**Ceramic Processing – Zirconia Toughened Alumina**

Zirconia toughened aluminas (ZTAs) are one of the most important engineering ceramics with high melting points, excellent mechanical strength and chemical stability, and are commonly used as wear resistant and high-temperature components, as prosthetic implants and electric circuit substrates.

In this work, methods of processing fine-grained, dense, thin, free-standing (ZrO2)x(Al2O3)1-x films (x = 0-50 mol. %, ~40 μm thick) by sintering flame made nanopowders (NPs) to optimize the *t*-ZrO2 content, sinterability and microstructures under select conditions (1120-1500 °C/5 h in O2 or 95 %N2/5 %H2, short as N2/H2) were explored. In all cases, the final sintered products retain *t-*ZrO2 with average grain sizes (AGSs) of 0.1-1 μm. ZTA film thicknesses were increased to ~200 μm to assess potential as electronic substrates. Excellent fracture toughness (24 MPa m1/2) and small AGSs of 0.7 μm were found for ~200 μm thick ZTA films sintered at 1500 °C/5 h/N2/H2 using a three-step binder burnout process. Furthermore, homogeneous ZTA thin films (<5 μm thick) can be sintered on Si3N4 substrates (thickness ≈ 300 μm) to provide physical protection against oxidation under extreme conditions (1500 °C/1 h/O2), offering additional practical utility for high-temperature ceramics and power electronic substrates.

**ZTA Nanopowders and Ceramic Film Processing**

Nanopowder production

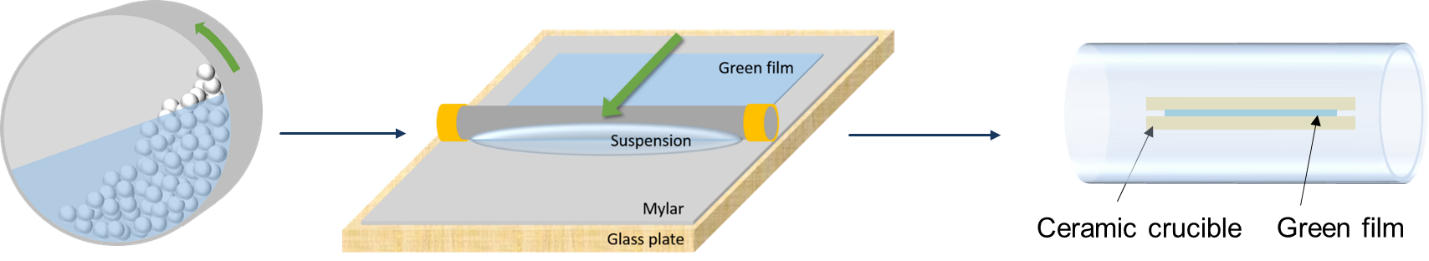
Nanopowders (NPs) were produced by **liquid feed-flame spray pyrolysis (LF-FSP)**, which was invented in the Laine group at the University of Michigan. It is a single-step continuous synthesis method for producing ceramic NPs. Typical metalloorganic precursors in this work include metal-carboxylates and metal-atrane compounds. Metalloorganic precursors at selected compositions were dissolved in alcohol and fed into an atomizing nozzle, and was aerosolized with oxygen into a quartz chamber, where it is ignited with methane/oxygen pilot torches on the spray head. Initial combustion takes place producing temperatures of ≥1500 °C followed by a quenching step that drops the temperature to 300-500 °C over 1.5 m to produce NPs. Powders are collected downstream in rod-in-tube electrostatic precipitators. The scheme below illustrates the LF-FSP apparatus for NP production.

Diagram, text

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As-produced NPs were then dispersed in ethanol by ultrasonication, and the supernatant was decanted and allowed to oven dry (60 °C/12 h) providing the starting ZrO2 doped *-*Al2O3 NPs.

The NPs were then processed following the steps below to produce target ceramic films.



Green film processing

LF-FSP synthesized NPs were mixed with polymeric additives such as binder, plasticizer, curing agent, and dispersant, in a selected solvent system by ball-milling with spherical Al2O3 as the milling media.

After ball-milling, the suspensions were cast on Mylar film using a wire-wound rod coater with control thickness to form green films. After solvents evaporated, dried green films were uniaxially pressed between stainless steel dies at 100 °C at 10 ksi/5-30 min to improve packing density.

Film sintering

Green films (typically 5 × 5 mm2) were placed between Al2O3 substrates and heated to 800 °C/1 h in extra dry grade O2 to remove polymeric additives (binder burnout). Subsequently, they were sintered to selected temperatures, times and ramp rates, using a tube furnace under controlled gas flow: 1120-1500 °C at 1-10 °C/min under O2 or 95%N2/5%H2 at 60 mL/min. For convenience, 95%N2/5%H2 is referred to as N2/H2.

**ZTA ~40 μm thin films**

In the first part of study, we investigated the sinterability, microstructures and phase compositions of ZTA thin films (~40 μm) with varying compositions and sintering conditions starting from (ZrO2)x(Al2O3)1-x (x = 0-50 mol.%) NPs by LF-FSP. Studies suggest that 1 wt.% MgO and TiO2 additives improve the sintering behavior, resulting in dense films (composition **D**: 10 mol.% ZrO2 doped Al2O3 with 1 wt.% TiO2 and MgO) with final AGSs of 0.5-1 μm at 1500 °C. Comparison of films sintered in O2 and N2/H2 suggests that the N2/H2 atmosphere improves film quality coincident with higher shrinkages and densities, as well as reductions in AGSs.

The table below lists different compositions **A**-**D** used in the study.

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The figure below compares SEM fracture surfaces of films **A**-**D** sintered at 1400-1500 ° C/5 h/N2/H2. Films **B** and **C** start to densify at 1400 ° C, obvious grain growth can be seen at 1500 ° C, especially for film **B**. Films **A** and **D** show similar sintering behavior, they densify at 1500 ° C, and exhibit finer grain sizes (0.5-1 μm) than **B** and **C** (≥1 μm). TiO2 promotes grain growth and densification, while MgO tends to diffuse to the grain boundaries and limits grain growth. After sintering at 1500 ° C, all films show some transgranular fracture behavior (marked with red arrows) suggesting improved mechanical properties.

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**ZTA ~200 μm thick films**

For potential applications as power electronic substrates, ZTA film thicknesses were increased to 150-250 μm. Since the thin film work show that films with composition **D** show small and uniform grain sizes (0.5-1 µm), and low porosity, the same composition was used for thicker films.

Sintered films exhibit hexagonal *α*-Al2O3 and *t*-ZrO2 phases, which in principle provide good mechanical properties, and was proven by single-edged precracked beam (SEPB) test that a high K1C value of ~24 MPa m1/2 is obtained. By investigating the effects of different sintering conditions, we were able to sinter crack-free 150-250 μm thick 10 mol.% ZrO2 doped Al2O3 films with AGSs of 0.7 μm by using BN insulation between films and Al2O3 substrates with a three-step binder burnout procedure.

Representative data are given below.

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**Coating Si3N4 substrates with ZTA thin films**

Similar to ZTA films, silicon nitride (Si3N4) films are also commonly used in structural applications including electronic substrates, owing to their good chemical, physical and thermal stabilities, and mechanical properties. However, Si3N4 is susceptible to oxidation even at ambient and may deteriorate over time. Although a surface oxide/oxynitride layer that forms can protect against further oxidation, to withstand high-temperature oxidation and/or active oxidation environments, additional protection is needed. In this work, we also investigated the possibility of applying sintered ZTA thin film (<5 μm) on Si3N4 substrates (≈300 μm thick) as protective coating layer against oxidation.

To coat Si3N4 substrates, ZrO2 doped *-*Al2O3 NP suspension was first cast on one side of Si3N4 samples with 25 μm spacers using the coating setup shown below. Then the films were thermally pressed at 100 ° C bottom, 60 ° C top, 4 ksi, and followed by sintering in two steps: binder burnout at 800 ° C/1 h/O2; and sintering at 1500 ° C/5 h/N2/H2. The other side of Si3N4 samples was then coated and sintered following the same procedure.



In conclusion, we found that sintered ZTA coatings (<5 μm) adhere well to Si3N4 substrates and were proven to be effective in providing physical protection against oxidation even under extreme oxidative conditions (1500 °C/1 h/O2). This demonstrates an alternate application of ZTA films for high-temperature ceramics and power electronic substrates.

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**For comprehensive analyses and discussions, please see the published paper:**