Ceramics International 17 (1991) 267–274

Molecular and Colloidal Engineering of Ceramics†

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(Received 24 June 1990; accepted 10 September 1990)

Abstract: During the last decade, significant advances have been made in the processing of ceramics by a combination of techniques utilizing molecular precursors and colloids for powder consolidation. Powder consolidation methods have mainly dealt with the formation of unagglomerated powders in the size range of 0·1–1 μm, the preparation of colloidal suspensions that are suitable for the formation of high density compacts by filtration and/or plastic forming techniques, the removal of the processing aids, and the role of consolidation methods on microstructural evolution. In contrast, the molecular and/or sol–gel techniques dealt with processing at a finer dimensional scale of 10–1000 Å with either molecularly homogeneous precursors or nanometer-sized particulates that are used in the preparation of gels that display linear viscoelastic behavior. Similar to green compacts of micron-sized powders, these gels are then converted to dense ceramics by heat treatment. This review summarizes the concepts that are common to both of these regimes and points to the synergistic benefits of coupling molecular precursors with colloids in a process path. The emphasis is on the control of the structure of a final product at scale lengths ranging from molecular to micro- and macroscopic dimensions.

1 INTRODUCTION

Molecular and colloidal engineering of ceramics is by no means a new endeavour. The earliest and best examples of molecularly engineered ceramics and ceramic matrix composites are those produced in nature by a variety of very elegant low-temperature processes. Clay-based minerals are the best-known examples of nature's molecularly engineered ceramics in two-dimensional forms.[1–4] Traditionally in manmade ceramic products, these minerals have served as the primary constituent mainly because (i) they are easily fragmented to submicron-sized powders, and (ii) as such, when mixed with water, they yield some of the best examples of colloids for slip casting or plastic forming applications.[5]

Similarly, biological systems provide us with very elegant examples of molecularly engineered ceramics and ceramic–polymer composite architectures.[6,7] As exemplified in Fig. 1 with the cross-sectional view of an abalone shell, biological composites such as seashells and skeletal structures are unique for two key reasons: (i) they are produced by very low temperature processes, and (ii) the design of the entire system is controlled from molecular (<10 Å) to microscopic ($>100\,\mu$m) dimensions with a specifically engineered hierarchical structure suitable for multifunctional applications.

In contrast, many of the manmade advanced

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† Presented at the *World Congress on High Tech Ceramics* (*7th CIMTEC*), held in Montecaitni, Italy, 24–30 June 1990. The complete Proceedings of that meeting can be obtained from Elsevier Science Publishers, PO Box 211, 1000 AE Amsterdam, The Netherlands, under the title *Ceramics Today—Tomorrow's Ceramics*, P. Vincenzini (Ed.).

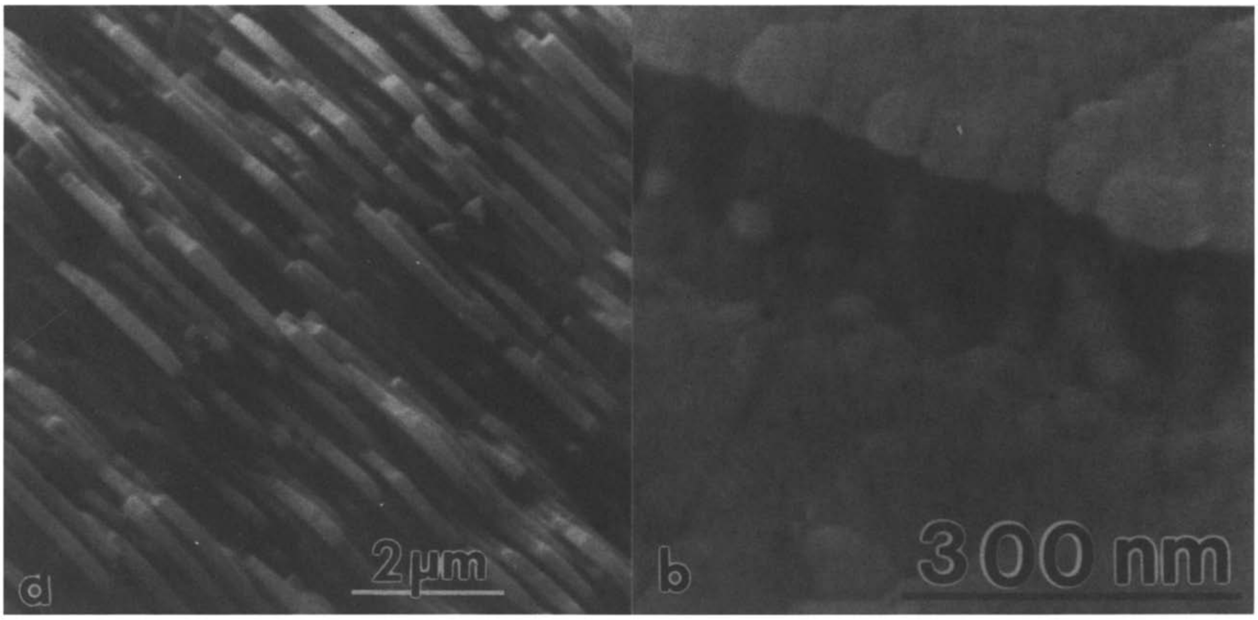

Fig. 1. (a) Scanning electron micrograph (SEM) image of the fracture surface of the nacre region of abalone shell. The $CaCO_3$ plates of ≈0·2 μm are stacked with a dense packing arrangement and constitute > 98 vol.% of the composite; (b) ligament formation between the $CaCO_3$ plates by the organic phase is responsible for a major portion of the toughening in the composite.[8]

ceramics are still processed at very high temperatures and also with far less specific design than that observed in biological systems. Exceptions are found primarily in the electronics field where lithographic techniques, coupled with thin film fabrication, have resulted in a variety of complex but specifically designed microcomposites, such as solid-state devices. However, in the case of composite processing via powder routes our level of understanding is not yet advanced enough to fabricate components with the same level of specificity found in biologically or lithographically designed systems. During the 1980s, a synergism developed between powder synthesis and colloidal processing efforts that not only is narrowing this gap in our understanding but also bringing the field of powder processing from a largely empirical state to a strong science and engineering base.[9-12] This paper reviews some of these developments.

A review of the key developments in processing with submicron-sized powders can be grouped into three categories: (i) synthesis of submicron-sized powders with controlled shapes, sizes and chemistries; (ii) the development and use of colloidal dispersion and consolidation techniques to control pore volume and pore size distribution in powder compacts; and (iii) the role of powders and powder compacts on the evolution of microstructures during heat treatment. Due to space limitations, the emphasis of this review will be on the second category with relevant conjectures to both the first and third categories. Our main goal will be to illustrate that for a given powder system a variety of techniques can be used to modify the structure of powder compacts and thus to influence the evolution of the microstructure during heat treatment. Problems that still remain and the future directions that should be taken to address these problems will be discussed in the final section.

2 THE ROLE OF PORES VERSUS PARTICLES

A common mistake in most powder processing efforts has been to downplay the role of pores in comparison to the role of particles. Following the predictions of Herring's scaling law,[13] it has been customary to expect that systems with a smaller particle size would sinter at lower temperatures than their counterparts with a larger particle size. The underlying assumption in this prediction is that the total pore volume and pore size in a powder compact must first be minimized by achieving the theoretical limit of packing density. Experimental limitations in reaching the theoretical limit have hindered the progress in utilizing smaller particle size systems. For instance, although the theoretical limit of dense packing for a monosized spherical particle system is 74 vol.%, there has been no recorded case where this limit has been achieved. With monosized spherical systems, the best recorded number is 68 vol.%[14] and the most commonly referenced packing densities are

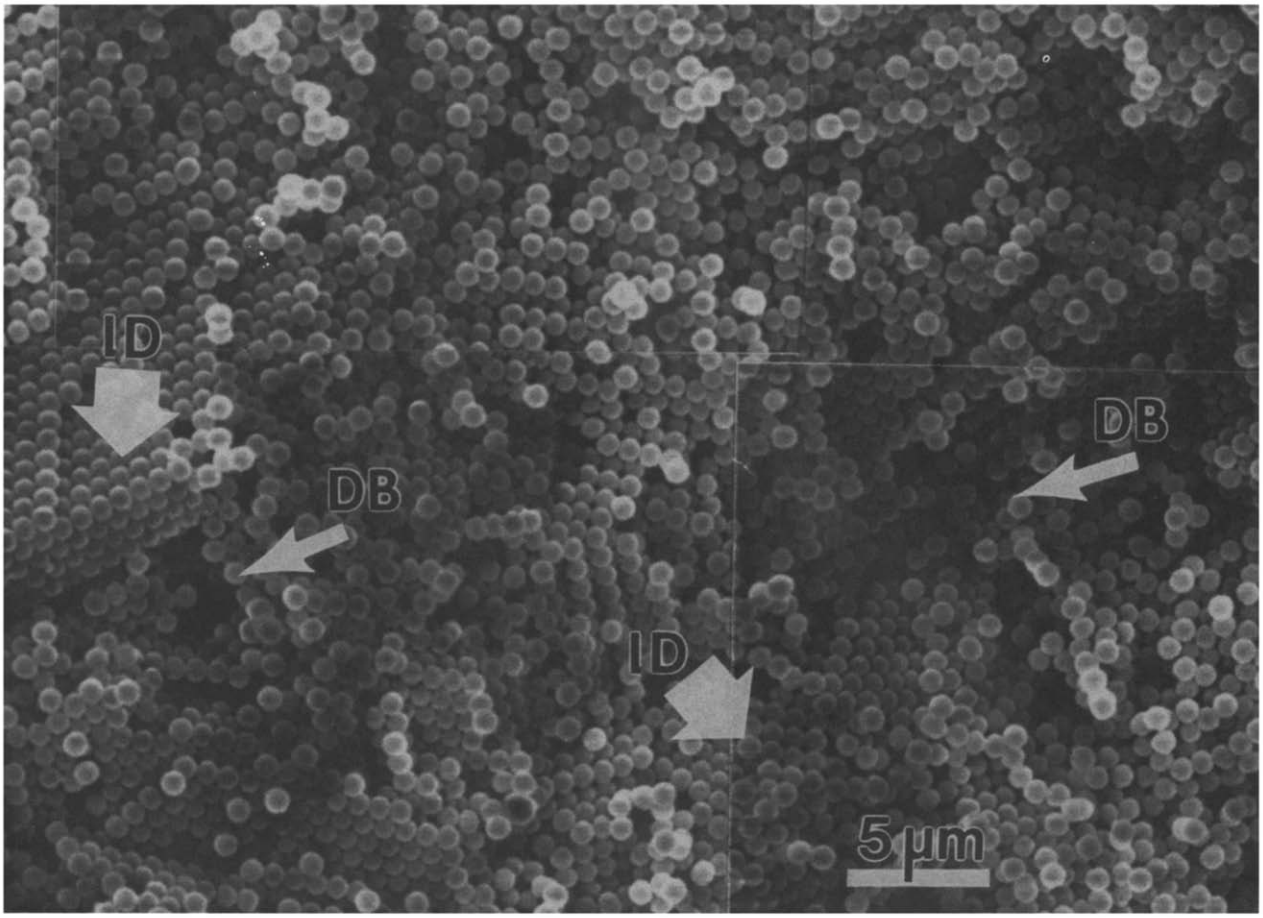

Fig. 2. Fracture surface of crystalline (opal-like) packing of monosized colloidal silica (SEM image). Notice that the packing structure is face-centered-cubic and polycrystalline. Intradomain (ID) regions are ≈ at 74% dense; however, the global density is only 64% due to the contributions of the porosity at the domain boundaries (DB).

those of random dense packing (i.e. 64 vol.%) (Fig. 2). An immediate consequence of this lower-than-theoretical limit of packing is that real powder compacts always display pore size variations. Thus, the sintering behavior of the overall compact reflects the combined effects of the differential sintering characteristics of local regions as affected by these pore size variations.[15]

Experiments with model systems confirm the validity of Herring's scaling law in local regions where particle clusters are densely packed and display only interparticle pores, i.e. pores smaller than the particles themselves. As illustrated in Fig. 3(a), in the case of α-Al_2O_3, a densely packed local region of 0·8 μm-size particles sinters to full density at 1200°C in 1 h. The full densification of the entire compact, however, always displays a shift to higher temperatures than are observed in local regions (Fig. 3(b)) due to the fact that pores larger than the interparticle pores may not be readily eliminated without some grain growth at a higher temperature regime.[15] The sintering temperature of the overall powder compact increases as the size of the intercluster voids increases. Consequently, in order to achieve low-temperature sintering, an immediate goal must be to decrease the size of the intercluster voids through innovative processing methodologies. Methods that have been effective are: (i) preparation of very highly concentrated (>50 vol.%) but sufficiently fluid (<1 Pa s) colloidal dispersions that can be used in casting or molding applications;[16–18] (ii) minimization of the pore size and volume by filling in the voids with smaller particles or ceramic precursors;[16] and (iii) reduction of the size of the intercluster voids through shear deformation processes as in injection molding.[19]

3 THE ROLE OF PARTICLE SIZE ON PACKING BEHAVIOR

It is important to note that the data presented in the previous section are for a very limited particle size range of 0·2–0·8 μm. Although the concepts presented are valid outside this range, experience has shown that when the size of the particles or packing units is reduced to the nanometer (1–100 nm) range,

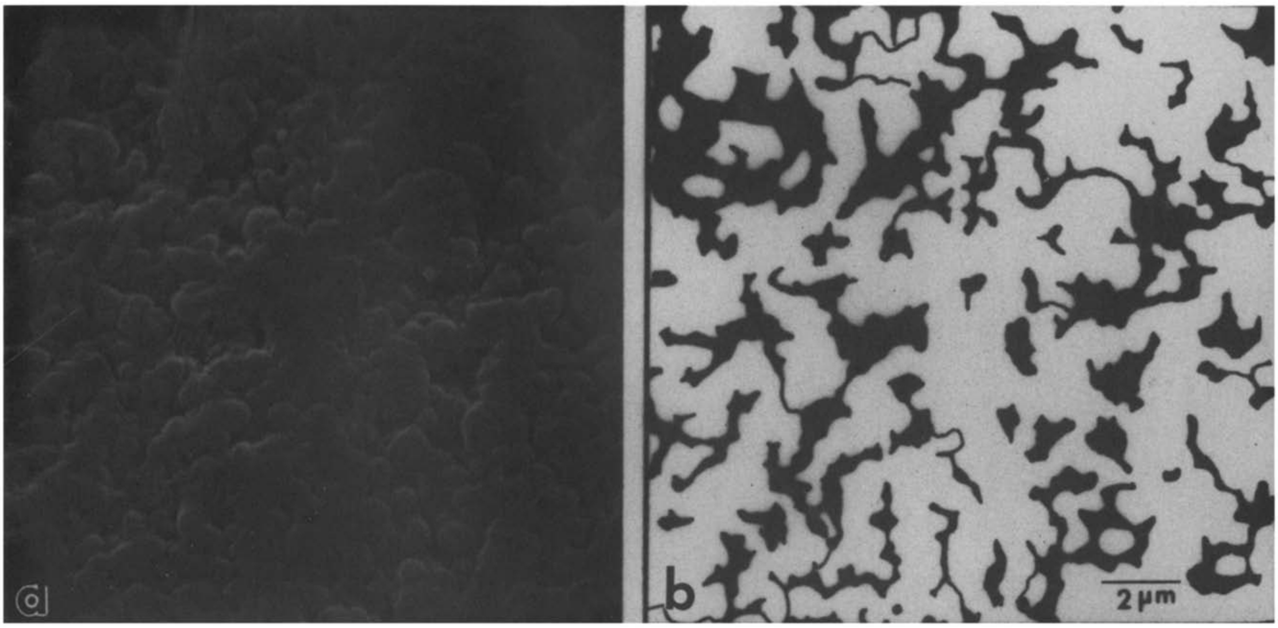

Fig. 3. (a) SEM image of 0·8 μm α-Al_2O_3 powder compact after partial sintering at 1200°C for 1 h; (b) interdomain regions that are still porous are highlighted in the negative image.

high density suspensions and compacts are very difficult to prepare since the tendency for very open network structure formation increases (Figs 4 and 5). This nanometer range is popularly known as the sol-gel processing regime.[20] In addition to the low-density network characteristics, other key features of gels are that, unlike the colloids of micrometer-sized particles, they can sustain a finite stress and are viscoelastic.[21]

Due to excessive shrinkage and subsequent cracking problems during solvent extraction, sol-gel-based systems are mainly used in the processing of low-dimensional shapes, e.g. thin films or fibers. The utilization of sol-gel-based systems in the processing of monolithic shapes is expected to increase as techniques are developed to consolidate nanometer-sized particles and/or macromolecular units more efficiently. Our recent research has focused on this problem using two approaches: (i) increasing the packing density by first coating the particles with lubricating surfactants,[22] and/or (ii) restructuring the low-density gels to a higher density state prior to drying with pressure filtration techniques.[23]

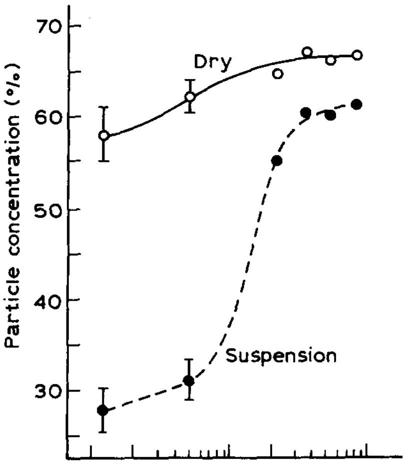

Fig. 4. The effect of particle size on the maximum particle concentration of electrostatically stabilized suspensions of α-Al_2O_3 (>0·1 μm) and AlOOH (<0·1 μm) without exceeding a suspension viscosity of 1 Pa s (broken line) and dried compacts (solid line). In the <0·1 μm range, gelation takes place at low particle concentrations and significant densification takes place during drying.

Coating of the particles with lubricating surfactants is necessary to prevent the formation of a strong chemical bond between the particles (Fig. 6(a)).[22] It is important to note that this chemical bond formation may not be a unique characteristic of nanometer-sized particles. However, in comparison to the micrometer range, chemical bond formation between particles plays an especially important role in the nanometer range since for a given particle concentration, the number of particle–particle contacts increases by six orders of magnitude as we decrease the particle size by only one order of magnitude (from the micro- to the nanometer range). This significant increase in the contact density alone is sufficient to explain the high modulus of gels.

In the selection of the surfactants, there are two important factors to consider: (i) surfactants must be

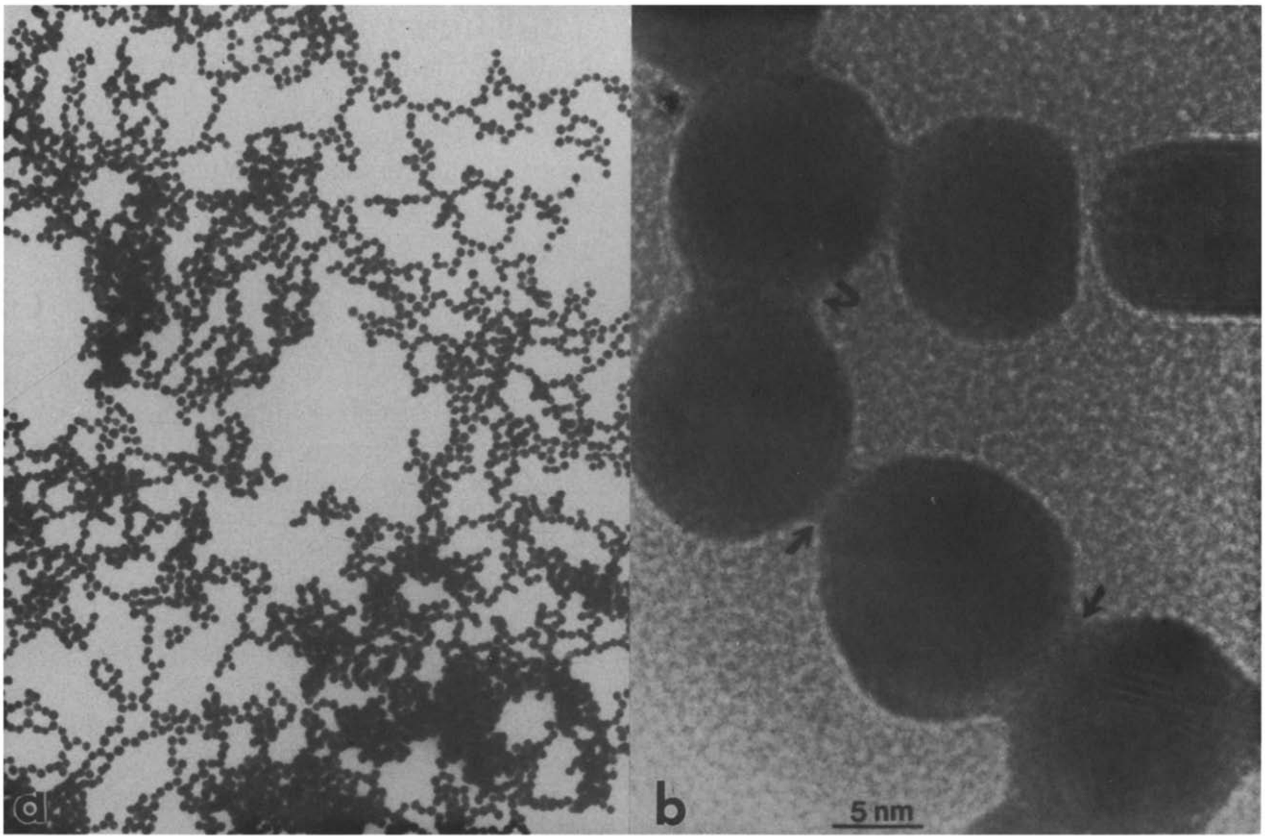

Fig. 5. (a) Transmission electron microscope (TEM) image of a low density (fractal) aggregate of nanometer-sized (≈15 nm) gold particles; (b) high resolution transmission electron micrograph (HRTEM) image revealing the structure of interfaces between particles in this gold aggregate. The solid bond between the particles prevents the restructuring of the aggregate to a denser packed state.[22]

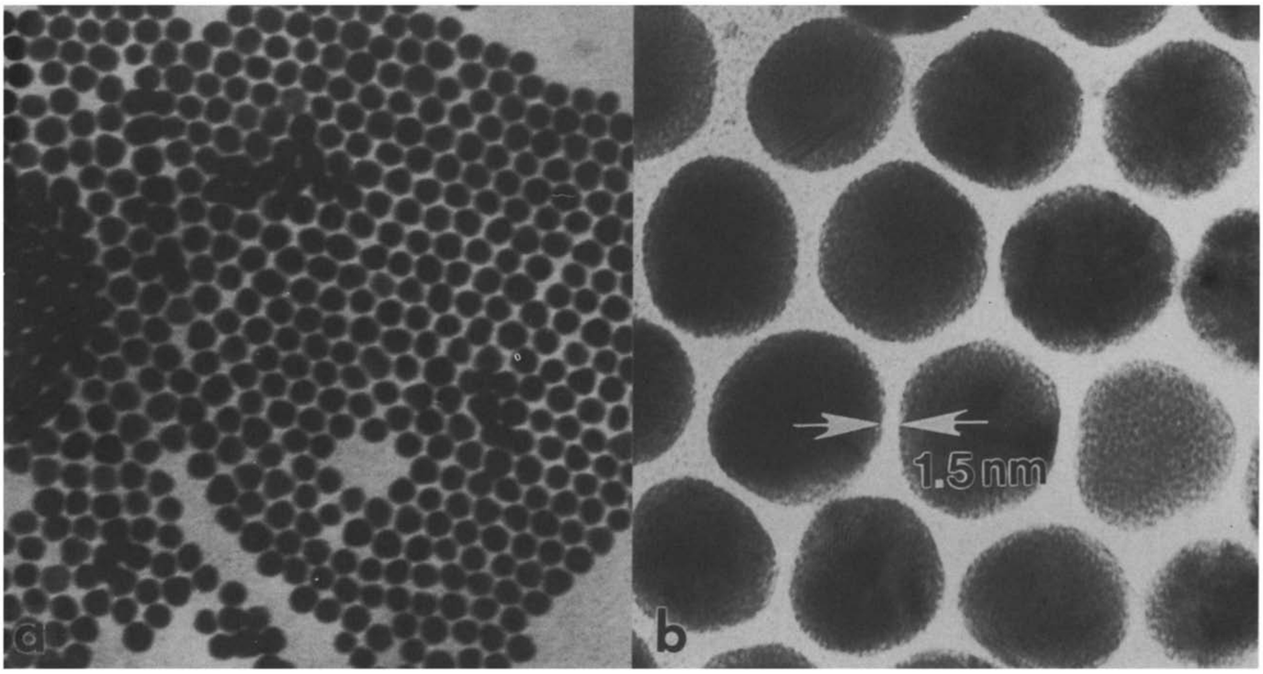

Fig. 6. (a) TEM image of closely packed gold particles that are first coated with a protective monolayer of surfactant; (b) HRTEM image of the same system highlighting the 1–3 nm gap region between the particles.

effective in reducing the interaction energy between the particles, and (ii) the thickness of the coating should be sufficiently small to avoid a significant increase in the size of the particles. Macromolecules that work effectively as dispersants with micrometer-sized particles are not suitable in the nanometer range because the thicknesses of the protective coatings may be much larger than the particles themselves. For nanometer-sized particles, what is needed is thin monolayers of molecular coatings that keep the particles separated by only a few nanometers.[24] Typical examples include molecules with polar and nonpolar head groups and an interior moiety which is often an alkyl chain. The polar group is used to anchor the molecule to the surface of the particle. As shown in Fig. 6(b), with these types of coatings, particles can be kept apart by only 1–3 nm and consequently restructure to a densely packed state.

It is also important to note that in the case illustrated in Fig. 6(b), dense packing took place in a flocculated suspension, contrary to the prevailing view that flocculated suspensions cannot yield dense packings.[15] Our observations support the theory that dense packing can be achieved even with flocculated suspensions as long as the interaction energy between the particles is low enough to provide restructuring.[22]

4 THE HOMOGENEITY OF MULTICOMPONENT COLLOIDS

Most colloids and molecular systems used in the processing of ceramics are multi-component from the point of view of thermodynamics.[25,26] Only the very idealized systems illustrated in Fig. 2 can be regarded as a single component colloid. For instance, commercial powders always display a finite particle size distribution and thus cannot be treated as single component colloids. Similarly, colloids that are used in the processing of micro- and nano-composites are mixtures of more than one type of particle or macromolecular unit and are governed by the mixing rules of solution thermodynamics. Therefore, the degree of mixing in a multicomponent system is controlled not only by external field effects (e.g. particle segregation due to the gravitational field but also by thermodynamic as well as kinetic factors. In the following, we briefly summarize the methodology for controlling the scale of homogeneity in multicomponent systems.

Particle interaction energies play the most significant role in thermodynamic mixing and thus determine the degree of homogeneity. The smallest length scale of homogeneity that can be achieved is the length scale of the packing units themselves. In order to reduce the homogeneity scale to this lowest

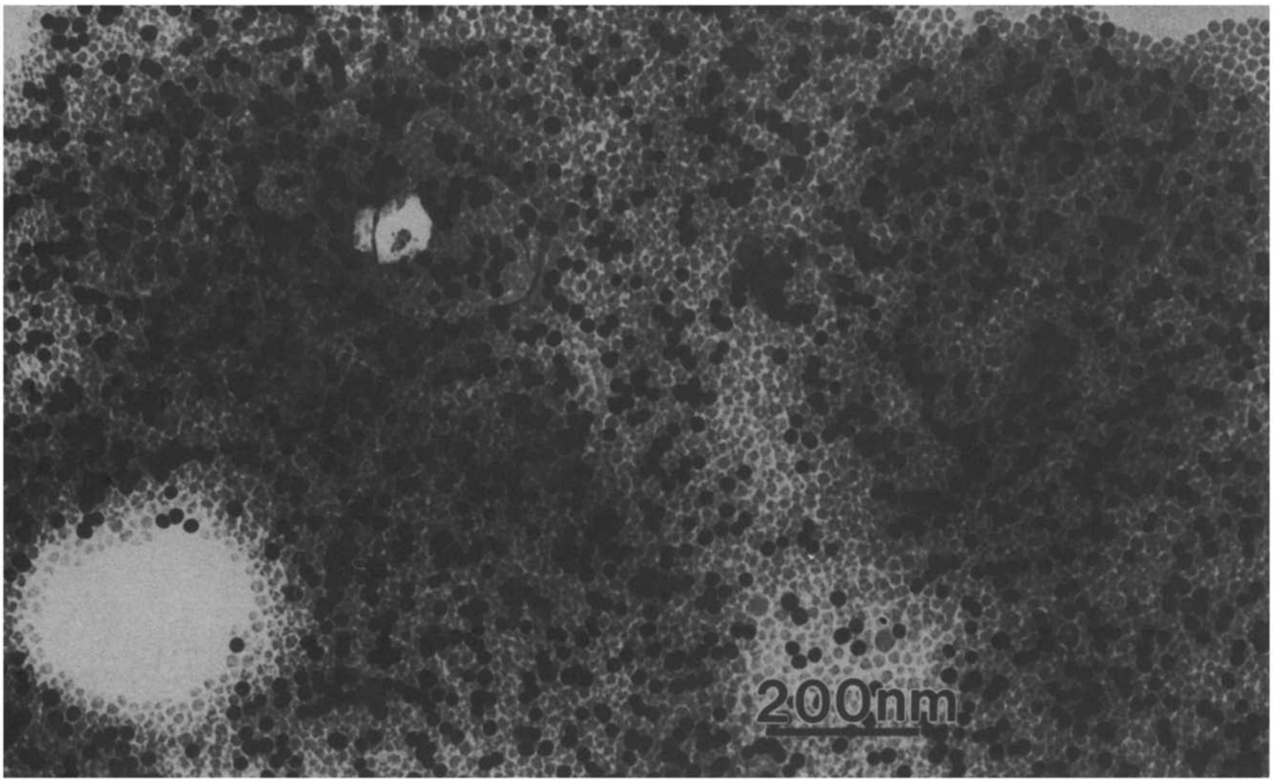

Fig. 7. Colloidally mixed nanometer-sized gold and silica composite. The long-range segregation of the particles was minimized by retaining attractive interactions between the particles.[27]

level, all particles must first be dispersed through shear mixing techniques. Systems with repulsive particle interactions are ideal for this purpose since repulsive interactions yield stable and low-viscosity suspensions.[17,18,27,28] The disadvantage of this approach, however, is that particles also tend to segregate either due to external field effects or differences in interaction energies.[25-27] A partial solution to this problem is to lower the rate of segregation by working with highly concentrated systems. The other extreme is to work with highly attractive particle systems and take advantage of the fact that particles, once thoroughly mixed, cannot segregate from each other at low shear rates.[29] This second approach provides a solution to the segregation problem but creates difficulties due to the very high energy input required in shear mixing to overcome the solid-like suspension viscosity at low particle concentrations. Thus, high packing densities are not easily attained with this approach.[15(b)] The compromise is to work at a range where particles are sufficiently attractive to yield spontaneous flocculation but, at the same time, allow ready restructuring of the clusters without any long-range segregation due to the weak nature of the interactions.[22,30] As illustrated in Fig. 7, under these conditions, not only is the scale of homogeneity kept to a minimum but high packing densities are also achieved.

5 FUTURE DIRECTIONS

Nanoscale heterogeneities have been shown to result in unique properties in a variety of new classes of materials.[31-33] We expect that the processing methodologies summarized in the previous sections will be useful not only in improving the properties of these materials but also in tailoring newer classes of micro- and nanocomposites for multifunctional applications. It should, however, be pointed out that the techniques summarized in this paper are not yet adequate (i) for net-shape forming, and (ii) for achieving a specific control of the composite structure. The solution to the first problem will require the development of techniques where a given volume can totally be filled with ceramic phases through low temperature reactions. On the second problem, efforts in molecular and colloidal engineering must concentrate on the development of procedures for tailoring nanocomposites with specific designs. The optimism that these goals can be achieved stems from the fact that many of the biologically processed composites are engineered to a net shape with the type of specificity that we wish to practice in the laboratory.

Studies on biological systems provide us with the following guidelines: (i) ceramic phases nucleate at the surfaces of organic substrates and grow until a specific volume is filled; and (ii) these organic substrates appear to dictate the formation of a specific architectural arrangement of the ceramic phases through epitaxy.[7] These process guidelines are to a limited extent already being practiced in certain commercial applications where either a liquid or a vapor phase is infiltrated into a matrix to form a composite material by high-temperature processes.[8,34,35] What we suggest, now, is the application of these concepts to low-temperature systems where we may truly be mimicking the biological composites.[36]

ACKNOWLEDGEMENTS

A major portion of this work was supported by the US Air Force Office of Scientific Research under Grant No. AFOSR-87-0114 and AFOSR-91-0040. The author gratefully acknowledges his colleagues, M. Sarikaya, J. Liu, W. Y. Shih and W.-H. Shih, who have contributed to many of the concepts presented in this paper.

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