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# Synthesis and Processing of Nanostructured Materials

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*A Collection of Papers Presented at the  
29th and 30th International Conference on  
Advanced Ceramics and Composites  
January 2005 and 2006,  
Cocoa Beach, Florida*

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# Contents

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Preface	vii
Introduction	ix
Nanoparticle Colloidal Suspension Optimization and Freeze-Cast Forming Kathy Lu and Chris S. Kessler	1
Synthesis, Characterization and Measurements of Electrical Properties of Alumina-Titania Nano-Composites Vikas Somani and Samar J. Kalita	11
Synthesis and Characterization of Nanocrystalline Barium Strontium Titanate Ceramics Vikas Somani and Samar J. Kalita	23
Nanoparticle Hydroxyapatite Crystallization Control by using Polyelectrolytes Mualla Öner and Özlem Dogan	33
Synthesis of Carbon Nanotubes and Silicon Carbide Nanofibers as Composite Reinforcing Materials Hao Li, Abhishek Kothari, and Brian W. Sheldon	41
3-D Microparticles of BaTiO <sub>3</sub> and Zn <sub>2</sub> SiO <sub>4</sub> via the Chemical (Sol-Gel, Acetate, or Hydrothermal) Conversion of Biological (Diatom) Templates Ye Cai, Michael R. Weatherspoon, Eric Ernst, Michael S. Haluska, Robert L. Snyder, and Kenneth H. Sandhage	49
Polymer Fiber Assisted Processing of Ceramic Oxide Nano and Submicron Fibers Satyajit Shukla, Erik Brinley, Hyoung J. Cho, and Sudipta Seal	57

<b>Phase Development in the Catalytic System <math>V_2O_5/TiO_2</math> under Oxidizing Conditions</b>	<b>69</b>
D. Habel, E. Feike, C. Schröder, H. Schubert, A. Hösch, J. B. Stelzer, J. Caro, C. Hess, and A. Knop-Gericke	
<b>Synthesis and Characterization of Cubic Silicon Carbide (<math>\beta</math>-SiC) and Trigonal Silicon Nitride (<math>\alpha</math>-Si<sub>3</sub>N<sub>4</sub>) Nanowires</b>	<b>81</b>
K. Saulig-Wenger, M. Bechelany, D. Cornu, S. Bernard, F. Chassagneux, P. Miele, and T. Epicier	
<b>High Energy Milling Behavior of Alpha Silicon Carbide</b>	<b>89</b>
M. Aparecida Pinheiro dos Santos and C. Albano da.Costa Neto	
<b>Synthesis of Boron Nitride Nanotubes for Engineering Applications</b>	<b>95</b>
J. Hurst, D. Hull, and D. Gorican	
<b>Comparison of Electromagnetic Shielding in GFR-Nano Composites</b>	<b>103</b>
W.-K. Jung, S.-H. Ahn, and M.-S. Won	
<b>Densification Behavior of Zirconia Ceramics Sintered Using High-Frequency Microwaves</b>	<b>113</b>
M. Wolff, G. Falk, R. Clasen, G. Link, S. Takayama, and M. Thumm	
<b>Manufacturing of Doped Glasses Using Reactive Electrophoretic Deposition (REPD)</b>	<b>121</b>
D. Jung, J. Tabellion, and R. Clasen	
<b>Shaping of Bulk Glasses and Ceramics with Nanosized Particles</b>	<b>129</b>
J. Tabellion and R. Clasen	
<b>Author Index</b>	<b>137</b>



# Preface

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This proceedings contains a collection of papers submitted from the Functional Nanomaterial Systems Based on Ceramics focused session, held during the 29th International Conference and Exposition on Advanced Ceramics and Composites, January 23–28, 2005 and the Synthesis and Processing of Nanostructured Materials symposium, held during the 30th International Conference and Exposition on Advanced Ceramics and Composites, January 22–27, 2006. in Cocoa Beach, Florida.

Thanks and appreciation goes to those who attended and participated in these nanomaterial sessions, to the authors who submitted a paper for this volume, and to those who helped in the review process.

WILLIAM M. MULLINS



# Introduction

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This book is one of seven issues that comprise Volume 27 of the Ceramic Engineering & Science Proceedings (CESP). This volume contains manuscripts that were presented at the 30th International Conference on Advanced Ceramic and Composites (ICACC) held in Cocoa Beach, Florida January 22–27, 2006. This meeting, which has become the premier international forum for the dissemination of information pertaining to the processing, properties and behavior of structural and multi-functional ceramics and composites, emerging ceramic technologies and applications of engineering ceramics, was organized by the Engineering Ceramics Division (ECD) of The American Ceramic Society (ACerS) in collaboration with ACerS Nuclear and Environmental Technology Division (NETD).

The 30th ICACC attracted more than 900 scientists and engineers from 27 countries and was organized into the following seven symposia:

- Mechanical Properties and Performance of Engineering Ceramics and Composites
- Advanced Ceramic Coatings for Structural, Environmental and Functional Applications
- 3rd International Symposium for Solid Oxide Fuel Cells
- Ceramics in Nuclear and Alternative Energy Applications
- Bioceramics and Biocomposites
- Topics in Ceramic Armor
- Synthesis and Processing of Nanostructured Materials

The organization of the Cocoa Beach meeting and the publication of these proceedings were possible thanks to the tireless dedication of many ECD and NETD volunteers and the professional staff of The American Ceramic Society.

ANDREW A. WERESZCZAK  
EDGAR LARA-CURZIO  
General Editors

*Oak Ridge, TN (July 2006)*

# NANOPARTICLE COLLOIDAL SUSPENSION OPTIMIZATION AND FREEZE-CAST FORMING

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## ABSTRACT

Nanoparticle suspension and forming are important areas. In this paper, the stability and rheology of  $Al_2O_3$  nanoparticle suspensions at different dispersant concentration, suspension pH, and solids loading were studied. The most desirable suspension conditions were 7.5-9.5 for pH and 2.00-2.25 wt% of  $Al_2O_3$  for poly(acrylic acid) (PAA) dispersant. 45.0 vol%  $Al_2O_3$  solids loading can be achieved while maintaining good suspension flow for freeze casting. The maximum solids loading of the  $Al_2O_3$  nanoparticle suspension was predicted to be 50.7 vol%. The preliminary results of the freeze-cast sample showed that suspension pre-rest before freezing was critical for achieving defect free microstructures.

## INTRODUCTION

To overcome agglomeration and low packing density issues, colloidal processing is the preferred approach for nanoparticles. The unique ionic properties of water allow addition of ions to overcome the problematic particle-particle attraction; this ion-related stabilizing mechanism is called electrostatic stabilization. Another approach is to add a polymer dispersant to the suspension; polymer chains adsorb onto the particle surfaces and extend into water, and physically repel one another; this method of stabilization is called steric stabilization.<sup>1</sup> More effectively, an ionic polymer dispersant and the ionic properties of water can be used simultaneously to obtain a well-dispersed suspension; this method is called electrosteric stabilization.<sup>2</sup> A delicate balance must be maintained in the pH and the dispersant concentration. Inappropriate pH will result in particle attraction, not repulsion.<sup>3</sup> The adsorbed polymer must be thick enough to prevent close particle contact and counteract van der Waals forces. Too little polymer will cause bridging flocculation; too much polymer will cause depletion flocculation.<sup>4,5,6,7</sup> Ideally, the adsorbed polymer layer should be just thick enough to prevent van der Waals bonding. Since nanoparticles have much larger specific surface area than micron size particles, more polymer molecules will be adsorbed to cover the nanoparticle surface of the same mass; this will correspondingly reduce the solids loading of the nanoparticles even with ideal polymer layer thickness.

Viscosity measures the ability of the solid particles to flow relative to one another. A decrease in the particle size leads to suspensions of high viscosity because the effective solids loading is increased in the nanoparticle suspensions. The effective solids loading increase occurs because the particle diameter decrease creates large electrical double layer or adsorbed polymer layer volume that accounts as part of the effective solids loading. For high solids loading, the polymer concentration must be controlled with a much higher precision for the nanoparticle suspension than for the conventional suspensions.<sup>8</sup> The suspension must flow well into the mold and fill in the complex details or cavities of the mold. Intuitively, the higher the solid loading,

the more viscous and difficult the flow will be. However, high solids loading is necessary to get a fully dense component. A balance must be achieved to address these opposite demands.

Freeze casting is a process that pours the suspension into a nonporous mold, freezes the suspension, demolds the component, and then dries the component under vacuum. Very desirably, freeze casting avoids defect formation by eliminating capillary force during drying and saves tremendous effort in binder removal. The technique is ideally suited for complex shapes and costs very little on tooling, which is a huge saving compared to dry pressing, isostatic pressing, or shock wave compaction.<sup>9,10,11</sup> Flexibility in forming complex shapes at minimal cost is also very suitable for rapid prototyping. Freeze casting also has the advantage of using less expensive and non-toxic dispersing medium, water.

The work reported here is focused on understanding PAA dispersant concentration, suspension pH, and Al<sub>2</sub>O<sub>3</sub> solids loading effects on PAA adsorption onto Al<sub>2</sub>O<sub>3</sub> nanoparticles and the stability and rheology of the nano-Al<sub>2</sub>O<sub>3</sub> suspensions. By measuring the suspension rheology under different conditions, the maximum solids loading for the Al<sub>2</sub>O<sub>3</sub> nanoparticle suspension is predicted. Based on the optimized dispersion conditions, the 40 vol% solids loading suspension has been freeze-cast. The preliminary characteristics of the freeze-cast components are reported.

### EXPERIMENTAL PROCEDURE

Al<sub>2</sub>O<sub>3</sub> nanoparticles with average particle size of 38 nm and specific surface area of 45 m<sup>2</sup>/g were used in this study (Nanophase Technologies, Romeoville, IL). The Al<sub>2</sub>O<sub>3</sub> was reported from the vendor to have 70:30 of  $\delta$ :  $\gamma$  phases. Even though the average particle size was much less than 100 nm, the particle size distribution was wide and there was a small percent of large particles close to 100 nm. PAA (M<sub>w</sub> 1,800, Aldrich, St Louis, MO) was used as a polymer dispersant with the polymer segment as [-CH<sub>2</sub>CH(CO<sub>2</sub>H)-].

For the preparation of the Al<sub>2</sub>O<sub>3</sub> suspensions, 10 wt% glycerol (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>, water basis, Fisher Chemicals, Fairlawn, NJ) was mixed with water and the mixture was homogenized for 5 min using a ball mill. Glycerol was used to lower the freezing temperature of the suspension and refine the ice microstructure for homogeneous component formation during freeze casting.<sup>12</sup> Al<sub>2</sub>O<sub>3</sub> powder was added for a specific solids loading in 10 g increments along with an appropriate amount of PAA dispersant. Since low pH promotes PAA dispersant adsorption onto the nano-Al<sub>2</sub>O<sub>3</sub> particles, HCl solution was added to lower the pH to 1.5.<sup>13</sup> The suspension was ball milled for 12 hrs with periodic adjustment of pH to 1.5. This procedure was used to make suspension of approximately 20 vol% Al<sub>2</sub>O<sub>3</sub>. NH<sub>4</sub>OH was then used to adjust the suspension to the desired pH level. Depending on the final solids loading desired, nano-Al<sub>2</sub>O<sub>3</sub> was added again in 10 g increments, along with the appropriate amount of PAA dispersant and the adjustment of the suspension pH. The suspension was then mixed for 24 hrs for complete homogenization. NH<sub>4</sub>OH was again used to adjust the suspension to the desired pH level.

For suspension characterization, the pH of the suspensions was measured by a pH meter (Denver Instrument, Arvada, CO). Potentiometric titration was used to determine the amount of PAA dispersant adsorbed onto the Al<sub>2</sub>O<sub>3</sub> particles in a suspension.<sup>14,15</sup> pH was adjusted to 9.5±0.05 before titrant HCl solution was added in order to promote the dissociation of PAA dispersant in water. Adsorption curve was developed for known PAA concentration blank solutions first. To measure the adsorption of PAA dispersant in an actual suspension, the suspensions with PAA dispersant and different solids loading were centrifuged at 2,500 rpm for 45 min before collecting the resulting supernatants. A known volume of the supernatant was

titrated and the amount of un-adsorbed PAA dispersant was determined using the standard curve from the blank PAA solutions. The viscosities of the suspensions were measured by a rheometer with a cone-plate geometry (AR 2000, TA Instruments, New Castle, DE). All the suspensions were pre-sheared at  $200 \text{ s}^{-1}$  to impart similar shear history. The measurements were performed at equilibrium shear with controlled shear rates.

Slurries of 40 vol% solid loading were used for freeze casting. Freeze casting molds were developed using poly (dimethylsiloxane) epoxy (RTV 664, General Electric Company, Waterford, NY) and a fully dense flexural test specimen as a pattern. After curing, the flexural test specimen was removed, leaving a cavity in the epoxy. A transfer pipette was used to place the well dispersed  $\text{Al}_2\text{O}_3$  suspension into the mold to reduce air bubbles and promote filling. The  $\text{Al}_2\text{O}_3$  suspension filled epoxy mold was placed in a freeze dryer (Labconco Stoppering Tray Dryer, Labconco, Kansas City, MO) and cooled to  $-35^\circ \text{C}$  for 2 hrs. The samples were demolded after freezing and then exposed to low pressure ( $<10 \times 10^3 \text{ Pa}$ ) for 36 hrs to allow the ice to sublimate. The microstructures of the freeze-cast samples were examined by a LEO 1550 field emission scanning electron microscope (Carl Zeiss MicroImaging, Inc, Thornwood, NY).

## RESULTS/DISCUSSION

### 1) PAA Adsorption and Suspension Rheology

Hydrogen bonding is a ubiquitous mechanism for polymer adsorption onto hydrophilic surfaces. Mathur et al. studied the nature of oxide surface hydroxyls and indicated that isolated surface hydroxyls constitute the surface of  $\text{Al}_2\text{O}_3$ .<sup>16</sup> Based on this understanding, PAA adsorption onto  $\text{Al}_2\text{O}_3$  is expected to be affected by the PAA concentration. However, how such adsorption mechanism plays a role in high solids loading suspensions has not been examined. To study the PAA concentration effect on its adsorption onto  $\text{Al}_2\text{O}_3$  nanoparticles in a high solids loading suspension, the solids loading of the suspension was fixed at 30 vol% while the PAA concentration was varied between 1.00-2.50 wt% of  $\text{Al}_2\text{O}_3$  as shown in Fig. 1. As the PAA concentration increases up to 2.00 wt% of  $\text{Al}_2\text{O}_3$  PAA concentration, the adsorbed PAA amount onto  $\text{Al}_2\text{O}_3$  particles also increases. As more PAA is added to the suspension, the adsorbed PAA amount reaches a plateau at  $0.31 \text{ mg/m}^2$ . The adsorption plateau represents a saturation adsorption level at which the  $\text{Al}_2\text{O}_3$  particle surfaces are fully covered by PAA dispersant. For the studied system, the minimum PAA concentration needed is 2.00 wt% of  $\text{Al}_2\text{O}_3$ . On the other hand, the relative amount of PAA adsorbed onto the  $\text{Al}_2\text{O}_3$  nanoparticles decreases monotonically as more PAA is added, due to the blocking of some active sites from the adsorbed PAA polymer onto the solid surface; this means free PAA concentration increases along with total PAA concentration increase. After the adsorbed PAA amount reaches the saturation plateau for monolayer coverage, additional PAA dispersant only exists as free polymer in the suspension, resulting in 'overdispersing'.