Effect of Mechanical Activation on the Sintering of Transition Nanoscaled Alumina

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Abstract:
Consolidation of transition nanoscaled alumina (γ, δ, θ, and α-phase) at P=500 MPa and T=1500°C, gave compacts with density of 70% TD and a vermicular structure. After mechanical activation by attriting, the transformation rate of \(\gamma-Al_2O_3 \rightarrow \delta-Al_2O_3 \rightarrow \theta-Al_2O_3 \rightarrow \alpha-Al_2O_3\) was reduced from 1126 to 1079°C. The density of the sintered compacts at 1500°C was 96% TD. The \(\alpha-Al_2O_3\) microstructure exhibited a grain size distribution from 100 to 900 nm.

Keywords: Transition alumina, Nucleation, Sintering, Grain size, Microstructure

Introduction

\(Al_2O_3\) nano powder is a superfine ceramic powder which can be widely used in the field of electronics, fine ceramics, composite materials, biomaterials etc. A lot of different processes for production of ceramic nano powders have been developed such as thermal spraying, coprecipitation, heterogeneous azeotropic distillation, sol-gel, laser induced chemical vapour deposition etc.

Studies on producing nanocrystalline ceramics from nano powders have highlighted the problem of achieving high densities without excessive grain growth. It is particularly true for transition alumina powders which are currently produced with a very high specific surface area and ultra fine crystalline size. In some cases, a solid-state phase transformation has been exploited to aid sintering at these temperatures to produce high-density polycrystalline alumina with submicron grain size.

It is known that many transformations in ceramics proceed by a nucleation and growth process. To initiate the transformation sufficient energy must be supplied to the system to exceed the nucleation barrier. After nucleation the transformation occurs rapidly, by growth.

Kumagai et al [1,2] showed that the nucleation step may effectively be eliminated by supplying nuclei to the system. This process known as seeding, involves adding ceramic particles of the high-temperature phase to the ceramic matrix to be transformed. By eliminating the nucleation step less energy is required for the transformation and it can occur at a lower temperature. They showed that \(5 \times 10^{13}\) seeds/cm³ or 1.5 %wt \(\alpha-Al_2O_3\) with particle
size of 0.1µm represents an optimum concentration for θ-α transformation, while Legros [3] estimated 2⋅10^{14} seeds/cm$^3$ of α-Al$_2$O$_3$ with a particle size of 0.15 µm.

A number of researchers have attempted to influence the transformation to α-Al$_2$O$_3$ using additives. Wakao and Hibino [4] reported that the temperature of θ to α-Al$_2$O$_3$ was reduced with CuO and Fe$_2$O$_3$, lowering the transformation temperature to as low as 1050°C. Bye and Simpkin [5] added chromium and iron via a solution technique to a γ-Al$_2$O$_3$ powder. They showed that the transformation temperature was lowered to 1100°C with 2% Fe and to 995°C with 5% Fe.

The goal of this paper is obtaining of α-Al$_2$O$_3$ dense ceramics starting from transition nanocrystalline alumina, which contains some amount of α−Al$_2$O$_3$. Using mechanical activation, the present inactive α-Al$_2$O$_3$ can be activated and together with the created lattice defects can act as heterogeneous nucleation sites in the system, controlling the transformation to α-Al$_2$O$_3$ and enhancing densification.

**Experimental Procedure**

The nano aluminium oxide powder (99.98%) used in this study was obtained from IBU-tech, Germany. This powder was obtained from aluminium tri-sec-butylate at 850°C by a pulse reactor technique. Characteristics of the as received powder are reported in Tab. I.

**Tab. I Characteristics of a transitional alumina nano powder**

<table>
<thead>
<tr>
<th>Specific surface area (BET), m$^2$/g</th>
<th>XRD phases</th>
<th>Tap density, g/dm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>124.0</td>
<td>δ, θ, γ, α</td>
<td>37.55</td>
</tr>
</tbody>
</table>

The powder morphology was observed via transmission electron microscopy (TEM). Specific surface area was measured using nitrogen gas adsorption (multipoint BET method) (Gemini, Micromeritics USA).

DTA/TG investigations were performed by NETZSCH STA 409C in air atmosphere in the temperature interval 20-1500°C using a heating rate of 10°min$^{-1}$.

Phase analysis of the alumina was carried out by X-ray diffraction (XRD) with Ni-filtered CuKα radiation.

Mechanical activation (wet milling) of the starting powder was performed by attritor mill NETZSCH using alumina balls at pH 5 for 0.5, 1 and 1.5h. The suspension with a solid load of 30%wt. was used. Viscosity of the slip was controlled using a Viscotester 6l/R, Haake.

After milling, the suspension was sieved with a 11µm sieve, dried in porous plates at RT, milled by agate mortar and dried at 105°C.

Pressing was carried out in two steps: First, uniaxially at P=2 MPa (WEBER PRESSEN KIP 100) and by cold isostatic pressing (CIP) at 500 MPa (WEBER PRESSEN KIP 500 E).

Samples in the form of 30x4x4 mm$^3$ rods were produced. Sintering was performed under a constant heating rate of 10°min$^{-1}$ in the interval RT-1500°C without soaking time.

The green density of the compacts was determined by measuring the mass and volume with the help of a micrometer to the nearest of 0.001 cm and the final density was determined by the Archimedes displacement method.

Shrinkage was followed by dilatometry (NETZSCH TMA 402E) in air atmosphere, using a heating rate of 10°min$^{-1}$ in the temperature interval 20–1500°C.
Microstructure and grain sizes were observed by scanning electron microscopy (Leica IS 110) on fractured and polished surfaces. The polished samples were thermally etched at 100°C below sintering temperature for 1h to reveal the grain structure.

**Results and Discussion**

TEM micrographs show the spatial arrangement of nano particles. The size of primary alumina particles was 5-50 nm. One part of these primary particles is aggregated in the as received powder and the aggregate size was in ranged from 100-600 nm (Fig.1).

![Fig.1 TEM photograph of the starting transition alumina powder (bar 30 nm)](image)

XRD shows that the powder consisted of δ,θ,γ and α phases or using their common name “Greek-letter-alumina” [6].

The dominant phases are δ and γ-Al₂O₃. The θ-crystalline phase which is the last metastable transition alumina with a cubic close packing of oxygen ions and stable α-phases with hexagonal oxygen packing, are present in approximately the same quantities cca 10±1% (Fig.2).

DTA investigation of the starting powder showed one exo-peak at 1304°C that corresponds to the α-Al₂O₃ transformation. Cold isostatic pressing of 500 MPa, shifted the exo-peak to 1126°C. The transformation temperature is reduced for 178°C. According to [7], the effect of pressing is to reduce the apparent incubation time and to increase the constants of the transformation kinetics.

The green density of the compacts after CIP was 2.01 g/cm³ that is 0.56TD. After sintering in the interval RT-1500°C, without soaking time at the final temperature, the density was 2.78 g/cm³ that is 0.70TD. Open porosity was 28%.

The sinterability of the compacts formed from the starting powder is shown in Fig.3, where ΔL/L₀ is plotted as a function of the temperature (ΔL= L₀-L), where L₀ is the initial length of the sample and L is instaneous sample length. The temperature at which measurable shrinkage begins is 970°C and it is comparable to that commonly observed for compacts of
sub micrometer $\alpha$-$\text{Al}_2\text{O}_3$ powders [8]. The densification of transition alumina shows two regions of densification during the constant heating rate.

![X-ray diffraction patterns of starting transition $\text{Al}_2\text{O}_3$](image)

**Fig. 2** X-ray diffraction patterns of starting transition $\text{Al}_2\text{O}_3$

The first one is a distinctive feature of the sintering kinetics, with rapid shrinkage in the temperature region 1020 – 1150°C, with a maximum shrinkage rate at 1097°C. This densification is associated with the phase transformation of $\gamma$-$\text{Al}_2\text{O}_3$ via $\delta$ and $\theta$ to a stable $\alpha$-phase. The second region of shrinkage above 1150°C is densification of the $\alpha$-$\text{Al}_2\text{O}_3$ at higher temperatures. At the temperature of 1500°C the shrinkage value was $\Delta L/L_0= 13.7\%$, where the density of 0.70TD was achieved.

![Shrinkage ($\Delta L/L_0$) and shrinkage rate of the compact formed of the as-received powder, during sintering at 10°min$^{-1}$ to 1500°C](image)

**Fig. 3** Shrinkage ($\Delta L/L_0$) and shrinkage rate of the compact formed of the as-received powder, during sintering at 10°min$^{-1}$ to 1500°C
The microstructure of the sintered sample up to 1500°C is shown in Fig. 4. The microstructure is of a vermicular network in which both, the pores and the pore channels are the same scale as the \( \alpha-\text{Al}_2\text{O}_3 \) grains. The elongated pores have a size of 0.5-1.8 \( \mu m \).

Based on these results, one can conclude that starting nanosized transition alumina powder possesses low activity related to their sinter parameters. The kinetics of the \( \alpha \)-transformation has been studied by Dynys and Halloran [7], who reported that the rate of transition to \( \alpha-\text{Al}_2\text{O}_3 \) strongly depends on the mechanical pre-treatment of the powder. They showed that mechanical milling of the powder (ball mill for 13h) can reduce the time for complete transformation at 1150°C.

Mechanical activation causes changes in a materials structure, which has a direct influence on properties dependent on structure-transport and reactive properties [9-12].

During wet milling chemical and physical interactions occur between the alumina particles surface and the surrounding medium. This interaction can be influenced by surface changes, the type and concentration of surface defects, unsaturated bonding states and the morphology of the particle surface. In wet grinding the reological and colloid chemical behaviour of the particles is crucial in respect to the process flow and resulting material properties. The fine particles become electrically charged when they are dispersed in an aqueous system charged in the order of the state of the lattice, which are caused by formation of the lattice distortion, surface defects and decreasing crystallite size [9,10].

The mechanical activation was realized by wet milling- attriting at pH 5. At this pH value the viscosity of the slip was minimal.

According to Dynys and Halloran [7] after milling, the nucleation frequency increased \( 10^4 \) times.

The specific surface area of the mechanically activated powders was 126.5 m\(^2\)/g after 0.5h milling, 123 m\(^2\)/g after 1h milling and 83 m\(^2\)/g after 1.5h milling. The observation that the BET surface area is a little affected by milling of 0.5h, suggests that a small amount of new surfaces was created. It is possible, that even this small new surface provides potent sites for nucleation.

One of the reasons for the reduction of the specific surface area after milling of 1 and 1.5h is the appearance of agglomeration. The obtained powders possess a high surface energy that is one of the reasons for agglomeration during attriting. Several studies showed that agglomerates and aggregates cause particle packing inhomogenities in the green
microstructure [13]. The packing inhomogeneities cause porosity inhomogeneities in the sintered microstructure, which impede successful densification.

After milling of 0.5h, uniform distribution of the $\alpha$-$\text{Al}_2\text{O}_3$ present occurs among the metastable $\delta, \gamma$ and $\theta$-$\text{Al}_2\text{O}_3$. DTA of the mechanically activated and pressed powder at 500 MPa showed phase transformation to $\alpha$-alumina at 1079°C.

It appears that both, milling and compaction involve creation of large contact stresses, which cause an increase in the internal energy of the material. The created lattice defects, act together with $\alpha$-$\text{Al}_2\text{O}_3$, as heterogeneous nucleation sites for the transformation.

The starting powder thermally treated at 1200°C/4h showed the presence of $\gamma$, $\delta$, $\theta$, and $\alpha$-$\text{Al}_2\text{O}_3$, Fig.5. Powder mechanically activated for 0.5h, thermally treated at 1100°C/4h showed the presence only of $\alpha$-$\text{Al}_2\text{O}_3$, that meant a complete $\gamma\to\delta\to\theta\to\alpha$-$\text{Al}_2\text{O}_3$ transformation, Fig.6.

![Image](image.jpg)

**Fig. 5** X-ray diffractogram of the starting powder thermally treated at 1200°C/4h, crystalline phases: $\gamma$-$\text{Al}_2\text{O}_3$, $\delta$-$\text{Al}_2\text{O}_3$, $\theta$-$\text{Al}_2\text{O}_3$, $\alpha$-$\text{Al}_2\text{O}_3$

The results given in Fig. 5 illustrate that $\alpha$-$\text{Al}_2\text{O}_3$ present in the starting powder with a concentration of 10±1% w, has no seeding effect at the temperature/time of RT- 1200°C/4h. After mechanical activation of the starting powder, pressing and annealing at 1100°C/4h, due to the generated sites of nucleation, a complete transformation to $\alpha$-$\text{Al}_2\text{O}_3$ was realised, Fig.6.

The green density of the isostatic pressed bodies of the mechanically activated powder was 2.14 g/cm$^3$ (0.59 TD) for the milling time of 0.5h. The shrinkage during sintering of the compacts formed from of mechanically activated powder is shown in Fig.7.

The shrinkage in the temperature interval RT-1500°C is 22%. The first region of densification associated with the phase transformation to $\alpha$-$\text{Al}_2\text{O}_3$ has a maximum shrinkage rate at 1038°C that is 59°C lower than for the starting powder. The second maximum of the shrinkage rate, associated with the densification of $\alpha$-$\text{Al}_2\text{O}_3$ is at 1400°C. The density of the sintered samples at 1500°C was 3.82 g/cm$^3$ (0.96TD). The same value of relative density was obtained by Karagedov and Lyakhov [15].
Fig. 6 X-ray diffractogram of the mechanically activated powder, thermally treated at 1100°C/4h, crystalline phase: α-Al₂O₃

Fig. 7 Shrinkage (ΔL/L₀) and shrinkage rate of the mechanically activated systems, during sintering at 10°min⁻¹ to 1500°C

The microstructure of the samples sintered in the region RT-1500°C without soaking time is shown in Fig 8.
The α-alumina microstructure exhibits grain size distribution from 100 to 900 nm. There is no intra-granular pore formation which indicates that the densification rate may have been faster than the grain growth rate at the processing temperature (1500°C) (14).

There are some inter-granular pores adjacent to grains indicating that these pores are probably formed during α-Al₂O₃ discontinuous grain growth. The size of the pores located at the grain boundary is 100-300 nm.

Conclusions

Transition nano alumina powder obtained by the pulse reactor technique besides γ, δ, θ - Al₂O₃ contains also cca 10±1 %wt. α-Al₂O₃. This α-Al₂O₃ has no seeding effect. System consolidation was achieved by applying isostatic pressure of 500MPa and non-isostatic sintering RT-1500°C, obtaining compacts with a vermicular structure and a density of 0.70 TD. The pores and pore channels are on the same scale as the α-Al₂O₃ grains The elongated pores have a size of 0.5-1.8 µm. Using mechanical activation, realised by attriting for 0.5h treatment, an active nano-powder was obtained, in which the transformation into α-Al₂O₃ was carried out at 1079°C. The consolidated system, RT-1500°C has a density of 0.96 TD and a grain size of 100-900 nm.

References


Садржај: Консолидација прелазне нано алумине (γ, δ, θ и α-фазе) на P=500 MPa и T=1500°C дала је испреске са густином од 70% од теоријске густине и вермикуларном структуром. После механичке активације априцијом брзина трансформације γ-Al₂O₃→δ-Al₂O₃→θ-Al₂O₃→α-Al₂O₃ је редукована од 1126 до 1079°C. Густина синтерованих испресака на 1500°C је била 96% од теоријске густине. Микроструктура α-Al₂O₃ је показала расподелу величина зрна од 100 до 900 нм.
Кључне речи: Прелазна алумине, нуклеација, синтеровање, величина зрна, микроструктура.