

NANODESIGNING OF MULTIFUNCTIONAL CERAMIC COMPOSITES

J. LIU, M. SARIKAYA, W. Y. SHIH, W.-H. SHIH, and I. A. AKSAY

Department of Materials Science and Engineering; and
Advanced Materials Technology Center, Washington Technology Centers,
University of Washington, Seattle, WA, USA 98195

Nanodesigning of multifunctional ceramic composites with colloids is discussed from a fundamental point of view. We start with one-component systems, where packing density is the primary concern. Then we extend the discussion to binary systems and deal with the problem of homogeneity. We show that the structure is controlled by the nature of bonding between the particles and by the particle-particle interaction. Surfactants are used to modify these properties, by, first, protecting the active particle surfaces to prevent solid bond formation, and, second, altering the interparticle interaction to provide a "lubricating" effect. In weakly attractive multicomponent systems, not only are we able to achieve high-density packing through restructuring, but we can also control the scale of homogeneity.

1.0 INTRODUCTION

There has been a growing interest in the colloidal processing of nanocomposites because of the advantages of using nanometer-sized particles.¹⁻³ For example, it is possible to mix different components on a nanometer scale and achieve improved electronic and structural properties for multifunctional applications.³⁻⁵ Another advantage is that the materials can be processed to full density at much lower temperatures than by conventional methods.

Previous literature has discussed some of the advantages and difficulties in colloidal processing with nanometer-sized particles compared to the processing of micrometer and submicrometer-sized particles.^{1,2} The most significant difficulty is that nanometer-sized particles in general result in the formation of low-density gels which display large shrinkages during solvent extraction and, therefore, cracking during drying or sintering.^{6,7} In this paper, we discuss this problem from a more fundamental point of view and summarize our recent work in this area. We then extend our discussion to binary systems, which have not been understood as well. The study and understanding of multicomponent systems is essential for processing composite materials with two or more components. Through such an understanding, high-packing density can be realized, and also the distribution of species can be controlled so that regularity in the structure and the scale of homogeneity in composition can be predicted.

2.0 RESULTS AND DISCUSSION

2.1 One-Component System: Effect of Restructuring

In processing with micrometer or submicron-sized particles, the microstructure and density of green compacts can be controlled via colloidal processing routes.^{8,9} When particle interactions are repulsive, suspensions can be consolidated to high packing density compacts.^{2,8,9} In contrast, highly attractive particle systems result in low packing density compacts.^{2,8,9} In the attractive

region, low-density fractal clusters or powder compacts could restructure to a higher density at later times under weak attraction conditions.^{10,11} This restructuring is controlled by the interaction energy E and the relaxation time τ_R . However, experience has shown that with nanometer-sized particles this restructuring is not easily accomplished without the application of high pressures.¹ Therefore, we conducted systematic studies to determine the unique characteristics of nanometer-sized particles. We used conventional and high-resolution transmission electron microscopy (HRTEM) to study the general structure of the aggregates and the particle-particle interfaces in order to investigate the aggregation behavior of nanometer particles in colloid systems. We also calculated the particle-particle interaction by a modified DLVO theory.¹² First, we found that there is effectively no secondary minimum away from the particle surface in particle-particle interactions for nanometer-sized particles.¹³ When nanometer-sized particles begin to aggregate, they fall into the primary minimum and direct contact takes place. Second, solid bonding forms between the particles. For example, Figure 1 shows the interfaces between gold particles in a low-density aggregate; when particles touch one another, solid bonding is formed at the particle contacts. This high binding energy makes it very difficult for the particles to break away and relax to a high density once the aggregates are formed. The low-density (< 30 vol. %) aggregate corresponding to Figure 1 is very strong and cannot be easily consolidated to a higher density. For these two reasons, nanometer-sized particles are different from larger (> 0.1 μm) particles.

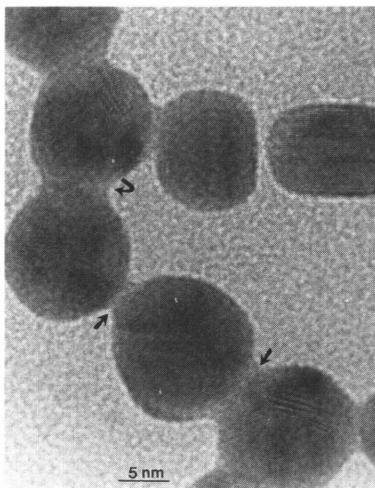


Figure 1. High resolution transmission electron microscope (HRTEM) image revealing structures of interfaces between particles in a colloidal gold aggregate. The solid bonding between the particles makes it difficult for the clusters to relax to a high density.

An obvious solution to the problem stated above is that the active particle surfaces must be protected so that solid bonding cannot occur between the particles. Coating the particles with a layer of surfactant prevents the particle-particle contact. Figure 2 illustrates the high-density packing achieved when a layer of surfactant is adsorbed onto the particle surface. The

particles now are separated by a distance of about 1 to 3 nm, which roughly corresponds to the size of the surfactant. This separation is caused by the adsorption of the surfactant, which spatially protects the particle surface. Yet, in order to have dense packing, the particles must be able to move around freely. Thus, the surfactant must also act as a lubricant.¹¹

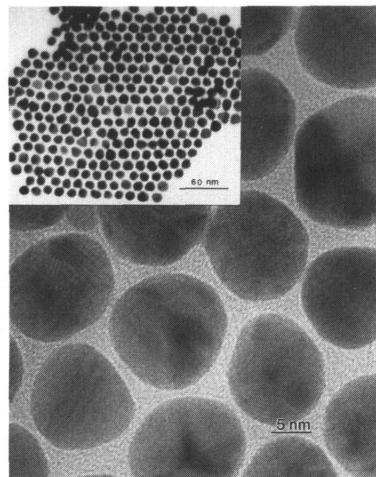


Figure 2. Transmission electron microscope (TEM) images revealing the close packing of gold particles when the particle surfaces are protected by a layer of surfactant. The particles are separated by a distance of 1 to 3 nm, about twice the length of the surfactant.

In order to understand the role of surfactants, the aggregation behavior of the particles was studied at different surfactant concentrations.¹⁴ In this study, a cationic surfactant was added to the colloidal solution containing the negatively-charged gold particles. The surfactant induces aggregation by neutralizing the charges on the particle surface, and since the surfactant layer has a certain thickness, the particles cannot come in contact with one another. The interaction between the particles is thus controlled by the amount of surfactant added to the solution. We then measured the fractal dimension, D , of the aggregates, which is a measure of the packing density, by light scattering and transmission electron microscopy (TEM). The particle interaction was calculated by the modified DLVO theory^{12,15} and the attraction energy E was taken as the energy of closest approach (taken as 1.5 nm in our case). The relation between D and E is plotted in Figure 3, with the computer simulation result¹⁰ plotted as triangles. The experimental results agree very well with the simulation. That is, D is directly related to E . Under a weak attraction condition, a high fractal dimension and, thus, high density is obtained. If the attraction energy E is large (such as in the presence of solid bonding), restructuring is impossible and low D is observed. Therefore, it is important to provide a small attraction energy to make restructuring possible. This study shows that a surfactant provides a means to help achieve high-density packing for nanometer-sized particles.

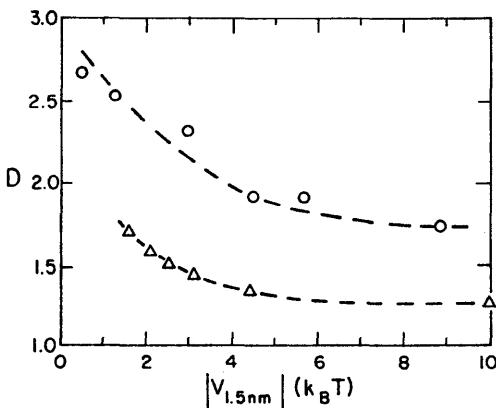


Figure 3. Relationship between the fractal dimension of gold aggregates with surfactants and the binding energy between the particles. The circles are the experimental results and the triangles are the results of the computer simulation in two-dimensions. The fractal structures vary from ramified to compact objects, depending upon the binding energy.

In the case of large particles, macromolecular coatings are used to stabilize suspensions and achieve high solids loading.¹⁶ However, for nanometer-sized particles, macromolecules are not desirable since the amount of the surfactant needed to cover the particle surface increases significantly as the particle size is decreased to the nanometer range, and the effective solid density decreases. There are two methods for solving the problem of excess surfactant. One is to find a surfactant that is short, but very effective, so that the total amount of surfactant incorporated into the system is much less. However, short surfactants may not be large enough to stabilize the particles, but if they have good lubricating properties, the weak aggregates can easily restructure to high density. Studies are underway to identify such surfactants.¹⁷ The second method is to fabricate surfactants (inorganic precursors) which would be transformed into ceramics at a later stage of processing so that they do not need to be eliminated completely. With this method, a nanocomposite could be fabricated in which a surfactant precursor would form the matrix and particles would form the dispersoids.

2.2 Binary Systems

In this section, we present theoretical work on binary systems in which the relationship between particle-particle interactions, stability, and phase separation is considered. We then compare the theoretical work with the experiments. The principles discussed here will apply to both large particles and nanosized particles.

2.2.1 Model

2.2.1.1 Repulsive Regime¹⁸⁻¹⁹ Phase diagrams of highly repulsive colloidal suspensions have been calculated by comparing the free energies of the different phases (specifically, liquids,

and solids with small or large particle-rich phases) in which the particle-particle interactions have been considered. If the particle concentration is not too high or the temperature is not too low, the effective interactions between the colloidal particles are treated with the Debye-Hückel approximation and the stable phase is considered to be the one with the lowest free energy. The free energies of various phases are calculated by means of a variational principle based upon the Gibbs-Bogolyubov inequality.¹⁸ Einstein oscillators are used as the reference system for the solids and a binary hard sphere mixture is used as the reference for the liquids. The solid phase is considered as fcc or bcc substitutional alloys.

2.2.1.2 Attractive Regime²⁰ For attractive interactions, we studied the kinetic effect in systems where the equilibrium state should yield phase separation. A computer simulation was done on a two-dimensional square lattice by using the Monte Carlo method. N_1 represents the number of particles of type 1 with interaction E_{11} , and N_2 is the number of particles of type 2 with interaction E_{22} . The particles are placed randomly in a $M \times M$ lattice with periodic conditions. E is the interaction between particles. The particles then perform Brownian motion according to the Boltzmann probability $e^{-\Delta E/RT}$, where ΔE is the energy change due to the motion. Once two particles come together, they form one cluster and move as a whole. In the same way, larger clusters are formed. The mobility of a cluster is assumed to be inversely proportional to the mass of the cluster. In addition, particles can unbind from a cluster according to the Boltzmann probability, $e^{-\Delta E/RT}$, where ΔE is again the energy change associated with the unbinding.

The free energy of such systems is also calculated according to the cluster variation method (CVM)²¹ in which the free energy F is written as a function of x_1 , x_2 , as well as the pair parameter y_{ij} . Here x_1 is the concentration of particle 1; x_2 is the concentration of particle 2; and y_{ij} is the probability of forming pairs of particle i and particle j (including vacancy). y_{ij} can be obtained by minimizing F for the equilibrium condition. After y_{ij} is found, the structure of the suspension is then simulated on a two-dimensional lattice again according to x_1 , x_2 , and y_{ij} .²² The results of the CVM calculation and simulation are compared to the Monte Carlo simulation.

2.2.1.3 Results and Discussions

1. Packing Density

Phase diagrams of repulsive binary systems are presented in Figure 4. Large particles have a radius of 545 Å and a surface charge $Z_i = 300$. Small particles have a radius $R = 491$ Å, 445 Å, 409 Å, 382 Å in Figures 4(a), 4(b), 4(c), and 4(d), respectively. X is the number fraction of the large particles and D is the total number density. The particle diameter ratio is defined as R_{small} / R_{large} . The line is the boundary between the solid and liquid phase. It can be seen from the D - X phase diagram that the boundary line begins to show a maximum as the diameter ratio deviates from unity. The maximum becomes more pronounced as the diameter ratio deviates more from unity, a phenomenon confirmed by experiments.²³ For a diameter (or charge) ratio of 0.7, the solid-liquid boundary almost opens up vertically toward high number densities. The shrinking of the crystalline phase region also signifies the phase separation of the crystalline phases at high concentrations.¹⁸⁻¹⁹ The results of these phase diagrams show that the fluid phase is stable up to a much higher density in a binary system than can be achieved with a one-component system.

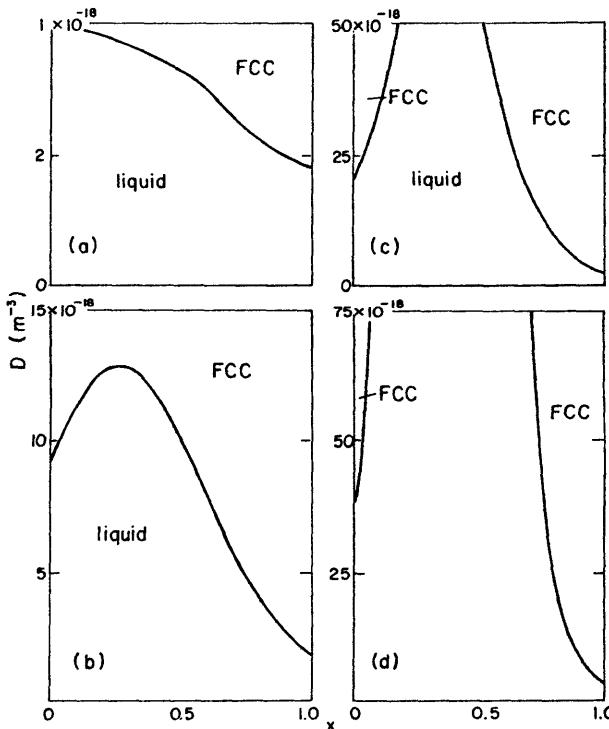


Figure 4. Phase diagrams for repulsive binary systems of large and small particles. Y-axis is density and the x-axis is the number fraction of small particles. From (a) to (d) the diameter ratio of the small to large particles decreases. It can be seen that the fluid region increases to high density as the diameter ratio becomes smaller.

On the other hand, in attractive systems, flocculation is often encountered. In our case, where $E_{11} < 0$, the first species flocculates before the second species ($E_{12} = E_{22} > 0$). The addition of the second species has a large effect on the aggregation of the first species. Results from the Monte Carlo simulation are represented in Figure 5. Initially, the addition of the second species always enhances the rate of aggregation. Cluster sizes become larger as the concentration of the second species is increased. However, at a high concentration of the second species, the cluster size begins to decrease again. There is a maximum in the aggregation rate with respect to the second species concentration. This is in agreement with experimental observations.¹⁶ Also to be noted is the effect of aging; as time passes, the clusters become large and the peak position shifts towards a higher concentration of the second species.

From this discussion, it seems that a repulsive system has an advantage over an attractive system since an attractive system flocculates and may show low density. In a repulsive binary system, the fluid phase can still exist at a very high number density, which is helpful in colloidal processing where a high green density compact is desired.⁸ However, high density is not always

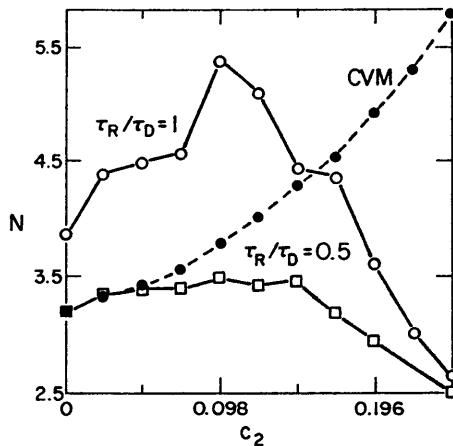


Figure 5. Cluster size vs. second species concentration, c_2 , for comparison between Monte Carlo simulations and CVM calculations where $E_{11} = -1$, $E_{12} = E_{22} = 8$, and $c_1 = 0.245$. (\bullet) represents CVM, (\circ) for $\tau_R/\tau_D = 1$, and (\square) for $\tau_R/\tau_D = 0.5$, representing simulations at $t = 300\tau_D$. Note that while the simulations show the slowing in the cluster rate at high c_2 , the CVM calculations do not, indicating that the restabilization at higher c_2 is a kinetic effect. In the simulations, a smaller value of τ_R/τ_D represents more sufficient relaxations.

the only requirement for a nanocomposite; one has to also consider the scale of mixing of several components. This aspect of colloidal processing will be discussed in the following section.

2.2.2 Scale of Homogeneity

For a nanocomposite, ideally the two components should be distributed with a predictable scale of homogeneity. However, repulsive systems often undergo phase separation, as illustrated in Figure 6. This phase diagram was calculated in a manner similar to Figure 4. It clearly shows that in a binary system, there is a wide two-phase region, one phase rich in small particles, and the other rich in large particles. As the particle concentration increases, phase separation behavior is more pronounced. This indicates that the composite material produced under repulsion conditions will have large domains of different phases of different composition. This then results in an increase in the scale of homogeneity. The phase separation behavior of highly charged particles at high densities has been observed in our experiments. Figure 7 shows colloidal gold and colloidal silica particles mixed under repulsive conditions. The pH of the solution is about 7. Under this condition, the zeta potentials of silica and gold particles are about 60 and 100 mV, respectively, as measured by Doppler shift laser light scattering.^{1,14} Given the diameters of both gold and silica particles as 150 Å, the estimated effective charge of a gold particle is about 42 electron charges and that of a silica particle is about 25. The charge ratio is smaller than 0.7. As discussed above, the system should phase separate at high densities. Indeed, this is the case. It can be seen that the gold particles and the silica particles tend to phase-separate into regions consisting of either silica or gold particles. In order to obtain the properties desired for a composite material, the distribution of different components

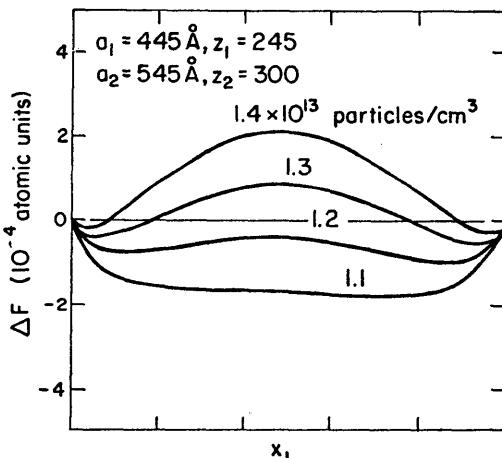


Figure 6. Excess free energy of repulsive binary systems as a function of concentrations of smaller particles, x_1 . A wide two-phase region is usually observed. One atomic unit equals 27.2 eV.

as well as the degree of phase separation, i.e., the scale on which the phase separation takes place--must be controlled. Further understanding of the kinetic process is needed to achieve this control.

From the above discussion, it can be seen that there is a disadvantage in highly repulsive systems due to phase separation. In that sense, weakly interactive systems may have an advantage. A high degree of homogeneity can be achieved in weakly flocculated systems at higher densities.²⁴ The high degree of homogeneity at high densities is due to slow kinetics, not to equilibrium conditions as shown by aging and also by the comparison of the cluster size calculated by the Monte Carlo method at finite time with that calculated by the CVM method shown in Figure 5. Therefore, in a weakly interactive system, a high degree of homogeneity can still be achieved by slow kinetics at high densities although the equilibrium state should phase separate. The CVM calculation shows that the cluster size increases monotonically with the concentration of the second species. The free energy curve also shows that phase separation should occur over all the concentration ranges. However, the Monte Carlo simulation shows that the aggregation is slowed at high concentration, and there is a maximum. The slowing of the aggregation rate is attributed to the kinetic effect, i.e., the particles (or clusters) are trapped in a kinetic cage and cannot relax to a lower energy state (phase separation state). As the system ages, it moves towards a state of equilibrium.

However, for nanometer-sized particles, aggregate structures formed by adding salt are difficult to consolidate because of the formation of solid bonding between particles. It is necessary to use surfactants to protect the particle surfaces in attractive systems. Under this condition, not only can we achieve a finer scale of homogeneity, but we can also achieve high-density packing through restructuring, as discussed earlier.

To demonstrate the advantage of weakly attractive particles coated with a surfactant, a binary suspension was prepared (Figure 8). A cationic surfactant was introduced into a colloidal suspension consisting of gold and silica particles in order to protect the particle surface and to neutralize the negative charge. This created weakly attractive forces between particles, as evidenced by flocculation. Not only do we achieve a high-packing density (as discussed in Figure 2), but we also find the gold particles to be distributed more homogeneously among the silica particles in what is principally a nanocomposite.

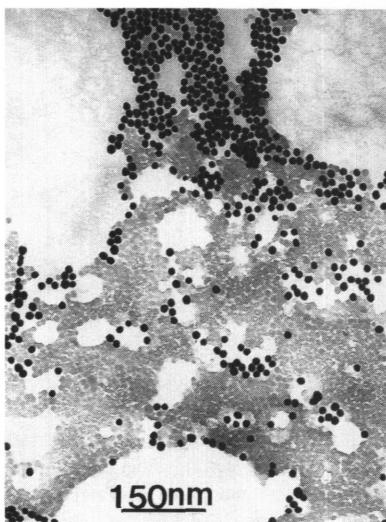


Figure 7. Phase separation of colloidal gold and silica particles under repulsive conditions. The dark particles are gold and the light particles are silica.

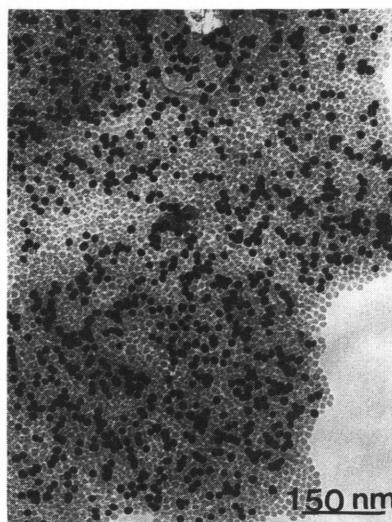


Figure 8. A finer scale homogeneous mixture of gold and silica particles under a slightly attractive condition.

3.0 SUMMARY

The density and homogeneity of nanocomposite materials can be controlled by regulating the particle-particle interaction. Specifically, we have concluded that a weakly attractive system may be advantageous over a repulsive system: first, it is possible to achieve high density by the restructuring of the clusters in weakly attractive aggregates; second, a weakly attractive binary system can have a finer scale homogeneous distribution of the components regardless of whether the equilibrium state is a phase separation or a mixture. In the case where the equilibrium state is a phase separation, homogeneity is provided by slow kinetics at high densities. The control of particle-particle interaction is realized by using surfactants. The surfactants have two functions. One is to protect the active particle surface to prevent direct particle bonding, which is especially important for small particles. The other is to modify the interparticle interaction, making it possible for the particles to relax to a high-density configuration within the clusters.

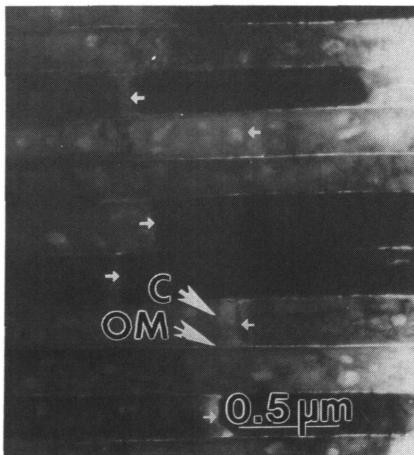


Figure 9. TEM micrograph revealing the typical microstructure of the nacre section of an abalone shell. The microstructure consists of organic material (OM) and ceramic layers (C) arranged in a regular laminated structure.

We should point out that although we have made considerable progress in understanding the properties of nanoparticle systems, as yet we have not been able to achieve precise control of the microstructure. In the above cases of colloidal processing, the final product is a result of a microstructure of small particles randomly configured under certain kinetic conditions. Therefore, the structure is basically determined by entropy. Full control of the final product is extremely difficult, if not impossible, to achieve. However, it is possible to control the processing precisely enough to achieve a final product with a predetermined, highly regular microstructure. In natural processes, there are abundant examples of highly regular microstructures. An example is given in a TEM image in Figure 9 where a cross-sectional view of an abalone shell, consisting of organic (thin-phase, 200 Å) and inorganic (thick-phase, 250 nm) layers, is seen. The phases are arranged in the form of a brick (CaCO_3) and mortar (organic) microarchitecture. In this case, a highly-ordered microstructure is processed at the molecular level by certain biological process(es) where energy plays the most important role in the *specific* arrangement of the phases.²⁵ Other than Nature's method, such processes, so far, can only be achieved synthetically in molecular processes such as molecular-beam epitaxy and liquid-phase epitaxy to fabricate materials with a full degree of control at the nanometer level.

ACKNOWLEDGMENTS

This research was supported by the Air Force Office of Scientific Research (AFOSR) and the Department of Advanced Research Projects Agency (DARPA) and monitored by AFOSR under Grant No. AFOSR-87-0114.

REFERENCES

1. B. J. Tarasevich, J. Liu, M. Sarikaya, and I. A. Aksay, "Inorganic Gels with Nanometer-Sized Particles," in *Better Ceramics Through Chemistry III, MRS Symp. Proc.*, Vol. 121, edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich (Materials Research Society, Pittsburgh, Pennsylvania, 1988), p. 225.
2. I. A. Aksay, W. Y. Shih, and M. Sarikaya, "Colloidal Processing of Ceramics with Ultrafine Particles," in *Ultrastructure Processing of Advanced Ceramics*, edited by J. D. Mackenzie and D. R. Ulrich (Wiley, New York, 1988), p. 393.
3. See, for instance, papers in *Multicomponent Ultrafine Microstructures, MRS Symp. Proc.*, Vol. 132, edited by L. E. McCandlish, D. E. Polk, R. W. Siegel, and B. H. Kear (Materials Research Society, Pittsburgh, Pennsylvania, 1989).
4. R. E. Newnham, "Composite Electroceramics," *Ferroelectrics*, **68**, 1 (1986).
5. K. Uchino, E. Sadanaga, and T. Hirose, "Dependence of the Crystal Structure on Particle Size in Barium Titanate," *J. Am. Ceram. Soc.*, **72** [8] 1555 (1989).
6. E. M. Rabinovitch, D. W. Johnson, J. B. McChesney, and E. M. Vogel, "Preparation of High-Silica Glasses from Colloidal Gels: 1. Preparation for Sintering and Properties of Sintered Glasses," *J. Am. Ceram. Soc.*, **66** [10] 683 (1983).
7. C. J. Brinker and G. W. Scherer, "Relation Between the Sol-to-Gel and Gel-to-Glass Conversions," in *Ultrastructure Processing of Ceramics, Glasses, and Composites*, edited by L. L. Hench and D. R. Ulrich (Wiley, New York, 1984), p. 43.
8. I. A. Aksay, "Principles of Ceramic Shape-Forming with Powder Systems," in *Ceramic Powder Science II, Ceramic Transactions*, Vol. 1, edited by L. E. Messing, E. R. Fuller, Jr., and H. Hausner, (American Ceramic Society, Westerville, Ohio, 1988), p. 663.
9. I. A. Aksay and R. Kikuchi, "Structures of Colloidal Solids," in *Science of Ceramic Chemical Processing*, edited by L. L. Hench and D. R. Ulrich (Wiley, New York, 1986), p. 513.
10. W. Y. Shih, I. A. Aksay, and R. Kikuchi, "Reversible-Growth Model: Cluster-Cluster Aggregation with Finite Binding Energies," *Phys. Rev. A*, **36** [10] 5015 (1987).
11. D. Gallagher, Ph.D. Thesis, University of Washington, Seattle, Washington (1988).
12. For example, see J. Th. G. Overbeek, "Recent Developments in the Understanding of Colloid Stability," *J. Colloid Interface Sci.*, **58**, 408 (1977).
13. J. Liu, Ph.D. Thesis, University of Washington, Seattle, Washington (1990).
14. J. Liu, M. Sarikaya, W. Y. Shih, and I. A. Aksay, "Fractal Colloidal Aggregates with Finite Interparticle Interaction: Energy Dependence of the Fractal Dimension," *Phys. Rev. A*, **41** [4] 3206 (1990).

15. W.-H. Shih and D. Stroud, "Theoretical Study of Miscibility and Glass Forming Trends in Mixtures of Polystyrene Spheres," *J. Chem. Phys.*, **80** [9] 4429 (1984).
16. J. Cesarano III, Ph.D. Thesis, University of Washington, Seattle, Washington (1989); M. Yasrebi, Ph.D. Thesis, University of Washington, Seattle, Washington (1988).
17. G. L. Graff, M.S. Thesis (in progress), University of Washington, Seattle, Washington (1990).
18. W. Y. Shih, W.-H. Shih, and I. A. Aksay, "The Stability of Binary Charged Colloidal Crystals," *J. Chem. Phys.*, **90** [8] 4506 (1989).
19. W. Y. Shih, I. A. Aksay, and R. Kikuchi, "Phase Diagrams of Charged Colloidal Particles," *J. Chem. Phys.*, **86**, 5127 (1987).
20. J. Liu, W. Y. Shih, R. Kikuchi, and I. A. Aksay, "On the Clustering of Binary Colloidal Suspensions," in press, *J. Colloid Interface Sci.* (1990).
21. R. Kikuchi, "Ternary Phase Diagram Calculations - I - General Theory," *Acta Metal.*, **25** 195 (1977).
22. R. Kikuchi, "Crystal Growth Model of Lattice-Order Simulation and the Cluster-Variation Method," *Phys. Rev. B*, **22** [8] 3784 (1980).
23. P. M. Chaikin and P. A. Pincus, unpublished.
24. C. Han, I. A. Aksay, and O. J. Whittemore, in *Advances in Materials Characterization II*, edited by R. L. Snyder, R. A. Condrate and P. F. Johnson (Plenum, New York, 1985), p. 339.
25. M. Sarikaya, K. E. Gunnison, M. Yasrebi, and I. A. Aksay, "Mechanical Property-Microstructural Relationships in Abalone Shell," in *Materials Synthesis Utilizing Biological Processes, MRS Symp. Proc.*, Vol. 174, edited by P. C. Rieke, P. D. Calvert, and M. Alper (Materials Research Society, Pittsburgh, Pennsylvania, 1990).