changes in the sintered properties of the specimens could be observed with further increasing magnesia beyond 1.0 mol%. In the case of added AlOOH, there was a first decrease of AP, but the BD was almost unaffected by the content of this additive (Figs. 4(A)). The beneficial effect of MgO can be attributed to its twofold

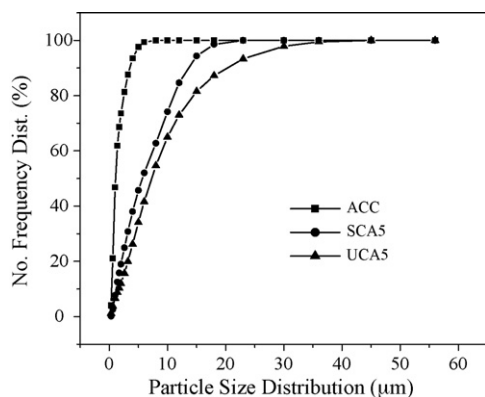


Fig. 2. Particle/agglomerate size distribution of as purchased ACC, and ground SCA5 and UCA5 powders (see Table 1).

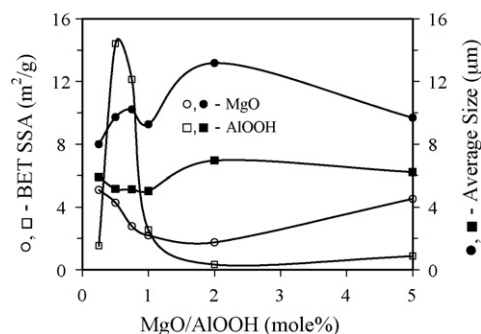


Fig. 3. Effects of MgO-doping and AlOOH-adding on BET surface area and measured average size of urea-combustion synthesized Al<sub>2</sub>O<sub>3</sub> powders.



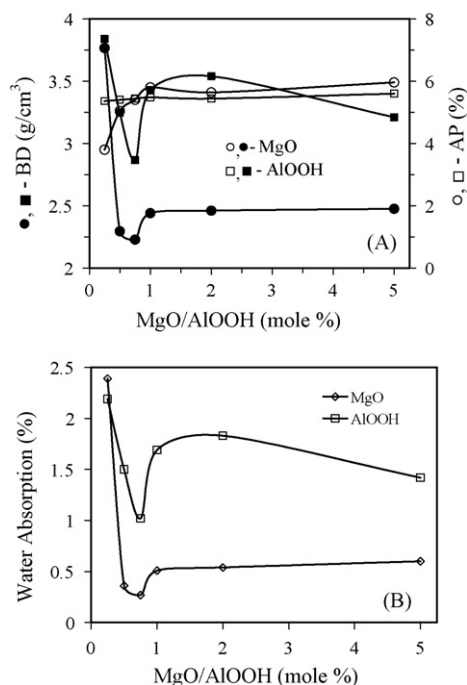


Fig. 4. Effects of MgO-doping and AlOOH-adding on BD and AP (A), and on WA capacity (B) of compacts derived from urea-combustion synthesized  $\text{Al}_2\text{O}_3$  powders after sintering at 1625 °C for 2 h.

role as sintering aid and grain growth inhibitor [7]. The increase of porosity with increasing MgO concentration could be related to the formation of  $\text{MgAl}_2\text{O}_4$  phase. 5.0 mol% MgO will react with alumina leading to the formation of 7.2%  $\text{MgAl}_2\text{O}_4$  spinel in  $\text{Al}_2\text{O}_3$  matrix during combustion/sintering processes as the standard stoichiometric  $\text{MgAl}_2\text{O}_4$  spinel contains 71.7%  $\text{Al}_2\text{O}_3$  and 28.3% of MgO. Further, according to the phase diagram of binary MgO– $\text{Al}_2\text{O}_3$ ,  $\text{MgAl}_2\text{O}_4$  is the only phase formed at temperatures up to 1600 °C. At this temperature, the solid solubility of MgO and  $\text{Al}_2\text{O}_3$  in the spinel is 2 and 6%, respectively. After sintering at 1625 °C for 2 h, the amount of  $\text{MgAl}_2\text{O}_4$  spinel formed in the alumina matrix would be more than ~7.2%. The formation of  $\text{MgAl}_2\text{O}_4$  is also associated with a volume expansion of about 8% [20]. Therefore, the beneficial effect of MgO as a sintering aid could be offset by the volume expansion associated with spinel phase formation for MgO concentrations >1.0 mol%.

The values of BD, RD, AP and WA capacity of sintered (1625 °C for 2 h) samples derived from ACC, UCA5 and SCA5 powders are presented in Table 1 together with green density of the compacts, crystallite size, average (particle/agglomerate) size and major XRD phases present in the powders. It can be seen that the compacts derived from ACC powder exhibits superior sintering ability in comparison to those derived from combustion synthesized powders, UCA5 and SCA5, achieving a relative densities of about 95, 87.88 and 88.28%, respectively. It has been reported that the  $\gamma\text{-Al}_2\text{O}_3$  undergoes an extensive phase-transformation associated with rapid grain growth, which does not allow attaining higher densification [21]. This could apply to the SCA5 powder that consists of  $\gamma\text{-Al}_2\text{O}_3$ , but not to the UCA5 powder. Therefore, besides the reasons

presented in the previous paragraph, the poor densification ability of the combustion synthesized powders in the present work can also be attributed to the presence of hard and porous agglomerates formed under the high temperatures achieved upon synthesis. These hard agglomerates are difficult to destroy and the remaining large inter-agglomerate pores cannot be eliminated upon sintering. This explains why even the SCA5 powder with a high specific surface area ( $\sim 51.2 \text{ m}^2/\text{g}$ ) exhibits poor densification ability.

Fig. 6 shows the SEM micrographs of sintered samples derived from urea-combustion synthesized  $\text{Al}_2\text{O}_3$  powders doped with 0.1 and 5.0 mol% MgO (Fig. 5(A) and (B)), or with added 0.1 and 5.0 mol% AlOOH (Fig. 6(A) and (B)). The shape of the grains in Fig. 5(A) and (B) is the same and their size (5–10  $\mu\text{m}$ ) decreases somewhat for the higher amount of MgO. The same trend is observed for the AlOOH-containing materials, but the grains are coarser (8–20  $\mu\text{m}$ ), (Fig. 6(A) and (B)). The values of apparent porosity for the compacts derived from 0.1 and 5 mol% AlOOH (Fig. 4) were not affected by the presence of AlOOH, probably due to its partial conversion into  $\alpha\text{-Al}_2\text{O}_3$  during combustion synthesis.

The SEM micrographs of the sintered (1625 °C for 2 h) compacts derived from ACC and SCA5 powders are compared in Fig. 7. Both micrographs reveal the presence of closely packed grains, but the grains are much finer in the sample made of commercial powder. These results suggest that a well-deagglomerated powder is essential for enhancing densification and limit the grain growth and that higher densification levels could be obtained for the compacts derived from all the powders, provided that an efficient deagglomeration process was achieved. This has not been the case after 1 h of planetary ball mill used in the present work, since almost full dense

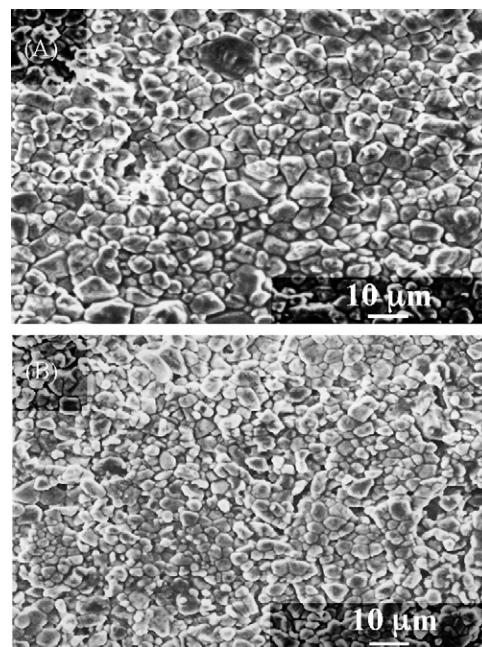


Fig. 5. SEM micrographs of sintered (1625 °C for 2 h) compacts derived from urea-combustion synthesized  $\text{Al}_2\text{O}_3$  powders doped with 0.1 mol% MgO (A), and from 5.0 mol% MgO (B).

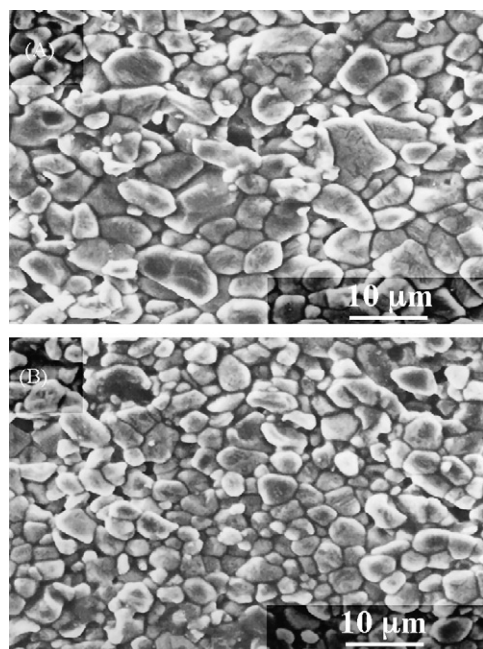


Fig. 6. SEM micrographs of sintered (1625 °C for 2 h) compacts derived from urea-combustion synthesized  $\text{Al}_2\text{O}_3$  powders containing 0.1 mol%  $\text{AlOOH}$  (A), and from 5.0 mol%  $\text{AlOOH}$  (B).

bodies should have been obtained from commercial powder if the agglomerates have been efficiently broken down. However, the aim of the present work was not to optimise the deagglomeration process, but to process the different powders in the same manner to draw conclusion about the influence of the combustion synthesis on the sintering ability of the powders.

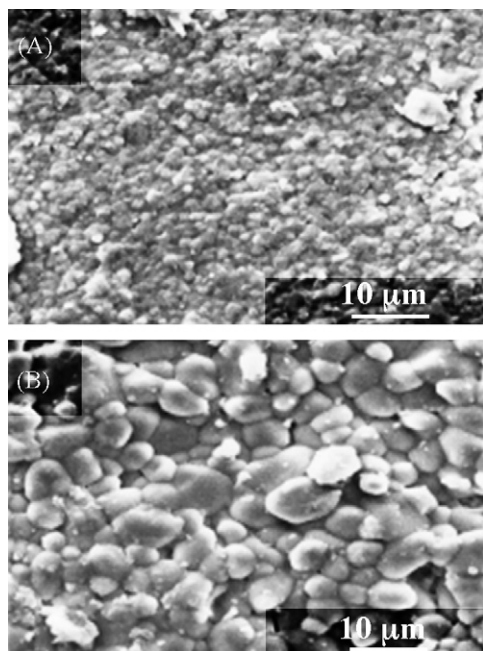


Fig. 7. SEM micrographs of sintered (1625 °C for 2 h) compacts derived from ACC (A) and SCA5 (B) powders (see Table 1).

#### 4. Conclusions

The following conclusions can be drawn from the present work:

- (1) Fully crystalline  $\alpha\text{-Al}_2\text{O}_3$  can be obtained by combustion synthesis using urea as a fuel. The use of sucrose as fuel leads to the formation of  $\gamma\text{-Al}_2\text{O}_3$  powder with high specific surface area. Even though both combustion synthesis routes have resulted in the formation of submicron sized individual particles, they form hard agglomerates that are difficult to destroy and hinder densification upon sintering. The potential advantages of the less extended agglomeration obtained when sucrose is used as fuel are lost in the case of alumina powders, because the transformation of  $\gamma$  to  $\alpha$ -phase is not efficiently retained upon sintering.
- (2) Small amounts of  $\text{MgO}$  (0.1–1.0 mol%) act as a grain growth inhibitor, while increasing bulk density of urea combustion synthesized  $\alpha\text{-Al}_2\text{O}_3$  powder upon sintering. Higher  $\text{MgO}$  concentrations led to the formation of  $\text{MgAl}_2\text{O}_4$  spinel phase, which is associated with a volume expansion of about 8% that offsets the beneficial effect of  $\text{MgO}$  as a sintering aid.
- (3) The decrease of the adiabatic temperature of the combustion reaction when urea is used as fuel by adding boehmite did not improve the sintering ability of combustion synthesized  $\alpha\text{-Al}_2\text{O}_3$  powder.
- (4) Considering that the formation of hard agglomerates during the combustion synthesis of alumina powders is the main drawback for the sintering ability, combustion synthesized  $\alpha\text{-Al}_2\text{O}_3$  powders could be preferentially recommended for producing porous ceramic materials.

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