Sintering of $\alpha$-$\text{Al}_2\text{O}_3$-seeded nanocrystalline $\gamma$-$\text{Al}_2\text{O}_3$ powders

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Abstract

This paper demonstrates that seeding nanocrystalline transition alumina powders is a viable option for producing high quality, alumina-based ceramics. By using $\alpha$-$\text{Al}_2\text{O}_3$ concentrations of $5.125$ wt.\% $\alpha$-$\text{Al}_2\text{O}_3$ seed particles (equivalent to $5 \times 10^{14}$ seeds/cm$^3$ of $\gamma$-$\text{Al}_2\text{O}_3$) the sintering temperature is reduced from $1600$–$14$ C for unseeded $\gamma$-$\text{Al}_2\text{O}_3$ to $1300$–$1400$ C in dry pressed powders. The scale of the sintered microstructure is related to $N_v^{1/3}$ and thus a $100$-nm grain size is obtained. It is apparent that seeding is necessary for producing dense, alumina-based ceramics from nanocrystalline transition alumina powders. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: $\text{Al}_2\text{O}_3$; Microstructure-final; Seeding; Sintering

1. Introduction

Alpha alumina ($\alpha$-$\text{Al}_2\text{O}_3$) is utilized in many areas of modern industry because of its unique mechanical, electrical, and optical properties. Since the properties exhibited by a ceramic are governed by its microstructure, refining $\alpha$-$\text{Al}_2\text{O}_3$ processing techniques to obtain superior microstructures is of great interest. Recently, transition alumina has attracted much attention because of its intrinsically nanocrystalline nature and because it can be synthesized by a variety of techniques. The most common transition alumina is $\gamma$-$\text{Al}_2\text{O}_3$ which forms from virtually all alumina precursors, except diaspore.

Upon heating, $\gamma$-$\text{Al}_2\text{O}_3$ undergoes a series of poly-morphic transformations:

$$\gamma$-$\text{Al}_2\text{O}_3 \rightarrow \delta$ $\rightarrow \theta$ $\rightarrow \alpha$-$\text{Al}_2\text{O}_3$$

The $\alpha$-$\text{Al}_2\text{O}_3$ phase transformation occurs by nucleation and growth. During the reconstructive transformation from theta to alpha alumina there is a specific volume reduction ($28.6$–$25.6$ cm$^3$/mol $\text{Al}_2\text{O}_3$), due to the difference in theoretical density ($3.6$–$3.986$ g/cm$^3$ $\text{Al}_2\text{O}_3$). A low intrinsic nucleation density results in large spacing between nucleation events and the formation of micrometer scale, single crystal $\alpha$-$\text{Al}_2\text{O}_3$ grains with dendritic protrusions surrounded by continuous pore channels. The resultant vermicular microstructure requires sintering temperatures $>1600$ C to reach high densities. To obtain dense, fine-grained $\alpha$-$\text{Al}_2\text{O}_3$ at low temperatures, the scale of the vermicular microstructure must be minimized.

A number of papers report the effect of a small amount of ceramic oxide seed particles on microstructure evolution during the $\theta$ to $\alpha$-$\text{Al}_2\text{O}_3$ phase transformation. In unseeded boehmite, the intrinsic nucleation density is $10^{8}$–$10^{11}$ nuclei/cm$^3$ $\text{Al}_2\text{O}_3$ and $1200$ C is required to fully transform to alpha alumina. The addition of seeds, which are isostructural with $\alpha$-$\text{Al}_2\text{O}_3$, provides low energy sites for heterogeneous nucleation and thus reduces the energy barrier required for nucleation. The seeds have a number of contacts with $\theta$-$\text{Al}_2\text{O}_3$ and thus, provide multiple nucleation sites. In conjunction with the lower energy barrier and the larger number of nucleation sites, the phase transformation takes place at lower temperatures. For $5$ wt.% seeded $\gamma$-$\text{Al}_2\text{O}_3$ samples, the transformation temperature and activation energy were decreased by $75$ C and $170$ kJ/mol, respectively, compared to unseeded $\gamma$-$\text{Al}_2\text{O}_3$.

Kumagai and Messing reported that a seed concentration of $5 \times 10^{13}$ seeds/cm$^3$ $\gamma$-$\text{Al}_2\text{O}_3$ is optimal for controlling the microstructure evolution during the $\theta$ to $\alpha$-$\text{Al}_2\text{O}_3$ phase transformation. By using fine particles
of the sinterability of to achieve a green density of 63% in an effort to improve dense. Wu et al. used high-pressure cold isostatic pressing 1600 powder obtained from powders above the y-Al2O3 phase transformation and inhibited complete densification.

To circumvent the formation of dendritic shaped grains as a means for obtaining dense y-Al2O3 at lower temperatures, Wu et al. heated nanocrystalline y-Al2O3 powders above the θ to y-Al2O3 phase transformation temperature prior to compaction.8 The aim of the experiments was to investigate whether nanocrystalline y-Al2O3 powder obtained from y-Al2O3 would sinter better than commercially available α-Al2O3 powder. The transformed y-Al2O3 powders sintered to 95% density and a grain size of ~1 μm at 1350°C. Freim et al. used rapid heating with a microwave furnace to alter the transformation, but no significant benefit was reported.21

Tsai et al. investigated the effects of ceramic oxide dopants on the phase transformation and densification of colloidal gels made from high purity, fumed y-Al2O3.17 Undoped y-Al2O3 samples transformed to α-Al2O3 at 1260°C and sintered to 53% density at 1400°C and 75% at 1600°C. Densities for samples sintered at 1600°C for 4 h increased when doped with 2 wt.% TiO2 (98%), MgO (82%), and ZrO2 (80%) but there was no significant effect on the phase transformation. Many sesquioxide dopants (e.g. α-Fe2O3), that are isostructural with α-Al2O3, have been shown to nucleate the phase transformation.22,23

Unseeded boehmite (γ-AlOOH) transformed to 70% dense α-Al2O3 after 100 min at 1200°C, and reached 97% density after 100 min at 1600°C.11 Using commercial boehmite Kumagai and Messing showed that seeding with 1.5 wt.% α-Al2O3 resulted in 99% density after sintering for 100 min at 1200°C.10 In another investigation, they reported that they could achieve 95% density after 6 h at 1140°C by seeding a high purity, alkoxide-derived boehmite.14

From the previous investigations, it is evident that the number concentration of α-Al2O3 seeds, the homogeneity of the seed distribution in the transition alumina matrix and the purity of the starting materials have significant effects on the transformation kinetics. The use of commercial powders, which are inherently agglomerated, limits the attainable homogeneity of the seed distribution, but, avoids the costly and time intensive preparation of high purity sols from alkoxide precursors.

The objectives of this investigation, therefore, were to (1) investigate the effect of α-Al2O3 seed addition on the microstructure evolution, and densification behavior of high purity, commercial γ-Al2O3, and (2) determine the effects of agglomeration and green density on the effectiveness of α-Al2O3 seeding. The α-Al2O3 powder selected for this investigation is the same as that used by Tsai and Hsieh.17 The phase transformation kinetics of the seeded powder described in this paper was reported earlier.3

2. Experimental procedure

A high purity, nanocrystalline fumed γ-Al2O3 powder produced by flame hydrolysis of aluminum chloride, was selected for this investigation. A 2.5 wt.% dispersion was prepared by adding deionized water and adjusting the pH to 3.0 with 2 M nitric acid. To reduce the agglomerate size, the dispersion was stirred and periodically sonicated for three days. The dispersed agglomerate size, determined by dynamic light scattering was ~86 nm.

Commercial α-Al2O3 powder was used to obtain fine seed particles.4 A 10 wt.% dispersion was prepared by adding α-Al2O3 powder to deionized water and adjusting the pH to 3.0 with 2 M nitric acid. The dispersion was stirred for three days and periodically sonicated to break up agglomerates. The seeds were obtained by removing agglomerates by centrifugation for 45 min at 2000 rpm (0.2 m radius). The seed dispersion (i.e. the supernatant after centrifuging) was added to the γ-Al2O3 dispersion while stirring to obtain seed concentrations of 0, 1.25, 2.5 and 5 wt.% α-Al2O3, on a γ-Al2O3 weight basis. The seeded sols were rapidly dried in a rotary evaporator to prevent mass segregation of the α-Al2O3 seeds during drying.

After drying, the powders were ground into agglomerates <44 μm (~325 mesh) with a high purity alumina mortar and pestle. The powder was uniaxially pressed at 280 MPa in a zinc stearate lubricated hardened steel die. The pellets were then cold isostatically pressed in latex bags at 280 MPa for 30 min. The pellet dimensions were

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2 Aerosil® Aluminum Oxide C, Degussa Corp., Ridgefield Park, NJ.
3 Microtrac UPA, Leeds & Northrup, St. Petersburg, FL.
4 Taimei DAR, Taimei Chemical Industrial Co., Nagano, Japan.
5 Cold Isostatic Press, Autoclave Engineers, Erie, PA.
6.2 mm diameter and ≈3 mm thick. The green densities of the pressed pellets, determined by the dimensional technique, were ·54%, based on the γ-Al₂O₃ theoretical density of 3.2 g/cm³.

For comparison, a commercial alumina powder containing 35% δ-Al₂O₃ and 65% α-Al₂O₃ was also sintered. A dispersion was prepared by adding 10 wt.% powder to deionized water and adjusting the pH to 3.0 with 2 M nitric acid. The dispersion was stirred for three days and periodically sonicated to break up agglomerates. The dispersed agglomerate size, determined by dynamic light scattering, was ·0.3 μm. The powders were then rapidly dried in a rotary evaporator and lightly ground into agglomerates. The powders containing 35% δ-Al₂O₃ and 65% α-Al₂O₃ phase transformation samples were sintered in a box furnace. The furnace was heated at 5°C/min to 1000–1600°C and held for 30 min. The furnace was cooled at 15°C/min to 850°C and then at 15°C/min to the sintering temperature of 1000–1600°C and held for 30 min. The furnace was cooled at 15°C/min to 400°C and then turned off. To examine morphological development during the α to γ-Al₂O₃ phase transformation, samples were polished and thermally etched for 30 min at 500°C lower than the sintering temperature for samples sintered at ≤1200°C and 100°C lower than the sintering temperature for samples sintered at ≥1400°C. The powders were sputter coated with gold to prevent charging during SEM examination. Grain size was determined from micrographs using the mean linear intercept method and multiplying by 1.56.

### Table 1

<table>
<thead>
<tr>
<th>Particle size (nm)</th>
<th>Volume frequency (%)</th>
<th>Number frequency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300–400</td>
<td>0.1</td>
<td>0.0001</td>
</tr>
<tr>
<td>200–300</td>
<td>4.2</td>
<td>0.01</td>
</tr>
<tr>
<td>100–200</td>
<td>29.4</td>
<td>0.34</td>
</tr>
<tr>
<td>90–100</td>
<td>0.6</td>
<td>0.03</td>
</tr>
<tr>
<td>80–90</td>
<td>3.1</td>
<td>0.19</td>
</tr>
<tr>
<td>70–80</td>
<td>3.2</td>
<td>0.29</td>
</tr>
<tr>
<td>60–70</td>
<td>5.3</td>
<td>0.74</td>
</tr>
<tr>
<td>50–60</td>
<td>15.6</td>
<td>3.61</td>
</tr>
<tr>
<td>&lt;50</td>
<td>38.5</td>
<td>94.8</td>
</tr>
</tbody>
</table>

The seed frequency, \( f_s \), was calculated from the seed particle size distribution and the seed concentration as follows:

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f_s = \frac{N_s}{V_{tot}} = \frac{6m_a}{\pi\rho_a V_{tot}} \sum_{i=1}^{n} \frac{w_{fi}}{d_i^2}
\]

where \( N_s \) is the number of seeds added, \( V_{tot} \) is the total volume of the seed powder, \( m_a \) is the weight of seeds added, \( \rho_a \) is the theoretical density, and \( w_{fi} \) is the weight fraction of seeds with diameter, \( d_i \). The seed number densities were calculated from the data in Table 1. At a seed concentration of 1.25 wt.% the seed frequency is \( 5 \times 10^{14} \) seeds/cm³ γ-Al₂O₃ and the frequency increases to \( 2 \times 10^{15} \) seeds/cm³ γ-Al₂O₃ at a seed concentration of 5 wt.%. The seed frequency on the transition alumina powder is 115 m²/g. The transition alumina powder is a mixture of gamma and delta alumina. The major impurities are 320 ppm Fe, 170 ppm Si and 390 ppm Ti. The chlorine content was not measured but was listed by the manufacturer as <0.5%. Most studies on seeded boehmite have used gels stabilized at pH 3 and no effects of alumina solubility on the α-Al₂O₃ transformation have been observed.

All samples transformed to >95% α-Al₂O₃ when sintered at 1100°C for 100 min as seen in Fig. 1. The unseeded sample exhibits dendrite grain shapes (0.2 μm) and continuous pore channels; indicative of a vermi-

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7. High Temperature Furnace 46100, Barnstead/Thermolyne, Dubuque, IA.
8. Model CAPA-700, Horiba Instruments, Ltd., Irvine, CA.
cular microstructure. As seed concentration increases, the size of the dendrites decreases and the porosity becomes more uniformly distributed. The vermicular grains are a result of the more heterogeneous distribution of seeds in the matrix and the large agglomerate sizes in the γ-Al₂O₃ powder. The 5 wt.% seeded sample exhibits a homogeneous microstructure of 0.1 μm α-Al₂O₃ grains.

The microstructures of γ-Al₂O₃ samples with 0–5 wt.% seeds sintered for 100 min at 1200°C are shown in Fig. 2. All of the samples have completely transformed and have undergone grain coarsening with a two-fold
increase in grain size. Rapid grain coarsening of the fine-grained microstructure resulted in pore entrapment within some of the grains. However, the size and number of entrapped pores decreases with increasing seed concentration. In addition, the grain morphologies appear more equiaxed at higher seed concentrations.

The microstructures of $\gamma$-$\text{Al}_2\text{O}_3$ samples seeded with 0–5 wt.% $\text{a}$-$\text{Al}_2\text{O}_3$ and sintered for 100 min at 1400°C are shown in Fig. 3. The unseeded sample contains continuous pore channels and large irregular grains of ~0.8 µm. The seeded samples have sintered to high densities with equiaxed grains (0.5–2 µm). The microstructures of $\gamma$-$\text{Al}_2\text{O}_3$ samples seeded with 0–5 wt.% $\text{a}$-$\text{Al}_2\text{O}_3$ and sintered at 1500°C for 100 min are shown in Fig. 4. Grains become more equiaxed in the unseeded sample as the matrix continues to densify. A few large pores are still present; however, a majority of the porosity is isolated at grain boundary junctions. Since seeded samples achieved high densities at 1400°C, sintering at higher temperature results in significant grain growth. The 5 wt.% seeded sample exhibits exaggerated grain growth resulting in a broad grain size distribution (1–12 µm). Without the use of grain growth inhibitors or dopants like MgO, the presence of impurities such as $\text{SiO}_2$ and $\text{TiO}_2$ in the as-received powder results in grain growth in preferential directions and the formation of faceted grains.24,25

The microstructures of the commercial $\delta/\text{a}$-$\text{Al}_2\text{O}_3$ powder sintered at 1400, 1500, and 1600°C for 100 min are shown in Fig. 5. The sample sintered at 1400°C exhibits a broad grain size distribution of 0.2–2 µm grains with a few large pores and less porosity located on grain boundaries. The sample sintered at 1600°C appears dense with a few small pores. Although there are heterogeneities in the seeded samples due to agglomeration of the nanocrystalline powders, a more homogeneous microstructure, compared to the $\delta/\text{a}$-$\text{Al}_2\text{O}_3$ mixture, of 0.5 µm grains was obtained at 1400°C from seeded transition alumina powder.

The densification of the seeded $\gamma$-$\text{Al}_2\text{O}_3$ and the commercial $\delta/\text{a}$-$\text{Al}_2\text{O}_3$ powder are shown in Fig. 6. The unseeded $\gamma$-$\text{Al}_2\text{O}_3$ samples sinter to 65% relative density at 1400°C and reached 90% at 1600°C. All of the seeded $\gamma$-$\text{Al}_2\text{O}_3$ samples sintered to ≥98% relative density at 1400°C and reached ~100% density at 1500°C. It is reasonable to conclude that >95% density would be obtained by sintering seeded $\gamma$-$\text{Al}_2\text{O}_3$ at lower temperatures for longer periods of time. The $\delta/\text{a}$-$\text{Al}_2\text{O}_3$ mixture

![Fig. 3. Microstructures of (a) 0 wt.%, (b) 1.25 wt.%, and (c) 5 wt.% seeded $\gamma$-$\text{Al}_2\text{O}_3$ samples sintered for 100 min at 1400°C.](image-url)
sintered to 88% relative density at 1400°C and reached 98% relative density at 1600°C.

The δ/α-Al₂O₃ mixture sintered better than the unseeded γ-Al₂O₃ sample due to a higher green density and the presence of α-Al₂O₃ particles which act to seed the phase transformation in the transition alumina. However, the density of the δ/α-Al₂O₃ mixture did not exceed the sintered densities of the seeded γ-Al₂O₃ samples. Sintering temperatures >1600°C were required to reach full density using the δ/α-Al₂O₃ mixture powders. The seeded γ-Al₂O₃ sintered better than the commercial δ/α-Al₂O₃ powder because the nucleation density in the sintered powders was significantly higher. Close examination of the commercial powder showed that the α-Al₂O₃ was ~1 μm diameter. Since the seed number density (Nᵥ) scales with dᵢ⁻¹/₃, the seed number density from the α-Al₂O₃ in the commercial δ/α-Al₂O₃ powder is at least three orders of magnitude lower than in the seeded samples. As shown here and in previous papers on seeded boehmite, the number frequency is the key parameter controlling the particle size of the transformed α-Al₂O₃, which in turn affects the sintering temperature.¹¹,¹⁴

Green density is known to affect the phase transformation. Therefore, seeded γ-Al₂O₃ powders were uniaxially pressed in a zinc stearate lubricated WC die to obtain pellets of 6.2 mm diameter and 0.2 mm height. The green densities of the pressed pellets, determined by the dimensional technique, were 48, 53, 56, and 59% (ρ₀ = 3.2 g/cm³) for samples pressed at 140, 280, 420, and 560 MPa, respectively. The densification behavior of seeded γ-Al₂O₃ pellets as a function of die pressure is shown in Fig. 7. At 1000°C, the sintered densities range from 43% for the 140 MPa pressed sample to 55% for the 560 MPa pressed sample. The pellets sinter rapidly between 1200 and 1400°C. The pellets reach full density at 1400°C when pressed at 280 and 1400°C. The pellets reach full density at 1400 and 1500°C when pressed at 280 and 140 MPa, respectively. By increasing the packing density of the γ-Al₂O₃ powders, the spacing between nucleation events in the matrix is slightly reduced and the number of particle contacts between the matrix phase and the seed particles is increased, both of which reduce the scale of the vermicular microstructure. As a result, higher sintered densities are attainable at lower temperatures. The sintered densities for samples die pressed at >280 MPa exceed any previous reports about pressureless sintering undoped γ-Al₂O₃ powders.

Fig. 4. Microstructures of (a) 0 wt.%, (b) 1.25 wt.%, (c) 2.5 wt.%, and (d) 5 wt.% seeded γ-Al₂O₃ samples sintered for 100 min at 1500°C.
4. Summary

The addition of $\alpha$-$\text{Al}_2\text{O}_3$ seeds to commercial $\gamma$-$\text{Al}_2\text{O}_3$ powders has a significant effect on microstructure evolution and densification. The addition of seeds provides a large number of nuclei for $\alpha$-$\text{Al}_2\text{O}_3$ formation and thus vermicular growth during the phase transformation was limited. The seeded $\gamma$-$\text{Al}_2\text{O}_3$ samples sintered to full density with a 1.5 $\mu$m grain size at 1400°C after 100 min. The results of this investigation are a significant improvement relative to earlier reports for densification of either pressureless or pressure assisted sintering of undoped boehmite and $\gamma$-$\text{Al}_2\text{O}_3$ samples.

Fig. 5. Microstructures of $\delta/\alpha$-$\text{Al}_2\text{O}_3$ mixture (CR-30) powders sintered at (a) 1400, (b) 1500, and (c) 1600°C for 100 min.

Fig. 6. Sintered densities of seeded $\gamma$-$\text{Al}_2\text{O}_3$ and $\delta/\alpha$-$\text{Al}_2\text{O}_3$ samples as a function of seed concentration and temperature (100 min).

Fig. 7. Sintered densities of 5 wt.% seeded $\gamma$-$\text{Al}_2\text{O}_3$ samples pressed at various pressures and sintered at various temperatures for 100 min.
The use of nanocrystalline $\gamma$-$\text{Al}_2\text{O}_3$ powders as a starting material provides a higher bulk density than boehmite gel systems and thus less shrinkage during sintering. In addition, the time consuming calcination step required for making bulk samples from boehmite powders was avoided. In comparison to a commercial $\delta$-$\text{Al}_2\text{O}_3$ powder, the seeded $\gamma$-$\text{Al}_2\text{O}_3$ samples sintered to full density at 1400°C, while the $\delta$-$\text{Al}_2\text{O}_3$ powder samples sintered to 98% density at 1500°C after 100 min. It is proposed that reduction in the agglomerate size (<50 nm), or removal of the agglomerates, will further lower the sintering temperature to less than 1400°C. We also conclude that seeding with other sesquioxides, which have been demonstrated to be effective for boehmite gels, would be successful for seeding the phase transformation and sintering of transition aluminas.

References