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Report Title

Final Report: Study of Self-Assembly Monolayers for Colloidal Processing of Ceramics and Textured, Super-Hydrophobic

ABSTRACT

Objectives are proposed concerning the molecules that form self assembled monolayers (SAMs) that can be used in colloidal powder processing and the fabrication of textured, super-hydrophobic ceramic surfaces. The first objective is to understand and control the steric forces between particles coated with hydrophilic (water loving) SAMs. This approach is new and will be exploited by industry in a variety of applications. The second is to use this knowledge
to produce ceramics with micron to submicron periodic surface features using elastomer molds that are produced by a new photolithographic methods. The third objective is to produce textured surfaces with hydrophobic (water hating) SAMs to produce super-hydrophobic surfaces (wetting angles > 165°) with unique features that include the biologically inspired self-cleaning properties of the lotus leaf, rain-repellent radomes with improved reliability during storms, surfaces designed to decrease the resistance to fluid flow (drug delivery in MEMS devices), and surfaces that either restrict or encourage selective liquid condensation. Progress towards these and other goals have been reported in the 15 technical reports. Many of these have been published in refereed journals.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Z. Zhang, B. Liu and F.F. Lange, “Increasing Wet Green Strength of Alumina Body During Microfabrication by Colloidal Isopressing,” J. Am. Ceram. Soc. 88 [6] 1411-1414 (2005).

RM Bock and FF Lange, “Effects of C(n)TAB chain length and concentration on the rehological properties of aqueous suspensions of alkylated alumina powder,” J. Amer. Ceram. Soc. 89 [3] 817-22 (2006)

Biao Liu, Fred F. Lange, "Pressure induced transition between superhydrophobic states: Configuration diagrams and effect of surface feature size, "Journal of Colloid and Interface Science 298 899–909 (2006)

Aninda J. Bhattacharyya, Joachim Maier, Ryan Bock, Frederick F. Lange, "New class of soft matter electrolytes obtained via heterogeneous doping: Percolation effects in “soggy sand” electrolytes," Solid State Ionics 177 (2006) 2565–2568

F. F. Lange "Plastic/Brittle Behavior of Consolidated Bodies: Role of Particle Pair Potential," Lessons in Nanotechnology from Traditional and Advanced Ceramics, Editor: J.-F. Baumard, publisher: Techna Group, It (2005)

F. F. Lange, "The Sophistication of Ceramic Science Through Silicon Nitride Studies," J. Ceramic Soc. of Japan 114 [11] 873-79 (2006)

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Shape Forming Via Colloidal Isopressing: Reformulating a Commercial Silicon Nitride Slurry with a Commercial Silane
Hannes Essmann, Ryan Bock, V. K Pujari, and F. F. Lange

Adsorption of Soluble Silica Species on Alumina Powders and Vice Versa
B. Liu and F. F. Lange

The Diffusion Path of Si in Au/Si System
B. Liu and F. F. Lange

Development and Characterization of Aqueous Mixed Network Slurries for use in Colliodal Isopressing.
R. M. Bock and F. F. Lange

Surface Modification of Alumina and Zirconia Powders using Monoalkyl Phosphates and Phosphonates.
T.C. Radsick and F. F. Lange

Slurry Consolidation and Mechanical Testing of Alumina and Zirconia Powders Modified with Monoalkyl Phosphates and Phosphonates
T.C. Radsick and F. F. Lange

Comparison of the Sintering Properties of Two Alumina Powders
Z. Zhang, K. Asici and F. F. Lange

Development and Characterization of Alkylated Slurries for use in Colloidal Isopressing using Salt to Control Interparticle Pair Potentials
R. M. Bock and F. F. Lange

Effects of CnTAB Chain Length and Concentration on the Rheological Properties of Aqueous Suspensions of Alkylated Alumina Powders
R. M. Bock and F. F. Lange

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Graduate Students

NAME	PERCENT_SUPPORTED	
Zhuo Zhange	1.00	No
Biao Liu	1.00	No
Ryan M. Bock	1.00	No
Lt. Col. T. C. Radsick	0.10	No
FTE Equivalent:	**3.10**	
Total Number:	**4**	

Names of Post Doctorates

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Names of Faculty Supported

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FTE Equivalent:	
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Names of Personnel receiving masters degrees

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Names of personnel receiving PHDs

NAME
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Shape Forming Via Colloidal Isopressing: Reformulating a Commercial Silicon Nitride Slurry with a Commercial Silane
Hannes Essmann, Ryan Bock, V. K Pujari, and F. F. Lange
Technical Report, to be published

Abstract: Colloidal Isopressing is a new shape forming method that requires a pre-consolidated slurry with a flow stress much less than that of a commercial throwing clay (< 0.1 MPa), so that it can be injected into a rubber cavity and isopressed. It is shown that the desired interparticle pair potential can be achieved with a commercial silane for a commercial Si_3N_4 aqueous slurry (NT 154-X12) containing densification aids. Unlike previous work, this silane has a relatively short molecular length and unlike previous results, the addition of salt was not needed to shorten the molecule and achieve the rheological behavior after pre-consolidation. The results of this study also show that the transition from a fluid-like to elastic-like behavior after consolidation was related to the relative density achieved during the pre-consolidation step, which was dependent on the consolidation pressure.

Adsorption of Soluble Silica Species on Alumina Powders and Vice Versa
Biao Liu, Xiaojun Liu, Carl D. Meinhart, and Fred F. Lange
Technical Report, Thesis Chapter to be published

Abstract: In an effort to texture a glass surface with alumina particles, we found that positively charged alumina particles were only attracted to the negatively charged silica substrates in aqueous solution for a very short period although the pH was between the iso-electric-point (IEP) of alumina and silica. Instead, experiments show that the glass surface attracted the dissolved species of alumina, which made the surface repel the alumina particles. It was observed that the IEP of the glass, which was exposed to the supernatant of centrifuged alumina particles, shifted toward the IEP of alumina: the magnitude of the shift depended on the concentration of the dissolved alumina, and vice versa for the IEP of the alumina exposed to a supernatant formed with glass powder. Therefore after a short exposure to an alumina slurry, the glass surface 'look' look like alumina, and the electrostatic attraction between glass and alumina particles will no longer exist.

Increasing Wet Green Strength of Alumina Body During Microfabrication by Colloidal Isopressing
Zhuo Zhang, Biao Liu and Frederick. F. Lange
Published: J. Am. Ceram. Soc., 88 [6] 1411–1414 (2005)

Abstract: Colloidal Isopressing involves formulating a slurry with a weakly attractive particle network that can be pre-consolidated to a high relative density by pressure filtration and still retain fluid-like characteristics. The pre-consolidated slurry is injected into an elastomeric mold and isopressed. Isopressing rapidly convert the slurry into an elastic body that can be removed from the mold without shape distortion. Not only is this process rapid, but since the water saturated compact produced by this method does not shrink during drying, it can also be converted into a dense body without a long drying period.

It is demonstrated that micron-size surface features, such as 5 μm wide channels with a depth/width ratio of 2, can be rapidly produced on the surface of alumina powder compacts. It was shown that surface features of this size were enabled when the saturated, isopressed body was strengthened. Namely, the fracturing of thin vertical portions of a micro patterned surface during pressure release and demolding is an obstacle to obtaining micron size features with high aspect ratios. It was shown that concentration controlled gelation of a PVA-Tyzor® TE additive effectively increased the strength of the

elastic, isopressed body, saturated with water, while maintaining the low viscosity of the pre-consolidated body, which is required for transfering the pre-consolidated slurry into a rubber mold prior to isopressing.

Investigation on Strain Recovery During Microfabrication by Colloidal Isopressing
Zhuo Zhang and F. F. Lange
Published: J. Am. Ceram. Soc., 89 [7] 2348–2351 (2006)

Abstract: During microfabrication of ceramics by the Colloidal Isopressing method, cracks were a major problem when features with high aspect ratios were molded into the surface. Since differential strain recovery (different elastic expansion of the polymer mold material relative to the consolidated powder compact) is one cause of stress that introduces cracks during pressure release, the strain recovery of the consolidated alumina body was investigated. Spheres of different materials with different elastic moduli were embedded within a pre-consolidated slurry and isopressed at different pressures. The strain recovery of the powder compact was also measured via a uni-axial compression test. Results showed that cracks did not form when the elastic moduli of the inclusions were greater than 3 GPa. Inclusions were made by consolidating wax (low modulus) and aluminum (high modulus) powers so that the elastic modulus of the composite was large enough to avoid crack during pressure release. The wax was removed via a low temperature heat treatment. This heat treatment also strengthened the powder compact so that the residual alumina powder could be removed by dissolving in a weak acid. Internal cavities could be formed in dense ceramics by this method.

Pressure induced transition between superhydrophobic states: Configuration diagrams and effect of surface feature size
Biao Liu and F. F. Lange
Published: Journal of Colloid and Interface Science 298 (2006) 899–909

Abstract: The stability of wetting states, namely the Cassie state (partial wetting) and the Wenzel state (complete wetting) of surfaces with protrusions, is determined by comparing the total free energy of a liquid drop in terms of their apparent contact angles for different protrusion features. It is found that when the area fraction of the topographical features and the intrinsic contact angle for a flat surface are large, the Cassie state is favored, but it can be either the metastable or stable state. It is shown that the transition from the Cassie state to the Wenzel state requires the application of a pressure to the meniscus between the surface protrusions. The critical transition pressure increases not only with increasing area fraction and intrinsic contact angle, but also with decreasing protrusion size. During the transition, a high-pressure gas can be trapped around the protrusions that can cause the Cassie state to be recovered after the release of the applied pressure. The analysis shows that a droplet can ‘hang’ upside-down when the protrusion size is very small; namely, the protrusions can pin the meniscus. These results are discussed relative to the advancing and receding contact angle.
Published: Journal of Colloid and Interface Science 298 (2006) 899–909

The Diffusion Path of Si in Au/Si System
Biao Liu, Jin Hyeok Kim and Fred F. Lange
Technical Report, Thesis Chapter, to be published

Abstract: Si diffuse through a deposited Au film and forms SiO_2 on top of the film at a low temperature in an oxidizing environment. The diffusion path of the Si is observed under Z-contrast TEM to the the Au grain boundaries. The oxygen counter diffuses inside and forms SiO_2 with the Si within the Au film.

Development and Characterization of Aqueous Mixed Network Slurries for use in Colliodal Isopressing.
R. M. Bock and F. F. Lange
Technical Report, Thesis Chapter, to be published

Abstract: The rheological properties of aqueous alumina slurries consisting of two interpenetrating particle networks, one produced with strongly attractive particles, and other, produced with repulsive particles, were studied. The repulsive particle network was formulated by first alkylating the particles with either decanol or octadecanol, and then dispersing the dried, alkyalted powder in water using a cationic surfactant, C12TAB. The attractive network was formulated in water at the isoelectric point of alumina. It was shown that the viscosity, at any give shear rate, increased with the volume fraction of the attractive network. Although the repulsive network exhibited Newtonian rheology, the mixed networks were shear rate thinning. Bodies consolidated from slurries formulated with octadecanol-alkylated powder and C12TAB exhibited a slightly higher relative density than their decanol-alkylated counterparts. In addition, bodies consolidated from decanol-alkylated plus C12TAB treated powder slurries were observed to undergo plastic deformation, whereas consolidated bodies from octadecanol-alkylated plus C12TAB slurries were brittle and fractured during loading. The plastic and brittle nature of the consolidated bodies is discussed relative to the length of the attached alkyl chain. Finally, it was shown that the yield stress of bodies consolidated from the mixed network increased with the volume fraction of the attractive network.

Surface Modification of Alumina and Zirconia Powders using Monoalkyl Phosphates and Phosphonates.
T.C. Radsick and F. F. Lange
Technical Report, Thesis chapter, To be published

Abstact: The interparticle pair potential of metal oxide powders can be influenced by the formation of a layer of adsorbed molecules. In the present study, two types of molecules, similar in several respects, were investigated. First, each of the two types were linear molecules containing one alkane chain with a length of 10 to12 carbon units. Second, each have an "anchor" functional group used to attach the molecule to the metal oxide surface. And third, each have a pendant functional group (either hydroxyl or carboxyl) to influence the hydrophobicity and apparent surface charge of the coated powder. The two types of molecules differed in the type of the "anchor" group that attached them to the surface of the metal oxide. The two molecular systems were:

(1) alkanes with a phosphorous-based "anchor" group,
(2) alkanes with a hydroxyl "anchor" group.

These molecules are illustrated in Fig. 2.1. The use of these systems in the preparation of ceramic slurries will be discussed in chapters 3 and 4, respectively.

Slurry Consolidation and Mechanical Testing of Alumina and Zirconia Powders Modified with Monoalkyl Phosphates and Phosphonates
T.C. Radsick and F. F. Lange
Technical Report, Thesis chapter, To be published

Abstract: This paper concerns the particle packing, or pressure consolidation, of slurries discussed in previous chapters. The mechanical behavior of the consolidated slurries will be determined and related to the consolidation pressure and the concentration of salt added to the slurries. Additionally, the behavior of the slurry after mechanical testing was qualitatively examined by subjecting post-test specimens to vibration and then examining the ease in which the consolidated bodies could be fluidized, which is required for new shape forming methods. While several different slurry compositions and adsorbing molecules were examined in Chapter 3, the present study focused on slurries containing 20 volume % of either alumina or zirconia powders, that have an adsorbed layer of COOH-terminated MAPn. Three

slurry preparation methods, “Aqueous A” (AQ-A), “Aqueous B” (AQ-B) and “Solvent” methods were used to formulate the slurries.

Comparison of the Sintering Properties of Two Alumina Powders
Zhuo Zhang and F. F. Lange
Technical Report, Thesis Chapter, to be published

Abstract: The densification behavior of two different alumina powders, TM-DAR and AKP-50 was studied and it was demonstrated that TM-DAR powder exhibits superior densification due to the smaller number of crystallites that compose the agglomerates within the powder. Heating, then cooling and reheating to a higher temperature produced a lower density relative to simply heating to a specific temperature in one step.

Development and Characterization of Alkylated Slurries for use in Colloidal Isopressing using Salt to Control Interparticle Pair Potentials
R. M. Bock and F. F. Lange
Technical Report, Thesis Chapter, to be published

Abstract: Aqueous slurries were formulated with alumina particles alkylated with decanol and dispersed by adding C_{12}TAB; these slurries were coagulated by adding different concentrations of NH_4Cl. The viscosity of these slurries was observed to increase as the concentration of the NH_4Cl increased. Shear thinning is also shown to occur with increasing concentrations of salt. The slurries were consolidated via pressure filtration and further evaluated. The packing density of consolidated slurries showed a slight dependence on salt concentration. Salt concentration had a large effect on the mechanical behavior of consolidated slurries. Namely, as more salt was added, consolidated slurries exhibited increasing plasticity

The Sophistication of Ceramic Science Through Silicon Nitride Studies
F. F. Lange
Published: J. Ceramic Soc. of Japan 114 [11] 873-79 (2006)

Abstract: The historical understanding of polyphase silicon nitride, abbreviated throughout as SiN, has been a multidisciplinary effort that contributed to the sophistication of Ceramic Science over the last 50 years. This understanding and the development of SiN leading to significantly improved properties has been linked by uncovering relations between phase equilibrium, processing science, microstructural development and properties. The understanding of how to represent phase relations between Si_3N_4, other phases, eutectics and other important constituents in different Si-N-O-M systems was pioneered by Gunter Petzow, his students, post-docs and co-workers at the Max-Planck-Institut fur Metallforschung in Stuttgart. It will be seen that this representation was one key to unlock the understanding of SiN properties as related to composition and its development into one of the modern ceramics of today. Major events and discoveries concerning these silicon nitride materials will be reviewed with reference major contributors to its science and technology .

Plastic/Brittle Behavior of Consolidated Bodies: Role of Particle Pair Potential
F. F. Lange
Published: Lessons in Nanotechnology from Traditional and Advanced Ceramics, Editor: J.-F. Baumard, publisher: Techna Group, It (2005)

Abstract: Colloidal powder processing can improve the reliability and strength of ceramics by reducing the size of strength degrading heterogeneities through filtering the powder prior to consolidation.

Removing heterogeneities greater than a given size is equivalent to a proof test, namely, truncating the strength distribution.
Although significant property improvements can be made with the colloidal approach, new forming methods-consistent with the removal of flaws, are still under development. This development requires knowledge relating the mechanical properties of saturated powder compacts to the forces between particles, similar to relating properties of crystalline materials to interatomic forces. The background to this program resides with the discovery that short-range repulsive potentials can be developed that, when combined with the pervasive attractive van der Waals potential, produce an interparticle pair potential characterized by a potential well. This development has lead to new shape forming methods that are discussed at the end of this review.

Effects of CnTAB Chain Length and Concentration on the Rheological Properties of Aqueous Suspensions of Alkylated Alumina Powders
R. M. Bock and F. F. Lange
Published: J. Amer. Ceram. Soc. 89 [3] 817-22 (2006)

Abstact: Alumina particles have successfully been alkylated via a condensation reaction between surface hydroxide sites and different, long chain alcohol molecules. These hydrophobic particles have been successfully dispersed in water using different C_nTAB surfactant molecules. The effect of the length of the surfactant molecule and its concentration was quantified by rheological experiments. Rheology and conductivity measurements were used to determine the minimum amount of the surfactant needed to disperse the alkylated powder. Slurries formulated with the alkylated powder and the proper amount of C_nTAB exhibited Newtonian rheology. Zeta potential measurements showed that the surface charge on the particles was always positive confirming that the C_nTAB molecules, with a positive head group, surrounded the alkylated particles. Such powder did not have an iso-electric point. In addition, the Newtonian behavior of the alkylated-alumina / C_nTAB slurry systems were independent of pH..

New class of soft matter electrolytes obtained via heterogeneous doping: Percolation effects in "soggy sand" electrolytes
Aninda J. Bhattacharyya, Joachim Maier, Ryan M. Bock and F. F. Lange
Published: Solid State Ionics 177 (2006) 2565–2568

Abstact: Percolation effects observed in the ionic conductivity variation with oxide volume fraction in "soggy sand" electrolytes are discussed in the light of conductivity and rheological measurements. The enhancement in ionic conductivity of the composites is attributed to the formation of a percolating attractive network of insulating particles.