

S. Synthesis of Nanocrystalline Ceramics

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Objectives

- Synthesize well-dispersed, concentrated aqueous suspensions of nominally 8–10 nm tetragonal ZrO₂.
- Form nano-grained green bodies from concentrated ZrO₂ suspensions.
- Dry nano-grained green bodies while avoiding crack formation.
- Sinter nano-grained green bodies to high theoretical density while maintaining nano-scale grain structure.

Approach

- Complex zirconyl nitrate with bicine in aqueous solution, which is then hydrothermally treated to precipitate 8–10 nm tetragonal ZrO₂.
- Increase ZrO₂ yield by increasing reagent concentrations.
- Form green bodies using constant-rate filter pressing.
- Dry green bodies under controlled humidity conditions or through a solvent exchange procedure.
- Fire green bodies at Oak Ridge National Laboratory using transient sintering cycles.¹

Accomplishments

- Hydrothermally synthesized 10–20 nm tetragonal ZrO₂ using a procedure developed by R.A. Kimel and J.H. Adair.
- Increased ZrO₂ yield from about 25 g/L to 100 g/L by increasing reagent concentrations and modifying the dispersant concentration to accommodate the higher surface areas in solution.
- Routinely made nano-grained green bodies ¾ in. in diameter and 1–4 mm thick using constant-rate filter pressing.
- Successfully dried nano-grained green bodies using controlled humidity drying.

- Successfully dried nano-grained green bodies by exchanging entrained water with acetone containing an acryloid binder.
- Sintered nano-grained green bodies to 100% theoretical density while maintaining grain sizes below 100 nm.

Future Direction

- Continue to produce nano-grained green bodies with constant-rate filter pressing.
- Compare constant-rate filter pressing to constant-pressure filter pressing.
- Optimize solvent exchange drying procedure to optimize green densities.
- Produce larger-diameter green bodies for sintering and mechanical testing.

Introduction

The main objective of this research was to manufacture bulk, dense ceramics with grain sizes of less than 100 nm. The material chosen for this purpose was ZrO_2 and Y_2O_3 -stabilized ZrO_2 because of its mechanical properties and its ease of production in the appropriate size scale.

Previously, nanoscale ZrO_2 and Y_2O_3 -stabilized ZrO_2 have been synthesized using a protocol developed by Kimel and Adair²⁻⁴ in which zirconyl nitrate (and yttrium nitrate) is complexed with bicine in aqueous solution through alkaline pH adjustment. Hydrothermal treatment at 200°C for 8 hours allowed particles of the tetragonal phase with sizes of between 8 and 15 nm to precipitate. The product suspension was then washed with an aqueous solution of oxalic acid to remove any remaining bicine and disperse the suspended particles. However, solid yield was only about 25 g/L using this method.

By increasing the concentration of reagents, yield was increased to about 50 g/L. The limiting factor in this protocol became the solubility of both bicine and the organic base used to adjust pH (tetraethylammonium hydroxide, TEAOH). To address this issue, dry zirconyl nitrate and bicine were mixed with an appropriate amount of solid organic base, tetramethylammonium hydroxide pentahydrate (TMAOH). Because of the water content of both the zirconyl nitrate and TMAOH, the mixture became an aqueous solution, which was hydrothermally treated to produce 10–30 nm ZrO_2 . Using this method, ZrO_2 yield was increased to 100 g/L.

Approach

The current task in this research has been the production of green bodies for sintering studies. This was accomplished with constant rate filter pressing, in which plungers moving at a constant rate apply a load to a concentrated suspension. Solution is then removed through filters at the bottom of the solution chamber (see Figure 1).

Once the wet pellets are removed from the filter press die, they must be carefully dried to avoid cracking within the body. This can be done either with controlled humidity or by exchanging water within the pellet with another liquid of lower surface tension (solvent exchange).

Results

With the current filter pressing protocol, pellet production has been increased to about four pellets per 4 hours (from four pellets per 12–18 hours). Humidity drying, the previously preferred method, has been limited as a result of difficulties with equipment. Therefore, solvent exchange drying has been investigated.

Initially, four solvents were chosen: methylethylketone (MEK), 40% MEK–60% ethanol (by weight), acetone, and isopropanol. Each of these solvents was pushed through a filter-pressed pellet immediately after pressing concluded. Upon removal from the die, the solvent-exchanged pellets were all cracked but dry. Density measurements by the Archimedes method revealed a marked increase in density (see Table 1). However, the dry pellets maintained little green strength.

Table 1. Archimedes density measurement results of solvent-exchange-dried ZrO₂ pellets

Solvent	Density (g/cm ³)	Theoretical density (%)
Methylethylketone (MEK)	3.99	66
40% Methylethylketone – 60% Ethanol (by weight)	4.01	68
Isopropanol	3.07	51
Acetone	3.61	60

It was then proposed that a binder be added to the solvent to add green strength to the dry body. An acetone-soluble acryloid binder (Rohm and Haas), which is typically used in dry pressing, was chosen. When the acetone-binder solution was pressed through wet filter-pressed pellets, cracks were still present, but to a smaller degree. Cracking was reduced further by introducing the acetone-binder solution to pellets that were not fully consolidated. Archimedes density determination on fragments of these pellets reveals, again, that pellets are achieving a high density after drying with the solvent exchange process (Table 2). Also, the high densities achieved with acryloid binder present require recalculation once the actual concentration of binder is determined by controlled thermolysis. It is likely that the very large values (in some cases greater than 70% theoretical density) will be in the 60% theoretical density range when the concentration of binder is known and accounted for in the density calculation. Whether cracking can be eliminated completely by beginning the solvent exchange drying process earlier in the filter pressing procedure is currently under investigation.

Conclusions

The research focus has centered recently on increasing yield during synthesis and producing green bodies for sintering studies. By modifying the previous synthesis procedure, ZrO₂ yield was increased fourfold. Pellet pressing times have also been decreased significantly. Solvent exchange drying was demonstrated to be an effective method of drying filter-pressed green bodies to a high density. Efforts are continuing to eliminate cracks after drying with the solvent exchange procedure.

Table 2. Archimedes density measurement results of solvent-exchange-dried ZrO₂ pellets (dried with a solution of acetone and an acryloid binder)

Sample number	Binder concentration	Density (g/cm ³)*	Theoretical density* (%)
a3	0%	4.32	72
a1	2% (relative to weight of solids)	4.48	74
a2	3% (relative to weight of solids)	4.17	69
b1	0%	4.71 (very small sample)	78
b2	1% (relative to weight of solution)	4.65	77
b3	2% (relative to weight of solution)	4.45	74
b4	5% (relative to weight of solution)	4.13	69
c1	1% (relative to weight of solution)	4.30	71
c2	2% (relative to weight of solution)	4.48	75
c3	5% (relative to weight of solution)	3.95	66

References

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