Processing thin (<10 μm), dense, flexible α-Al₂O₃ films from nanopowders

Makoto TAKEUCHI¹,³, Matthias NIEDERMAIER¹,², Monika JANSOHN¹, Noritsugu UMEHARA³ and Richard M. LAINE¹,⁷

¹Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109–2136, U.S.A.
²Chemistry and Physics of Materials, Paris-Lodron University Salzburg, Salzburg, A-5020, Austria
³Micro-Nano Mechanical Science and Eng., Nagoya University, Nagoya 464–8603, Japan

Normally, it is very difficult to process thin ceramic films (<10 μm) except by vapor deposition methods. This is because in traditional ceramics processing, initial powder particle sizes (typical average particle sizes, APSs > 200 nm) make it difficult to realize mechanically robust thin films after sintering to full density due to excessive grain growth. One solution to this problem is to start with nanopowders (APSs < 100 nm). Here we present efforts to use simple, easily available nano δ-Al₂O₃ (transition or t-Al₂O₃) nanopowders (NPs) to process the subject films. Thus t-Al₂O₃ NPs when properly dispersed, doped with 0.5–5 wt. % MgO and ball milled with a polymeric binder provide castable systems. Wire wound roller drawing/tape casting provides access to thin green films (10–30 μm) with ≈75 wt. % ceramic loadings. Following binder burnout and careful sintering to temperatures of up to 1500°C/7 h/air but preferably slightly lesser conditions leads to dense ≤10 μm films with average α-Al₂O₃ grain sizes of 500–800 nm. At higher MgO concentrations, spinel phase separates during sintering likely inhibiting grain growth. These relatively dense films are flexible and translucent. Such films, because of their flexibility, may offer utility as catalyst supports, electronic substrates or as hard facings for other materials.

©2019 The Ceramic Society of Japan. All rights reserved.

Key-words : Nanopowders, Thin films, Microstructure control, Alpha alumina, Flexible

1. Introduction

Alumina, because of its widespread abundance, has been explored extensively for use in processing diverse ceramic components ranging from cutting tools to sodium vapor lamp envelopes to spark plug bodies to radomes, electronic substrates and high temperature insulation.¹¹) Its attractiveness comes in part from its stability to very high temperatures, high hardness, corrosion resistance and consequently excellent durability.

The most abundant forms consist of a panoply of morphologies often lumped under the title transition aluminas (t-Al₂O₃). Therein lies one of the more difficult problems with processing alumina. The most stable form, α-Al₂O₃, differs in crystallographic morphology from the majority of t-Al₂O₃’s, requiring reconstructive transformation to the hexagonal α-phase. To effect this transformation from most t-Al₂O₃’s, sufficient energy must be provided to the green body to initiate nucleation of α-Al₂O₃. Very often the nucleation energy required is sufficient to coincidentally promote rapid grain growth immediately after nucleation leading to unwanted vermicular microstructures.¹⁰–¹⁸) Extensive studies have been undertaken by many groups to resolve this problem such that processing α-Al₂O₃ monoliths with good-to-excellent control of densification and grain growth is now well understood.

However, several important processing challenges remain. For example, efforts to produce transparent α-Al₂O₃ using pressure-less sintering remain incompletely resolved.¹⁹) Likewise processing thin <25 μm, dense, flexible α-Al₂O₃ films that may serve as electronic substrates, scratch resistant facings on other structures or as mechanically robust flexible catalyst supports¹³b remains a challenge.

Our recent successes in using metal oxide nanopowders to process a variety of thin, dense and flexible ceramic films for a wide variety of applications provides the impetus for the current work.¹⁹–²¹) Here we develop an approach to processing thin, dense, fine-grained α-Al₂O₃ films with minimal large flaws sufficient to engender flexibility starting from nano t-Al₂O₃. The challenge is to overcome the literature anticipated phase-transformation issues that might be expected to lead to excessive grain growth and poor densification.

A further exercise centers on doping the nano t-Al₂O₃ with MgO. While there are now numerous publications on the use of MgO doping to control grain growth during the
sintering of $t$-$\text{Al}_2\text{O}_3$; essentially all of these studies add MgO as a second phase either as MgO or as a simple chemical precursor.\(^{19,23-25}\) Our approach, described below, creates nano $t$-$\text{Al}_2\text{O}_3$ doped with Mg within the nanoparticle crystal structure rather than at its surface.\(^{26}\) As we show below, the presence of Mg ions in the gas phase affects the average particle sizes (APSs) produced during liquid-feed flame spray processing of the NPs themselves without changing the particle crystal structure.

2. Background

Here we briefly summarize previous work with a special emphasis on thin films. Like all efforts to optimize sintering, the reference papers are all concerned with optimizing APSs and size distributions, particle packing, sintering conditions, and characterization methods.\(^{19,23-25,27-30}\)

Particle packing optimization processes explored include float packing, slurry casting, slip casting, gel casting, pressure filtration packing and simple uniaxial pressing. As anticipated, in general, the smaller the APSs, the lower the sintering temperature to reach $>98\%$ of theoretical density. The lowest temperature required appears to be 1285°C to reach 99% density with 600 nm average grain size (AGS) starting from 80 nm APS particles of $\alpha$-$\text{Al}_2\text{O}_3$.\(^{31}\) Such particles require additional processing steps that might be eliminated if one could learn to use flame produced $t$-$\text{Al}_2\text{O}_3$ NPs. Flame produced $t$-$\text{Al}_2\text{O}_3$ are commercially available in multi-ton quantities.\(^{32}\)

Yang and Wu prepared ceramic films by tape casting.\(^{30}\) The objective of their work was to first optimize powder dispersions ($\gamma$-$\text{Al}_2\text{O}_3$) and stabilize solids loading in aqueous slurries. The gelling agent ISOBAM (alkaline hydro soluble copolymer of isobutylene and maleic anhydride) was shown to spontaneously function as dispersant, gelling agent and binder. Minimal water contents were used to minimize deformation and defects during the drying and firing processes. After degassing, slurries were tape-cast on Mylar. The isolated thin films were then sintered at 1750–1850°C for 3–5 h.

Transparent $\text{Al}_2\text{O}_3$ films were produced with good quality and defect-free surfaces at thicknesses of 150–600 µm with AGSs of 20–85 µm. Optimum binder content was 20 wt.% and a solids loading of 68 wt.% $\text{Al}_2\text{O}_3$. The obtained transparent films showed good quality and defect (pore)-free surfaces from vacuum sintering without polishing. The transmittance at 600 nm was 40%. Unfortunately, no powder diffraction studies were presented for either the starting materials or final products. We assume the finished product was $\alpha$-$\text{Al}_2\text{O}_3$. If it is, then at this thickness and grain size, based on the literature the resulting alumina films should be translucent\(^{19,20,29}\) unless some significant orientation of the grains was achieved.

A second pertinent reference explores packing effects using $t$-$\text{Al}_2\text{O}_3$ as the starting point.\(^{27}\) The goals of Azar et al.’s work were to compare slip casting with cold isostatic pressing (CIPping) in forming green films via a vis particle packing and in turn densification, phase transformation and microstructural evolution during sintering.

As expected, green bodies prepared by CIPping exhibited heterogeneous microstructures with large agglomerates and inter-agglomerate pores. In contrast, slip casting provided particle packaging with better homogeneity and uniform inter-particle pore sizes.

The homogenous microstructures of the initial green bodies improved particle rearrangement or reordering during transformation from $t$-$\text{Al}_2\text{O}_3$ to $\alpha$-$\text{Al}_2\text{O}_3$. Hence, transformation to the thermodynamically stable $\alpha$-$\text{Al}_2\text{O}_3$ and its further densification were enhanced. Microstructural evolution and transition temperatures as well as the number of macro defects (quantity and size of pores) remaining after the $t$ $\rightarrow$ $\alpha$ transformation could be reduced.

Slip cast films showed initial densification (coinciding with the $t$ $\rightarrow$ $\alpha$ transformation) at 1160°C for CIPped films at 1200°C. The second step (densification of $\alpha$-alumina) was more effective in slip cast films. A clear maximum in densification rate was observed at 1400°C. The final density of the sintered slip cast specimens was 98%, for the pressed specimens final densities were 80%.

Finally, we describe an approach similar to what we have used that the explored use of nano $\alpha$-$\text{Al}_2\text{O}_3$ powders derived from milling on the viscosity of slurries, the casting process, binder burnout, and sintering behavior.\(^{29}\) In these studies by Vozdecky et al. commercial $\alpha$-$\text{Al}_2\text{O}_3$ (150–200 nm) powders were further wet-milled to APSs of 50 nm. Slurries of these powders were milled in ethanol with a polymeric dispersing agent. Slurry compositions were evaluated to optimize rheology, optimal systems were tape cast and sintered. The anticipated benefits of using nano $\alpha$-$\text{Al}_2\text{O}_3$ were verified in that reduced sintering temperatures were found obtained.

Thus, the final optimized system used polyvinyl butyral as binder and benzyl phthalate as a plasticizer during grinding. The mixture was homogenized for 24 h, and slurries cast on silicon coated PET carrier film (700 mm/ min). Sintering was performed in air at 1450°C (maximum densification at 1365°C). The resulting films were flat, substrates up to 97% dense, translucent with submicrometer microstructures (low surface roughness $R_h = 170$ nm). Note that the translucency observed is as expected.\(^{28}\) To date, these results represent the best results obtained using commercial $\text{Al}_2\text{O}_3$, but at thicknesses (60 mm), not in the range we target.

3. Experimental materials and methods

3.1 Precursors synthesis

Magnesium propionate [Mg(OOCCH$_2$CH$_3$)$_2$] and aluminate [Al(OCH$_2$CH$_3$)$_3$N] were synthesized and mixed to produce nanopowders (NPs) of 0.0, 0.5, 1.0, 2.0, 3.0, and 5.0 wt.% MgO doped $\delta$-$\text{Al}_2\text{O}_3$ on combustion.

Magnesium propionate [Mg(OOCCH$_2$CH$_3$)$_2$] was synthesized by reacting magnesium hydroxide with propionic acid in a 1 L round bottom flask equipped with a still head at 140°C in N$_2$ atmosphere. Once a transparent liquid was obtained, heat was removed, and the liquid cooled to ambient temperature. Crystallized magnesium propionate was filtered off.
Alumatrane \([\text{Al(OCH}_2\text{CH}_2\text{N)}\text{]}\) was synthesized by reacting triethanolamine \([\text{N(CH}_2\text{CH}_2\text{OH)}_3]\), 99+%, Acros Organics, Morris Plains, NJ with aluminum sec-butoxide \([\text{Al}[\text{OCH(CH}_3\text{CH}_2\text{CH}_3)\text{]}], 97\%\), Alfa Aesar, Ward Hill, MA in a 1 L round bottom flask equipped with a still head at room temperature in N\(_2\) atmosphere. Residue was filtered off and alumatrane was obtained as a solution (ceramic yield 7.6 wt.%).

### 3.2 Liquid-feed flame spray pyrolysis (LF-FSP)

0.0, 0.5, 1.0, 2.0, 3.0 and 5.0 wt.% MgO doped \(\delta\)-Al\(_2\)O\(_3\) NPs were prepared by LF-FSP. As practiced at University of Michigan\((21-23)\) the LF-FSP apparatus consists of a precursor reservoir, a combustion chamber, and electrostatic precipitators (ESPs) (Fig. 1). The precursors magnesium propionate and alumatrane were dissolved in ethanol at selected molar ratios that provide an overall 3–5 wt.% ceramic yield. The precursor solution is aerosolized and combusted with methane/oxygen pilot torches on the spray head. Combustion at \(\geq1500^\circ\text{C}\) produced MgO doped \(\delta\)-Al\(_2\)O\(_3\) nanopowders that were collected downstream in ESPs operated at a DC potential of 10 kV.

The as-produced NPs were then dispersed in EtOH (200 proof, Decon Labs) using an ultrasonic horn (Vibra cell VC-505, Sonics & Mater. Inc.) at 100 W for 10 min. The suspension was allowed settle for 5 h to remove larger particles. The supernatant was decanted and allowed to oven dry providing the starting \(\delta\)-Al\(_2\)O\(_3\) nanopowders.

### 3.3 Film processing

Suspensions of 0.0, 0.5, 1.0, 2.0, 3.0, and 5.0 wt.% MgO doped \(\delta\)-Al\(_2\)O\(_3\) NPs, polyvinyl butyral, benzyl butyl phthalate, ethanol, and acetone at selected ratios were prepared in vials (Table 1). The suspensions were ball-milled using a ball tumbler (Thumler’s Tumbler Model B, True-Square Metal Products, Auburn, WA, United States) with 6 g of spherical Al\(_2\)O\(_3\) beads for at least 48 h. The suspensions were cast on Mylar film using a wire wound rod coater (1137, Sheen, Richmond Road, Kingston, United Kingdom). The cast thickness was adjusted to 100–125 \(\mu\text{m}\) in order to control the thickness of the final ceramic film.

### 3.4 Film sintering

Green films were placed between two Al\(_2\)O\(_3\) substrates \((D = 42 \text{ mm, films are } 5 \times 5 \text{ mm})\) and sintered to selected temperatures and times with a ramp rate of 10 \(^\circ\text{C}/\text{min}\) below 1000\(^\circ\text{C}\) and 5 \(^\circ\text{C}/\text{min}\) above 1000\(^\circ\text{C}\), using a vacuum tube furnace (GSL-1600X, Richmond, CA, United States). The substrates were used to prevent warping of the ceramic film. One aspect of the efforts reported here used one-step sintering [Fig. 2(a)] at \(t_1 = 1500^\circ\text{C}\) for \(h_1 = 0, 1, 3,\) and 5 h. When sintering in \(\text{N}_2\) or 95/5 \(\text{N}_2/\text{H}_2\) a preliminary binder burnout at 800 \(^\circ\text{C}\) in \(\text{O}_2\) was necessary.

### Table 1. Starting materials and composition of suspension of Al\(_2\)O\(_3\) (x wt.% MgO, x = 0.0–5.0)

| Components | Roles | Mass (g) | Wt. % | Vol. % |
|------------|-------|----------|-------|--------|
| MgO doped \(\delta\)-Al\(_2\)O\(_3\) Powder | 1.00 | 24.9 | 36.5 |
| Polyvinyl butyral Binder | 0.135 | 3.36 | 2.99 |
| Benzyl butyl phthalate Plasticizer | 0.135 | 3.36 | 2.99 |
| Ethanol Solvent | 1.38 | 34.1 | 42.6 |
| Acetone Solvent | 1.37 | 34.1 | 42.6 |

![Fig. 1. Schematic of LF-FSP for nanopowder production.](image1)

![Fig. 2. Schedule for one-step sintering 10 °C/min, above 1000°C: 5 °C/min.](image2)
3.5 Scanning electron microscopy (SEM) analysis

Particle and grain morphologies and sizes were characterized by a JSM-IT300 SEM (JEOL Ltd., Akishima, Tokyo, Japan). Since the samples lacked electrical conductivity, they were sputter coated with a gold/palladium film using a Technics Hummer VI sputtering system (Anatech Ltd., Alexandria, VA, United States) to avoid charging and to improve resolution.

3.6 X-ray diffraction (XRD) analysis

Measurements were carried out using a Rigaku Rotating Anode Goniometer (Rigaku Denki., LTD., Tokyo, Japan) at 40 kV and 100 mA with Cu Kα radiation (1.541 Å). Scan range was between 10 and 70° 2θ, using a scan rate of 5°/min with 0.02° intervals. The Jade program 2010 (Version 1.1.5 from Materials Data, Inc.) was used to determine the type of crystallographic phases, crystallite domain sizes from line broadening and weight fractions with the aid of Rietveld refinement. Peak positions and intensities were evaluated by comparison with ICDD files of δ-Al2O3, aluminum oxide (00-004-0877), α-Al2O3, corundum (98-000-0174), and MgAl2O4, spinel (98-000-3963).

4. Results and discussion

The objective of the work reported here is to learn to use t-Al2O3 (δ-Al2O3) NPs produced by liquid feed flame spray pyrolysis26) to process dense, flexible and thin α-Al2O3 films (<10 µm) with AGSs below 1 µm. Using the published literature on the sintering of translucent and transparent α-Al2O3 components as a guide to our efforts, we explored the use of MgO (0.0, 0.5, 1.0, 2.0, 3.0, and 5.0 wt.%) doped δ-Al2O3 NPs as a way to avoid excessive grain growth during sintering and the δ to α transformation. Our goal was not to make transparent materials; however, we consider the degree of transparency a qualitative method of evaluation in that it indirectly indicates the number of scattering centers.

Note that flame made, MgO doped δ-Al2O3 powders are single phase δ-Al2O3. As such, the Mg2+ ions are likely dispersed uniformly in the δ-Al2O3 lattice. Thus, our approach differs from all of the other studies cited wherein Mg was introduced to preexisting Al2O3 powders and as such was likely present as surface species during sintering. It is not clear from these studies if there is a difference; however, our ability to obtain dense films with very fine grain sizes suggests that there might be.

4.1 Powder characterization studies

We have previously detailed26) the synthesis and characterization of MgO doped δ-Al2O3 nanopowders finding that only at 10 mol.% Mg doping was a spinel phase observed, which also appears to be the case in the present studies as seen in Fig. 3. The 5 wt.% (13 mol.%) MgO composition powders clearly appear to be phase pure spinel; albeit at a composition not normally found for Mg spinel as noted previously.26)

![Fig. 3. XRD patterns of 0.0–5.0 wt.% MgO doped δ-Al2O3 NPs produced by LF-FSP.](image)

![Fig. 4. Normal distribution of particle sizes of 0.0–5.0 wt.% MgO doped δ-Al2O3 NPs produced by LF-FSP.](image)

| MgO (wt.%) | APS  |
|-----------|------|
| 0.0       | 39 nm|
| 0.5       | 37 mm|
| 1.0       | 44 mm|
| 2.0       | 33 mm|
| 3.0       | 27 mm|
| 5.0       | 25 mm|

Thus, our current efforts were simply to correlate Mg content with APSs.

To validate the APS of flame made Mg doped δ-Al2O3 powders at least 100 particles were measured per sample. The results are shown in Fig. 4 and tabulated in Table 2.

Perhaps the most important feature of the Fig. 4 data is the fact that at higher Mg concentrations the APSs are...
the finest and as can be seen, the particle size distributions become qualitatively narrower. This effect represents an indirect probe of the particle formation process. Occam’s razor, suggests that we consider the simplest explanation for the observed behavior. If we accept that the narrowest size distribution and smallest AGSs are found for what at 5 wt. % (13 mol %) is phase pure spinel, then we can argue that particle growth may be controlled by the ease of crystallization. So as gas phase nuclei collide and grow to critical sizes they stop coalescing earlier at this composition because they form a single phase.

In contrast, we might suggest that for lesser MgO contents, mixed phase nuclei form that stay molten or reactive for longer periods of time such that more collisions occur with subsequent coalescence before the particles reach an unreactive state. This would then explain the broader size distributions and larger AGSs with lesser Mg contents. Other possible explanations exist but are too speculative to be presented here. As discussed below, 1.0 and 2.0 wt. % MgO doped Al2O3 fi lms seem to offer the highest densities, are the most fl exible, and have the finest AGSs after sintering. After 5 h of sintering at 1500°C the grain size increased to about 530–580 nm, a 12- and 17-fold increase in size respectively.

4.2 Green fi lm processing
As detailed in the experimental section and using techniques developed previously,20–23 green fi lms were cast using a wire wound roller coating system. These dried fi lms can be between 10–30 μm but are most typically 20 μm thick. An SEM of a typical green fi lm is shown in Fig. 5. In Fig. 6, a typical thermogravimetric analysis (TGA) in air of a green fi lm, shows a ceramic loading of 79 wt. %. We fi nd that thermocompressing these fi lms in a warm press improves the interparticle packing and separation distances as witnessed by improved fi nal densities following sintering.

4.3 Film burnout and sintering studies
The Fig. 6 TGA suggests that most of the organic phase decomposes and is oxidatively removed on heating to 600°C. Because the fi lms are so thin, in our sintering studies in flowing O2 we actually did not have a stage wherein we hold the fi lms to promote binder burnout but instead directly heat the fi lms between two α-Al2O3 substrates at a low ramp rate. When sintered in N2 or 95/5 N2/H2 atmosphere, a preliminary binder burnout was done at 800°C in O2.

As part of our sintering studies we examined several variables (substrate, atmosphere, sintering schedule, temperature and time). Thus, we explored both one step (Fig. 2) and two step sintering. The two-step approach explored based on the work of Chen and Wang was found not be useful.33) The number of variables examined provides a large map of the sintering behavior in this system. Thus, examples of superior systems are presented in the following sections. Details concerning less efficacious processing studies are not presented.

For example, we explored using 2.0 wt. % MgO doped Al2O3 and mixing it with 0.0 wt. % MgO nanopowders to obtain 0.5 and 1.0 wt. %. To this end, we determined that this approach does not work as well as using directly synthesized MgO doped δ-Al2O3 NPs and as such these earlier efforts are not included here.

Initial efforts explored one-step sintering wherein fi lms were heated to a peak temperature of t1 = 1500°C for h1 = 0, 1, 3, 5, and 7 h in O2. Green fi lms were placed between α-Al2O3 substrates and sintered using a vacuum tube furnace. Sufficient densiﬁcation is achieved after 5 h. SEM fracture surface images of 20 μm green fi lms of 0.0, 0.5, 1.0, 2.0, 3.0, and 5.0 wt. % MgO doped Al2O3 are
shown in Fig. 7; film thicknesses are tabulated in Table 3. The 1.0 and 2.0 wt.% Mg doped Al₂O₃ exhibited especially dense films with a low number of pores.

Sintering for 7 h, does not result in significant increases in densification and films became rather brittle. Sintering in air vs. oxygen provided no differences in terms of the final microstructures.

The AGSs of film sintered for 0, 1, 3, and 5 h are presented in Fig. 8. The AGSs increase slightly with increasing sintering time and Mg content. The time component is as expected. The increases in overall grain sizes are to some extent contrary to the concept that MgO addition limits grain growth by a pinning mechanism. At present, we have no rational explanation for this behavior.

The greatest vertical shrinkages were seen with 2.0 and 3.0 wt.% Mg doped Al₂O₃ (20–40% of the pressed green film thickness, Table 3). Qualitatively, the most translucent

---

Table 3. Thickness of 0.0–5.0 wt.% 20 µm films after one-step sintering to 1500°C

| Wt.% MgO | Cast green film (µm) | Uniaxially pressed green film (µm) | 1500°C/0 h (µm) | 1500°C/1 h (µm) | 1500°C/3 h (µm) | 1500°C/5 h (µm) |
|----------|----------------------|-----------------------------------|-----------------|-----------------|-----------------|-----------------|
| 0.0      | 26 ± 2               | 27 ± 2                            | 18              | 11              | 17              | 14              |
| 0.5      | 26 ± 2               | 25 ± 2                            | 17              | 17              | 18              | 18              |
| 1.0      | 28 ± 2               | 26 ± 2                            | 16              | 19              | 17              | 21              |
| 2.0      | 38 ± 2               | 36 ± 2                            | 29              | 25              | 18              | 20              |
| 3.0      | 28 ± 2               | 26 ± 2                            | 19              | 15              | 27              | 17              |
| 5.0      | 28 ± 2               | 25 ± 2                            | 18              | 20              | 16              | 22              |
of the films produced seemed to be for the 2.0 and 3.0 wt.% MgO doped films.

While the observed densification seems best at 2 and 3 wt% doping, the Fig. 9 XRD data show no or almost no spinel phase forming for the samples with 1 or 2 wt% doping suggesting less phase segregation which of course increase the potential to scatter light. Furthermore, the best densities coupled with the smallest final grain sizes were found for the 1.0 and 2.0 wt.% Mg doped Al₂O₃ films which show AGSs below 600 nm. Hence all further studies were done using these doping levels.

As noted just above, MgO·Al₂O₃ precipitates as the films are sintered presumably to grain boundaries thereby pinning grain growth. As seen in Fig. 9, peaks associated with spinel appear in the 3.0 and 5.0 wt.% samples sintered at 1500°C/5 h/O₂. The APSs for these spinel inclusions were determined by X-ray line broadening as presented in Fig. 10 that suggest that the average spinel particle sizes are <100 nm.

If large pores were present, one might anticipate that they could serve as “fatal flaws” that would engender brittle properties to the final films. Given, as we discuss below, these films are flexible, one might choose to argue that such flaws are either internal or absent such that the resulting films are mechanically robust. The fracture surface SEMs seen in Fig. 13, below suggest that the majority of pores can be eliminated by sintering in 95N₂/5H₂ mixtures again supporting the robust nature of these films.

Careful optimization of initial processing parameters using 20 μm green films allowed us to explore tape casting green films of ≈10 μm thick. Selected data are presented in Table 4 and Figs. 11–15. These data provide a baseline comparison against materials sintered in 95/5 N₂/H₂.

![Fig. 9. XRDs of 0.0–5.0 wt.% MgO doped Al₂O₃ films sintered at 1500°C/5 h/O₂.](image)

![Fig. 10. Spinel (MgO·Al₂O₃) crystallite domain size in 0.0–5.0 wt.% MgO doped Al₂O₃ films sintered for different times at 1500°C in O₂.](image)

![Fig. 11. SEM fracture surface of 1500°C/5 h/O₂ sintered <10 μm 1.0 wt.% MgO doped Al₂O₃ film.](image)

![Fig. 12. Translucent <10 μm (a) 0.0, (b) 0.5, (c) 1.0, and (d) 2.0 wt.% MgO doped Al₂O₃ films sintered at 1500°C/5 h/O₂.](image)

Table 4. Thickness of 0.0–2.0 wt.% MgO doped Al₂O₃ 10 μm green films sintered via a one-step process at 1500°C in 95/5 H₂/N₂.

| Wt.% MgO | Cast green film (μm) | Uniaxially pressed green film (μm) | Film sintered at 1500°C/5 h (μm) |
|----------|----------------------|-----------------------------------|-------------------------------|
| 0.0      | 13 ± 2               | 11 ± 2                            | 8.7                           |
| 0.50     | 13 ± 2               | 12 ± 2                            | 9.2                           |
| 1.0      | 14 ± 2               | 13 ± 2                            | 8.3                           |
| 2.0      | 17 ± 2               | 16 ± 2                            | 11                            |
For completeness sake, we also sintered ball-milled mixtures of nano-δ-Al2O3 with nano MgO also produced by LF-FSP. These systems did not sinter to close to the densities (not shown) of the doped systems shown here. Presumably MgO outside the nano-δ-Al2O3 forms spinel coatings on the surface of these nanopowders and diffusion of Mg into the particles is then slowed by this higher melting phase.

Based on a literature comment that sintering α-Al2O3 in a hydrogen atmosphere improves densification and reduces porosity,29) we also explored this aspect of processing. As seen in Fig. 13, a finer, denser grain structure was obtained for studies in 95/5 N2/H2. The AGS was below 460 nm. The films are more flexible (Fig. 14) and more transparent (Fig. 15) than films sintered in O2.

It is important to reiterate that our primary goal in the work reported here is to make flexible thin α-Al2O3 films <10 µm thick. It was not to make fully transparent materials.

In part, these studies were also motivated by the finding that NiO-3Al2O3 cast green films on sintering transform to dense NiAl2O4/2α-Al2O3 flexible films that were found to be useful in developing regenerable catalysts for the production of carbon nanotubes. In that work, thinner films make better use of NiO and as such, our goal was to learn to make very thin, structurally robust films.18b)

4.4 Substrate effect
One most important question remains to be answered. All the above studies were done using α-Al2O3 substrates. It is easy to imagine that these substrates seeded the transformation of the initial t-Al2O3 NP composites to α-Al2O3 during the sintering process. A simple test was conducted wherein a set of samples was sintered in 1500°C/5 h/O2 using zirconia substrates. The resulting thin films were found to consist of α-Al2O3 with essentially identical AGSs and densities to those sintered on α-Al2O3 substrates. Consequently, no apparent influence of the α-

---

Fig. 13. SEM fracture surfaces for (a) 1.0 and (b) 2.0 wt.% MgO doped Al2O3 films sintered at 1500°C/5 h in 95/5 N2/H2 with an AGS smaller than 460 nm.

Fig. 14. Bend test for <10 µm (a) 1.0 and (b) 2.0 wt.% MgO doped Al2O3 films sintered at 1500°C/5 h in O2 and (c) 95/5 N2/H2 atmosphere (2.0 wt.% MgO doped Al2O3).

Fig. 15. Optical images of <10 µm 2.0 wt.% MgO doped Al2O3 films sintered at 1500°C for 5 h under O2, 95/5 N2/H2, and N2 atmosphere. Films are directly on paper or 1 mm away from lettering.
Al₂O₃ substrates on the δ-Al₂O₃ to α-Al₂O₃ transformation are apparent.

5. Conclusions
Optimization of phases and stoichiometries in mixed-metal oxide NPs is desirable for a number of applications, which can be achieved by controlling precursor compositions used for LF-FSP. Here, we demonstrate the use of LF-FSP to produce MgO doped δ-Al₂O₃ NPs to fabricate dense, flexible and thin (≤10 μm) Al₂O₃ films by tape-casting. APSs were observed to decrease with increasing MgO contents up to 5.0 wt.% whereas the phase remained as δ-Al₂O₃ per XRD studies as seen previously.26)

Surprisingly, sintering films with intermediate loadings of MgO between 0.0 and 2.0 wt.% simply by mixing 0.0 wt.% with various fractions of 2.0 wt.% did not give the same properties and sintering behavior as starting with NPs prefomed with the same Mg contents. These results suggesting that diffusion of MgO from MgO free particles into MgO rich films in that the AGSs did not give the same properties as starting with the same properties and sintering behavior as starting with NPs prefomed with the same Mg contents. These results suggest that diffusion of MgO from MgO free particles to MgO “rich” particles does not happen easily. One can therefore suggest that some form of lattice rather than surface doping must occur in flame made Mg doped Al₂O₃ NPs that provides superior sintering behavior.

We also find that as expected from the literature, sintering in hydrogen, improves the thin films in that the AGSs are somewhat smaller, 450 nm approaching the sizes below which it becomes possible to eliminate birefringence potentially leading to higher transparencies.34)

Acknowledgements This work was generously supported by a contract from Rogers Inc.

References
1) I. B. Cutler, C. Bradshaw, C. J. Christensen and E. P. Hyatt, J. Am. Ceram. Soc., 40, 134–139 (1957).
2) Chem. Eng. News, 35, 70–71 (1957).
3) E. S. Lukin, N. A. Makarov, I. V. Dodonova, S. V. Tarasova, E. A. Bad'ina, N. A. Popova and G. S. Perry, J. Mater. Sci., 1, 186–198 (1966).
4) X. S. Li and I. M. Low, J. Mater. Sci., 29, 3121–3127 (1994).
5) E. S. Lukin, N. A. Makarov, I. V. Dodonova and S. V. Tarasova, Refract. Ind. Ceram.+, 42, 261–268 (2001).
6) A. Aryanamayajala, N. X. Randall, M. H. Gordon and D. Bhat, Thin Solid Films, 517, 819–823 (2008).
7) P. C. Milak, F. D. Minatto, A. De Noni, Jr. and O. R. K. Monteiro, Cerâmica, 61, 88–103 (2015).
8) X. Zhang, J. Zhu, L. Zhang, K. Kishimoto, S. Y. Du and X. Yin, Surf. Coat. Tech., 228, S393–S396 (2013).
9) P. Kathirvel, J. Chandrasekaran, D. Manoharan and S. Kumar, Int. J. Light Electron Opt., 126, 2177–2179 (2015).
10) C. J.-P. Steiner, D. P. H. Hasselman and R. M. Spriggs, J. Am. Ceram. Soc., 54, 412–413 (1971).
11) R. B. Bagwell, G. L. Messing and P. R. Howell, J. Mater. Sci., 36, 1833–1841 (2001).
12) H.-L. Wen and F.-S. Yen, J. Cryst. Growth, 208, 696–708 (2000).
13) J. Echeberria, J. Tarazona, J. Y. He, T. Butler and F. Castro, J. Eur. Ceram. Soc., 22, 1801–1809 (2002).
14) J. M. Hale, A. Aurox, A. J. Perotta and A. Navrotsky, Science, 277, 788–791 (1997).
15) J. M. McHale, A. Navrotsky and A. J. Perotta, J. Phys. Chem. B, 101, 603–613 (1997).
16) M. Hongwei and A. Krell, Key Eng. Mat., 200, 43–46 (2002).
17) R. M. Laine, J. C. Marchal, H. P. Sun and X. Q. Pan, Nat. Mater., 5, 710–712 (2006).
18) B. Liang, Eongyu Yi, T. Sato, S. Noda, D. Jia, Y. Zhou, R. M. Laine, “Flame synthesized [NiO]₀.₂₅[Al₂O₃]₀.₇₅ and [NiO]₀.₅₀[Al₂O₃]₀.₅₀ nanopowders (NPs) provide thin, dense, flexible NiAl₂O₇-Al₂O₃ and Ni-Al₂O₃ composite catalytic films. Regeneration of a heterogeneous catalyst by oxidative re-adsorption into a heterogeneous substrate is demonstrated for carbon nanotube synthases, ACS Applied Nano Materials 2018, 1, 5483–5492.
19) D. Godlinski, M. Kuntz and G. Grathwohl, J. Am. Ceram. Soc., 85, 2449–2456 (2002).
20) E. Yi, W. Wang, S. Mohanty, J. Kieffer, R. Tamaki and R. M. Laine, J. Power Sources, 269, 577–588 (2014).
21) E. Yi, W. Wang, J. Kieffer and R. M. Laine, J. Mater. Chem. A, 4, 12947–12954 (2016).
22) E. Yi, W. Wang, J. Kieffer and R. M. Laine, J. Power Sources, 352, 156–164 (2017).
23) P. Bowen, C. Carry, D. Luxembourg and H. Hofmann, Powder Technol., 157, 100–107 (2005).
24) S. P. Bardakhanov, A. V. Kim, V. I. Lysenko and A. V. Nomoev, Inorg. Mater., 45, 335–339 (2009).
25) J. A. Wollmershauser, B. N. Feigelson, E. P. Gorzowski, C. T. Ellis, R. Goswami, S. B. Qadri, J. G. Tischler, F. J. Kub and R. K. Everett, Acta. Mater., 69, 9–16 (2014).
26) R. M. Laine, T. R. Hinklin, J. Azurdia, M. Kim, J. C. Marchal and S. Kumar, Adv. Mater., 20, 1373–1375 (2008).
27) M. Azar, P. Palmiero, M. Lombardi, V. Garnier, L. Montanari, G. Fantozzi and J. Chevalier, J. Eur. Ceram. Soc., 28, 1121–1128 (2008).
28) J. Yamashita, H. Nagayama and K. Tsukuma, J. Am. Ceram. Soc., 91, 2611–2616 (2008).
29) P. Nozdeev, A. Roosen, C. Knieke and W. Peukert, J. Am. Ceram. Soc., 83, 1313–1319 (2010).
30) Y. Yang and Y. Wu, J. Mater. Res., 29, 2312–2317 (2014).
31) A. Krell and J. Klimke, J. Am. Ceram. Soc., 89, 1985–1992 (2006).
32) See for example: http://www.cabotcorp.com/solutions/products-plus/fumed-metal-oxides/fumed-alumina.
33) I.-W. Chen and X.-H. Wang, Nature, 409, 168–171 (2000).
34) R. Apetz and M. P. B. van Bruggen, J. Am. Ceram. Soc., 86, 480–486 (2003).