

# Innovative Processing and Synthesis of Ceramics, Glasses and Composites IX

*Edited by*

J.P. Singh

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Antonio de Arellano López

***Proceedings of the 107<sup>th</sup> Annual Meeting  
of The American Ceramic Society,  
Baltimore, Maryland, USA (2005)***



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# Preface

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This volume contains papers presented at the symposium on Innovative Processing and Synthesis of Ceramics, Glasses, and Composites held during the 107th Annual Meeting, Exposition, and Technology Fair of The American Ceramic Society at Baltimore Marriott Waterfront, Baltimore, MD April 10-13, 2005. This symposium provided an international forum for scientists and engineers to discuss all aspects of processing and synthesis of ceramics, glasses, and composites. A total of 43 papers, including invited talks, oral presentations, and posters, were presented from 14 countries (USA, Australia, Belgium, Canada, China, Germany, India, Italy, Japan, Mexico, Slovenia, Spain, Taiwan, and the United Kingdom). The speakers represented universities, industry, and research laboratories.

This volume contains 14 invited and contributed papers, all peer-reviewed according to ACerS procedures. The latest developments in processing and characterization are covered including novel processing and microstructure-property relationships, electrophoresis, mechanisms and kinetics of processes, reaction forming, and in-situ and porous composites. All of the most important aspects necessary for understanding and further development of ceramic/composite processing and characterization are discussed.

The organizers are grateful to all participants and session chairs for their time and efforts, to authors for their timely submissions and revisions of manuscripts, and to the reviewers for their valuable comments and suggestions. Without the contributions of all involved, this volume would not have been possible. Financial support from the Engineering Ceramics Division and The American Ceramic Society is gratefully acknowledged. Thanks are due to the staff of the meetings and publications departments of The American Ceramic Society for their tireless efforts.

We hope that this volume will serve as a useful reference for the professionals working in the field of synthesis and processing of ceramics, glasses, and composites.

J. P. Singh  
Narottam P. Bansal  
Balakishnan G. Nair  
Tatsuki Ohji  
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# **Novel Processing and Microstructure-Property Relationships**

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## EFFECT OF ALUMINON AQUEOUS SOLUTION CHEMISTRY ON THE HOMOGENEITY OF COMPACTS BY COLLOIDAL FILTRATION OF $\alpha$ - $\text{Al}_2\text{O}_3$ DISPERSIONS

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### ABSTRACT

Colloidal filtration is successfully applied to produce dense-packed macro-defect free flat compacts from colloidally metastable dispersions of 300 nm  $\varnothing$   $\alpha$ - $\text{Al}_2\text{O}_3$  (AKP30) particles. Good homogeneity and <67% packing density are achieved by electro-steric stabilization of the dispersion with ammonium aurintricarboxylate (Aluminon) in combination with controlling  $p_H$  and ionic strength. An optimized solution chemistry was found by studying the influence of Aluminon, ammonia concentration and NaCl additions on rheological properties and zeta potential of 50 wt%  $\alpha$ - $\text{Al}_2\text{O}_3$  suspensions and compacts formed. The viscosity is found to be much higher at 0.1 wt% Aluminon than at 0.15 and 0.2 wt%. This indicates that the Aluminon does not cover the particle surface completely at a concentration of 0.1 wt%. Moreover, by adding a small amount of ammonia, the rheological behavior changes drastically from Bingham to a nearly Newtonian. It was found that, in order to prepare macro-defect free high-density compacts, the  $p_H$  must be 9.5 and the Aluminon concentration 0.2 wt %. Considerable improvements in microstructural homogeneity were found in particular at high ionic strength by NaCl addition. Since increasing ionic strength is expected to decrease colloidal stability, this effect cannot be explained by traditional DLVO considerations alone.

### INTRODUCTION

During the last decade, the application of inorganic ceramic membranes based on metal oxides such as alumina, mullite, cordierite, zirconia, silica and titania is increasing due to their excellent mechanical strength and resistance to harsh conditions like extreme  $p_H$ , intense oxidation and extreme temperatures [1, 2]. The use of ceramic membranes not only enhances the already existing applications but also opens new possible application such as high-flux water purification [3-5] and high-selectivity gas separation [6]. Generally, ceramic membranes are fabricated in a multi-layer configuration. The preparation of such multi-layer structures starts with a macro-porous support that is provided with one or more thin layers of other ceramic material [7]. As a consequence it is important that the support is sufficiently permeable but has a surface structure, suitable for deposition of the top layers. These layers should be macro-defect-free and very thin to achieve high separation factors in combination with high fluxes. As a consequence, the support must have a smooth fine-porous surface structure that allows for (colloidal) deposition of subsequent layers. Any macro-defects in the support surface are likely to cause similar defects in the subsequent layers.

Conventional forming methods such as extrusion, tape casting and dry pressing may not result in the desired surface structure necessary for ceramic membrane supports. Colloidal processing techniques, such as slip casting, colloidal filtration, and colloidal casting, generally

give better compact homogeneity and hence better surface quality. Practical membrane supports may ultimately be produced by a combination of conventional mass-production methods and colloid processing to improve surface quality. Colloidal processing has been successfully applied to the field of structural ceramics and several studies show that these methods result in minimal macro-defects in a quasi-homogeneous structure. They generally start from a homogeneous, colloidally meta-stable suspension of ceramic particles [8–11]. The particles in the dispersion are consolidated into a desired shape by the application of external forces such as gravity, convection or electro-statics.

A previous paper described the formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> compacts by colloidal filtration of 300 nm  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (AKP30) particles in aqueous HNO<sub>3</sub> with  $p_H = 2$  and sintering [12]. While this led to compacts with excellent surface quality, problems were met with the aggressive nature of the dispersion medium. It was also found that the use of polymer stabilizers such as APMA, instead of HNO<sub>3</sub>, led to increases of the dispersion viscosity that were incompatible with colloidal filtrations and poor compact homogeneity. It is for this reason that small molecule electro-steric stabilizers that operate in a more neutral  $p_H$  regime and do not affect viscosity are recently studied. In the first study, pyrocatechol-3, 5-disulfonic acid disodium salt (Tiron) was considered as an electrosteric stabilizer [13], and it was found that a fair compact quality could be obtained with proper optimization of the solution chemistry. The present paper describes the use and optimization of electro-steric stabilization by ammonium auringtricarboxylate (Aluminon) for the formation of homogeneous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> compacts.

## EXPERIMENTAL PROCEDURE

The starting material was high purity  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder, AKP-30 (Sumitomo Chemical Co. Ltd, Tokyo, Japan), with a narrow particle size distribution, a BET surface area of 6.2 m<sup>2</sup>/g, and an average particle size of 300  $\mu$ m, as stated by the manufacturer.

Dispersions of 50 wt. %  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in water were prepared with various amounts of added Aluminon, ammonia, NH<sub>4</sub>Cl or NaCl. Dispersion was promoted by using ultra sonic treatment for 10 min at an output power 60 W (Model 102C, Branson, USA) [11]. The suspensions were deaired by evacuating them in a desiccator and rheological properties were determined at 303 K with a rotational, stress controlled rheometer (MCR 150, Physica Messtechnik GmbH) with a plate/plate geometry. These measurements were performed with a shear rate that varied between 10<sup>-2</sup> and 10<sup>3</sup> s<sup>-1</sup>.

Electroacoustic measurements (ZetaProbe Analyzer<sup>TM</sup>, Colloidal Dynamic Inc., RI, USA) were carried out to evaluate the effect of  $p_H$  values on the zeta potential of alumina particles (AKP30). The tests were performed in diluted suspensions (5wt %) of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in water with 0.2wt % Aluminon. After ultrasonication for 10 min, the zeta potential was measured as a function of  $p_H$  by titrating the suspension with (1 N) HNO<sub>3</sub> or NaOH.

Colloidal filtration compacts were prepared with a set-up described elsewhere [12]. They had a thickness of ~2 mm and a diameter of ~42 mm, and were dried in their filtration cups under a controlled temperature of 313 K and humidity of 60%. The compacts were slightly sintered at 923 K for ~10 hrs using a 2K min<sup>-1</sup> heating rate. This procedure led to very little sinter shrinkage and provided the compacts with sufficient handling strength. The microstructure of the upper disk surface was examined by scanning electron microscopy (a Field-Emission Environmental SEM Philips XL30).

# RESULT AND DISCUSIONS

## Rheological properties of suspension

The shear stress vs. shear rate of dispersions with different Aluminon concentrations is shown in figure 1. The dispersion with 0.1 wt% Aluminon showed a much higher shear stress (viscosity) at any shear rate than the dispersions with 0.15 and 0.2 wt% Aluminon. This observation indicates that at 0.1 wt% Aluminon the  $\alpha\text{-Al}_2\text{O}_3$  surface is not yet completely covered by adsorbed Aluminon. The viscosity barely changed between dispersions with 0.15 and 0.20 wt% dispersant, indicating that the  $\alpha\text{-Al}_2\text{O}_3$  surface is likely to become fully covered at those concentrations. It is for this reason that 0.20 wt % was chosen as the concentration where Aluminon provides sufficient colloidal stabilization.

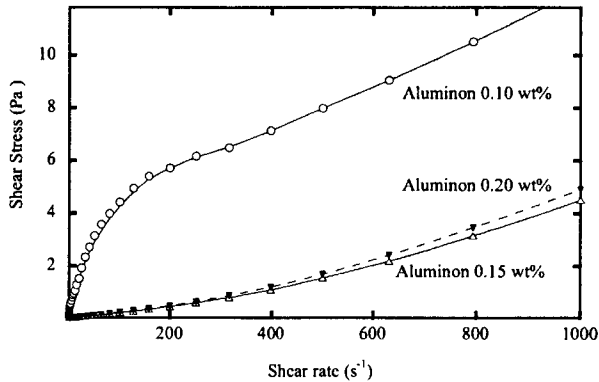


Figure 1: Shear stress vs. shear rate of a 50 % AKP30 suspension with different amounts of Aluminon added

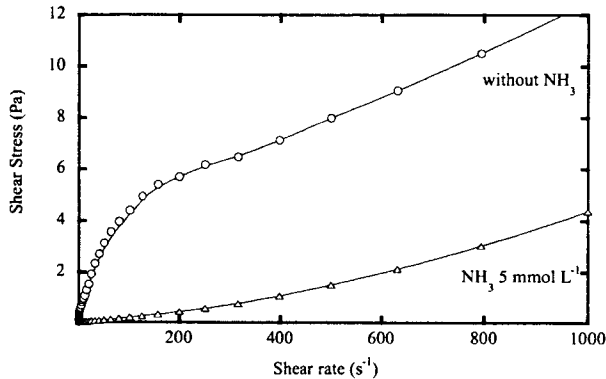


Figure 2: Shear stress versus shear rate of a 50 wt% AKP30 suspension with 0.1wt% Aluminon without and 5 mmol  $\text{L}^{-1}$   $\text{NH}_3$

Data reduction of the rheological parameters was performed with the Bingham equation for 0.1 wt%

$$\tau = \tau_0 + (\eta_B \dot{\gamma}) \quad (1)$$

and the Casson equation for 0.15 and 0.2 wt%

$$\tau = \left[ \tau_0^{1/2} + (\eta \dot{\gamma})^{1/2} \right]^2 \quad (2)$$

where  $\tau$  is the shear stress,  $\tau_0$  the yield stress,  $\eta$  the viscosity and  $\dot{\gamma}$  shear rate. Table I summarizes the rheological parameters, obtained by fitting to (1) and (2)

Table I: Rheological parameters

| Aluminon concentration | Viscosity at $(100\text{ s}^{-1})$ mPa·s | Fitting Parameter |                |          |
|------------------------|------------------------------------------|-------------------|----------------|----------|
|                        |                                          | $\tau_0$ [Pa]     | $\eta$ [mPa·s] | $R$      |
| 0.1                    | 44.1                                     | ~4                | 8              | 0.97 (1) |
| 0.15                   | 2.8                                      | 0.10              | 5              | 0.99 (2) |
| 0.2                    | 2.42                                     | 0.13              | 6              | 0.99 (2) |

The shear stress versus shear rate curves for the dispersion with 0.1 wt% Aluminon with and without  $\text{NH}_3$  added are shown in figure 2. From this figure it is clearly visible that the rheological properties of the dispersion with Aluminon strongly depend on the presence of the ammonia. In absence of any ammonia amount, the flow curve of the alumina water suspension shows a Bingham model.

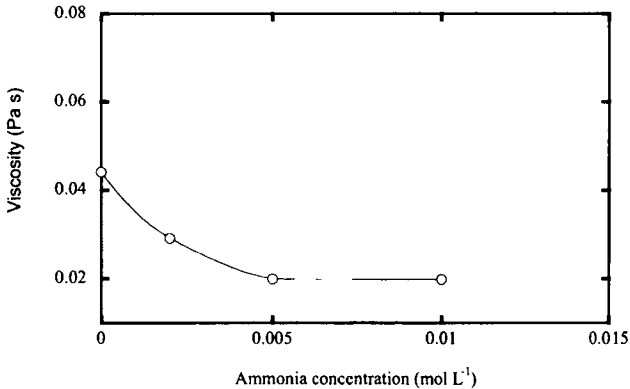


Figure 3: Apparent viscosity vs. ammonia content of a 50 wt% AKP30 suspension with 0.2 wt% Aluminon at a shear rate of  $100 \text{ s}^{-1}$

In figure 3, the apparent viscosity of dispersions with 0.2 wt% Aluminon at  $\dot{\gamma}=100 \text{ s}^{-1}$  is plotted as a function of ammonia content, showing that the viscosity of the suspension decreases with increasing ammonia amount. This indicates that colloidal stability increases with  $p_{\text{H}}$ . The