

PLASTIC/BRITTLE BEHAVIOR OF CONSOLIDATES BODIES: ROLE OF PARTICLE PAIR POTENTIALS

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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 led to new shape forming methods that are discussed at the end of this review.

1. INTRODUCTION

As reviewed by Horn¹, two different chemical routes that shroud the particles with a barrier layer have been identified to produce the short-range repulsive potential. The repulsive pair potential initiates when their barrier layers begin to interact. This interaction produces an attractive, but non-touching particle network in which particles "sit" in a potential well at an equilibrium separation distance. The depth of the potential well and the number of particles per unit volume (controlled by the volume fraction and particle size) governs the strength of the network. The strength of the network can be characterized by measuring the elastic modulus and yield stress (at a given stressing rate) of the slurry, and the response of the saturated powder body, formed by consolidating the same slurry, to stress. Brittle behavior (crack extension before flow) occurs when either the potential well is too deep, or

the particles are forced together (into a deeper potential well) during pressure consolidation. Plastic behavior, required for near net-shape forming, can also be achieved provided the potential well is not too deep. The conditions where the particles can be pushed together is the subject of the current paper. When a potential barrier exists between particles, they can be pushed into contact (over the potential barrier and into the deep, primary minimum) with a sufficient force. This force can be provided by the external pressure used during powder consolidation, e.g., during pressure filtration. When a large fraction of particles have been forced together the consolidated body can be brittle. The consolidation pressure that is required to produce brittle bodies (termed the plastic-to-brittle transition pressure) is related to the force (termed the critical force) needed to push particles over the potential barrier. This newly discovered phenomenon of converting a fluid-like slurry into an elastic body is the bases of a new forming technology called Colloidal Isopressing.²

2. INTERPARTICLE PAIR POTENTIALS

The van der Waals potential always causes particles with similar dielectric constants to be attractive when they are surrounded by a fluid with a different dielectric constant.¹ By itself, the van der Waals potential produces a network of particles in elastic contact; because they touch one another, such particles are more difficult to rearrange and consolidate due to friction. To keep the particles separated, they must be shrouded by matter that causes the system to increase its free energy as the shrouds of two approaching particles interpenetrate one another. Matter comprising the shroud must be of low mass so that the shroud itself does not significantly contribute to the attractive van der Waals potential, and thus, counteract the repulsive potential they provide. In effect, the interpenetrating shrouds keep the particles apart and, in effect, shield either a portion or all of the attractive van der Waals potential. When the electrostatic double layer method, approximated by the DLVO theory, is used to produce a repulsive potential, the shroud is comprised of counterions. When the steric approach is used, the shroud is composed of molecules that are either of either phys- or chem-adsorbed on the surface of the particles.

2.1. Electrostatic approach

In the electrostatic method where the shroud or barrier layer is produced with a cloud of ions, the density and 'thickness' of the cloud is controlled in an aqueous slurry by pH and salt concentration¹. In this approach, a dispersed slurry (i.e., particles are highly repulsive) is formed by reacting either H_3O^+ or OH^- (acid or base) with neutral surface sites ($-\text{M}-\text{OH}$) to produce charged surface sites (e.g. $-\text{MOH}_2^+$ or $-\text{MO}^-$). Oppositely charged ions,

called counterions, form a cloud around each particle in an attempt to neutralize the surface. As two particles approach one another, the concentration of counterions increase between the particles as the approaching counterion clouds penetrate one another. The increased counterion concentration increases the free energy of the system, which, in turn, produces a repulsive interparticle potential. The distance where the repulsion becomes significant depends on the thickness of the counterion cloud, generally described as the Debye length. Large Debye lengths (low counterion concentration) can produce a long-range repulsive potential where particles always repel one another.

Adding salt (adding counterions without changing pH) to a dispersed slurry decreases the Debye length such that strong interparticle repulsion only occurs at short interparticle distances. For this case, particles can be attractive to one another by the van der Waals potential, and only feel repulsion at very small separation distances. That is, when sufficient salt is added to significantly reduce the Debye length, the particles can reside in a potential well (generally referred to the secondary minimum, whereas the primary minimum is the condition were particles are in physical contact) where they retain an equilibrium separation distance. Classical DLVO theory, which treats countions as point charges without dimensions, does not teach this phenomenon. Instead, the DLVO theory teaches that the Debye length decreases to zero with large additions of countions to produce an interparticle potential identical to that at the isoelectric point where only the van der Waals potential is present. Velamakanni *et al*³ demonstrated that adding excessive amounts of salt only produces a weaker network, and much weaker than that observed at the isoelectric point where no repulsive potential exists between particles. Evidence suggests that at high salt concentrations the Debye length approaches a minimum value that is related to the work needed to produce dipoles in the surface of the particles, thus neutralizing the surfaces that approach and make contact.⁴

As discussed below, it has been discovered that the attractive but not touching particle network is of great importance to new shape forming technologies. Namely, it allows the flow stress of a slurry and the yield stress of a saturated powder compact to be manipulated by changing the interparticle potential.

2.2. Steric approach

In the steric method¹, two effects give rise to the repulsive potential produced by adsorbed molecules. The first arises when the adsorbed molecules on the surface of two approaching particles begin to mutually confine their configurational space. Confinement decreases their entropy, gives rise to an

increase in free energy, and thus, a repulsive interparticle potential. The second effect is due to the strain energy that arises when the confined molecules are further pushed together. The interparticle separation distance where the repulsive potential initiates is generally estimated as twice the length of the adsorbed molecules. Thus, very large molecules generally produce longer range repulsion where the molecular 'brushes' extending from the particle surfaces completely shield the attractive van der Waals potential. Whereas small molecules only produce strong repulsion at small interparticle separation distances and can only truncate the van der Waals potential. The short molecules thus produce a weakly attractive, but non-touching particle network, which has been found to be very useful for new shape forming technologies.

Many different types of molecules (hydrocarbon chains provided by alcohol molecules, surfactants, bi-functional molecules such as amino-silanes, di-block copolymers, etc) have been identified to produce that short-range repulsive potential which appears to be important for new shape forming technologies. Kramer and Lange⁵, who reacted simple alcohols with increasing molecular weight with the ceramic particle, shown that the strength of the particle network is inversely proportional to the length of the attached molecules. Molecules with shorter chains truncate the van der Waals potential at a very short interparticle distance to produce a deeper potential well and a stronger network, whereas longer molecules produce a shallow potential well and a weaker network. Kramer and Lange have also shown that the molecules must be strongly bound to the surface to avoid being pushed away during consolidation.

It has been shown that physisorbed molecules can easily be pushed away during particle packing^{6, 7}, whereas chemisorbed molecules are more robust and thus, more desirable for producing the repulsive potentials required for ceramic powder processing. It was shown that amino-silane molecules⁸, terminated at one end with RO-groups (R = alkyl), will hydrolyze in water and react with $-\text{Si-OH}$ hydroxyl sites on Si_3N_4 surfaces to produce strongly bonded, chemisorbed molecules that are difficult to push away during pressure consolidation. It was demonstrated that a diblock copolymer, PMAA-*block*-PEO chemisorbs on alumina powder to produce well dispersed, aqueous slurries over a wide range of pH⁹. At pH >4, the negative sites on the PMAA anchor block over compensate for the positive sites on the alumina surface to reduce the pH_{iep} (pH of the isoelectric point) of the coated powder from 9 to ≈ 5 . At pH 9, the particles are strongly dispersed due to repulsive potential produced by both the electrostatic repulsive potential produced by the net-negative surface charge, and by the steric effect of the polyethylene oxide (PEO) steric block of the copolymer. At pH 5, the pH_{iep} of the coated alumina particles, the aqueous slurries are also dispersed due to the steric effect of the PEO block.

3. RELATION BETWEEN RHEOLOGY, PARTICLE PACKING AND INTERPARTICLE POTENTIAL

Figure 1¹⁰ describes the potential and force between weakly attracted particles as a function of their separation distance. This schematic function for the force, shown in Fig. 1b, is the derivative of the particle pair potential shown in Fig. 1a with respect to the separation distance, 'h'. The force is zero at the equilibrium separation distance (h_{eq} , bottom of the potential well). The second derivative at h_{eq} is the 'spring' constant between the two particles, which is related to the elastic modulus (G') of the attractive particle network. When $h < h_{eq}$, the particles are repulsive, whereas, a tensile force is needed to separate the particles for $h > h_{eq}$. The maximum force needed to separate the particles and the number of particles per unit volume are related to the flow stress of the particle network, i.e., the stress were the network no longer behaves in an elastic manner, but breaks apart to initiate flow. Thus by measuring the flow stress and elastic modulus of the particle network in the slurry state, the first and second derivative of the pair potential can be estimated

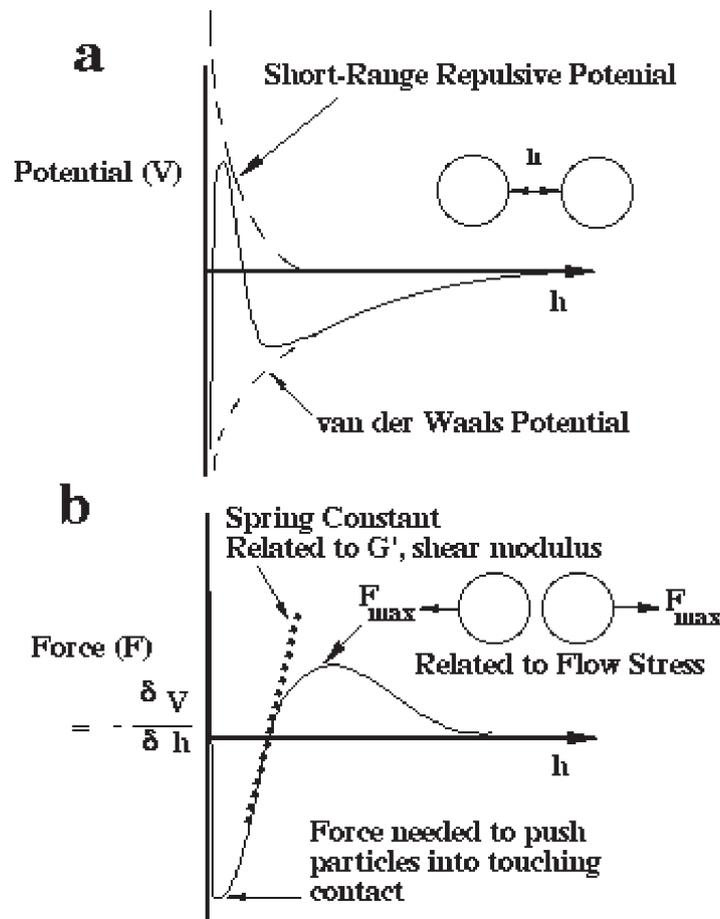


FIGURE 1 - Interparticle pair potential (a) and interparticle force (b) for weakly attractive particle.¹⁰

and related to systematic changes made in the chemistry used to form and alter the shroud around the particles for a given powder.

The interparticle potential shown in Fig. 1a is the sum of the van der Waals attractive potential and a short-range repulsive potential produced by the penetration of either two counterion clouds with a short Debye lengths, or two brushes of chem-adsorbed, short molecules. Assuming that the van der Waals potential is not strongly affected by changes in what is done to the surface to alter the short-range repulsive potential, it can be seen that the force needed to pull two particles apart will scale inversely to the depth of the potential well, viz., for a fixed van der Waals potential, a deeper potential well will produce a steeper slope at the inflection point. Thus, for a fixed volume fraction of particles, the strength of the attractive network can be changed by altering either the Debye length (adding more salt) or the length of the chem-adsorbed molecules.

For a given interparticle potential, the flow stress and elastic modulus of the attractive network will increase with the number of particles per unit volume, i.e., the volume fraction of powder within the slurry. Systemic measurements for slurries formulated with different salt contents and different volume fractions of powder show that for a given interparticle pair potential, the flow stress and elastic modulus are power law function of the volume fraction, with exponents of ≈ 3.5 and 4.5 , respectively¹⁰. That is, small changes in the volume fraction produce large changes in slurry rheology.

Although much more can be said about the relation between interparticle potentials and the rheology of the slurry state, the important result reported here will concern particle packing and the mechanical properties of the consolidated body that is still saturated with the liquid used to formulate the slurry. It is the consolidated state, produced, e.g., by concentrating the powder by pressure filtration, that must be shaped by either plastic deformation or made to flow into a mold and transform into an elastic body.

It has been discovered that the rheological behavior of a consolidated body was not only depend on the interparticle potential and the volume fraction of powder within the saturated compact, as expected, but also and unexpected, dependent on the consolidation pressure.¹¹ It was known that the particle packing density achieved during consolidation was related to the interparticle potential. Low relative densities result from slurries formulated for conditions where only the van der Waals potential prevailed, e.g., formulated at the iep, due to their resistance to rearrangement caused by the friction between the touching particles. Also as shown in Fig. 2, the relative density of bodies consolidated from these flocced slurries are also very pressure sensitive. On the other hand, slurries "lubricated" by a highly repulsive interparticle pair potential pack to the highest relative density that can be

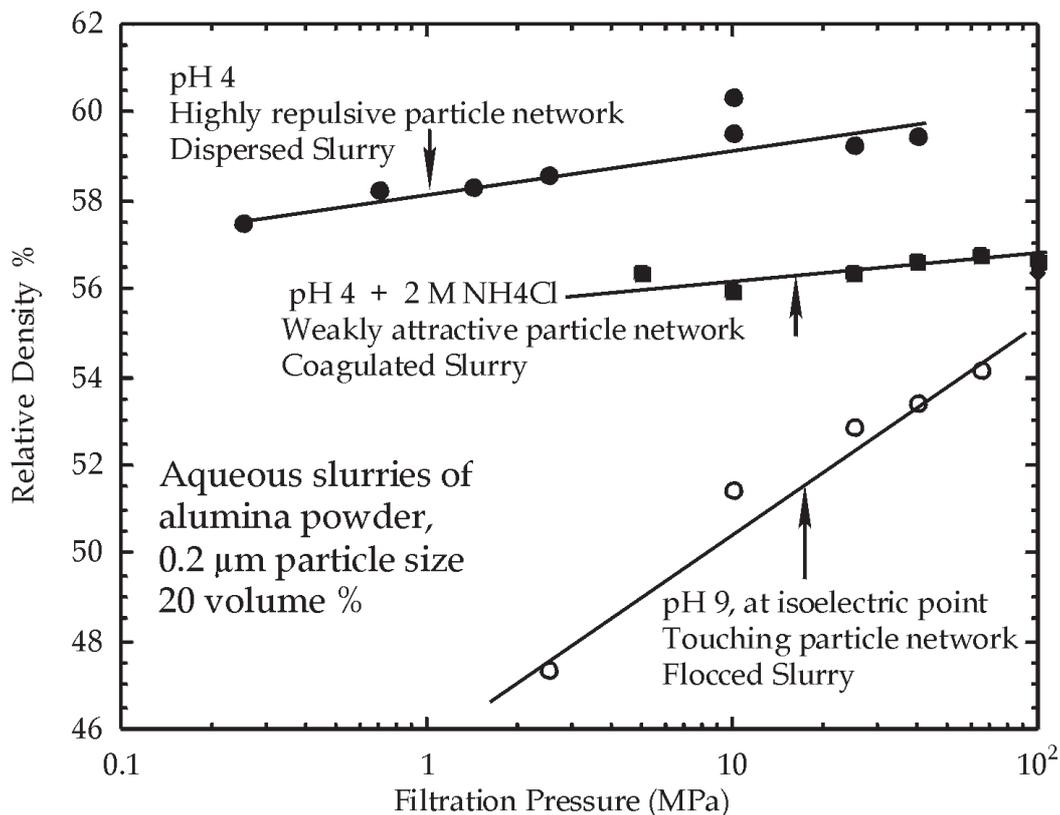


FIGURE 2 - Relative density of AKP-50 alumina as a function of consolidation pressure. Each data point is the average of between 2 and 5 specimens from the same powder lot.¹¹

achieved for a given powder. In addition, the relative density is not as sensitive to the applied pressure. Pair potentials that produce weakly attractive particle networks in the slurry state, e.g., by adding excess salt to a dispersed slurry, result in a relative density that is intermediate to the strongly repulsive and strongly attractive pair potential. The relative density of these weakly attractive particle networks is much less sensitive to the applied pressure relative to the strongly attractive networks. These effects are illustrated in Fig. 2, where the interparticle potential was produced by the electrostatic double layer method, with salt added to the dispersed slurry used to produce the weakly attractive particle network.

Franks and Lange¹¹ performed axial compression experiments on cylindrical specimens that were used to accumulate the relative density data shown in Fig. 2. They were able to classify the plastic and elastic nature of the different bodies with regard to the interparticle pair potential, relative density, and the applied pressure used to consolidate the bodies from the slurry state. Bodies consolidated from slurries formulated to contain a weakly attractive particle network, i.e., by adding excess salt to a dispersed slurry, the stress-

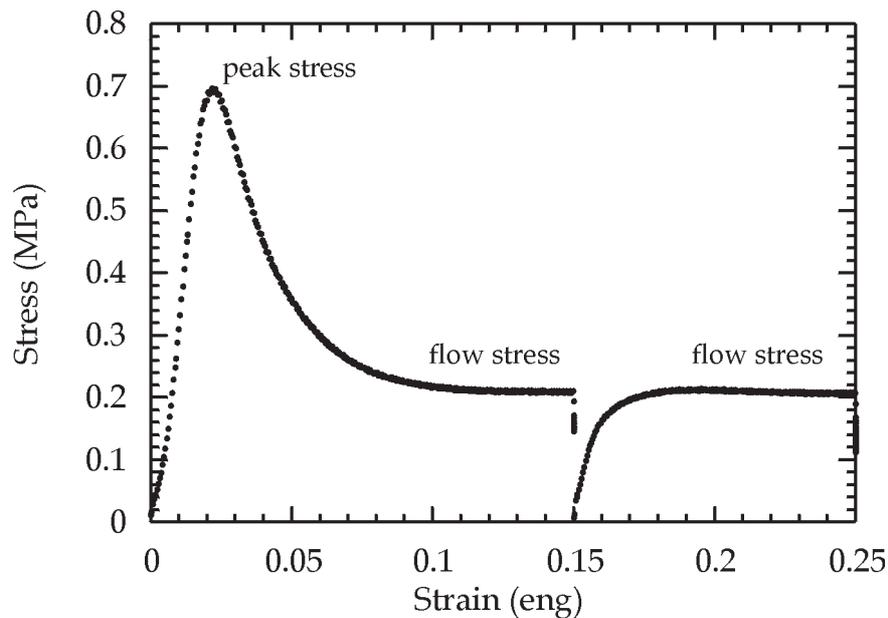


FIGURE 3 - Typical stress-strain curve for plastic specimen comparing peak stress and flow stress during initial and repeat loadings. Note the lack of peak stress on the second loading, while the flow stress remains constant.¹¹

strain behavior was typical to that shown in Fig. 3.¹¹ The initial stress-strain behavior was linear elastic to a maximum stress called the peak stress. Below a critical consolidation pressure, the bodies were plastic, where, after achieving a peak stress, the stress would drop to a flow stress. If the plastic body was unloaded and then reloaded, it would again exhibit the same flow stress as shown in Fig. 3, which could continue up to a strain of 50 % or more before strain hardening would occur due to the constraint imposed by the loading platens due to the decreased height to diameter ratio of the cylindrical body. When the consolidation pressure exceeded the critical value, the body was elastic; a load drop would only occur when the body cracked to break into pieces.

4. SHAPE FORMING TECHNOLOGIES ENABLED BY SHORT-RANGE REPULSIVE POTENTIALS

Above, it was shown that plastic powder compacts could be consolidated from slurries formulated to contain attractive, but non-touching particle networks. The short-range repulsive potential needed for these weakly attractive networks could be achieved with either the electrostatic double layer approach by adding excess counter ions to decrease the Debye length, or the steric approach by using relatively short, chem-adsorbed molecules. An experience person would suggest that the use of chem-adsorbed molecules,

which is the more robust approach.

Although not reviewed in detail here, the cited literature will show that the flow stress for a given powder system can be altered by changing the strength of the weakly attractive particle network.^{8,11,12} For the electrostatic approach, the network strength can be altered by changing the surface charge density (pH of slurry), the concentration of added counterions, and the type of counterion. For the steric approach, the network strength can be altered by using a different chem-adsorbed molecule, or by changing the apparent length of a given chem-adsorbed molecule by adding salt to the slurry. When both the electrostatic and steric approach are combined, as for example, by the use of a diblock copolymer⁹ where the charged “anchor” block can overcompensate the surface charge of the particle, while at the same time, the steric block can produce a strongly repulsive network. Using these methods of changing the strength of the weakly attractive particle network, one can produce consolidated bodies that can either have a flow stress too low to retain its shape when they are acted upon by gravity, just right to allow the application of clay-like plastic forming technologies.

Also noteworthy is that the methods described above to produce a plastic body are also consistent with the need to first produce a well dispersed slurry (highly repulsive particle network) needed to remove strength degrading inclusions by passing the slurry through a filter prior to consolidation and shape forming.

4.1. Shape forming via Colloidal IsoPressing²

Colloidal IsoPressing is a rapid method to form an engineering shape from the slurry state, previously filtered to remove strength degrading inclusions.¹ A slurry is formulated to produce a weakly attractive particle network with a short-range repulsive interparticle pair potential. The short-range repulsive potential is chosen such that the slurry can be consolidated to a high particle density that is easily fluidized by vibration. The role of the short-range repulsive potential is two-fold. First, it prevents particle from being pushed into contact while they are consolidated to a high relative density. Second, the interparticle pair potential is chosen such that the yield stress is very low, i.e., so low that after consolidation, the body does not retain its shape but still appears fluid-like, albeit with a much higher viscosity relative to the initial slurry state. The fluid-like body is injected into a rubber mold and subjected to a larger isostatic pressure to force particles into contact. The rubber mold contains a porous region so that the particle network within the mold can be compressed and the particle pushed into contact. Pushing the particles together causes the molded material to become a strong, elastic body with the shape of the rubber mold. Because the particles are forced

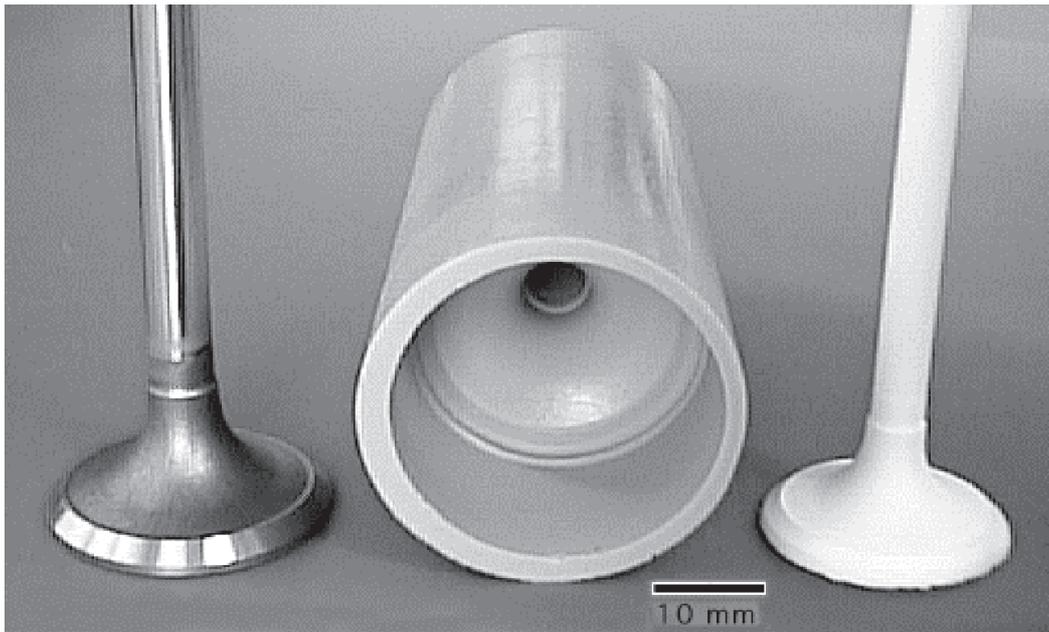


FIGURE 4 - Examples of alumina components produced by the Colloidal IsoPressing method. Metal engine valve (left), silicone rubber mold cast from the metal part (center), and sintered alumina valve (right)².

into contact at a high pressure, the liquid remaining within the component can be removed by evaporation without shrinkage. Drying without shrinkage allows direct heating to the densification temperature after shape forming. Figure 4 shows a metal car valve, the silicon rubber mold that replicates the valve, and the aluminum oxide valve produced from the rubber mold via the Colloidal IsoPressure method. Forming the valve within the rubber mold requires less than one minute at an isopressure of 100 MPa.

4.2. Fabricating Ceramic Matrix Composites via VibraIntrusion¹³

An important attribute of any ceramic, reinforced with very strong ceramic fibers, generally called a ceramic matrix composite (CMC), is that its strength be relatively insensitive to the presence of notches and holes. That is, the strength of a notched CMC component should be essentially identical to that of the un-notched body with the same, reduced cross section. Since the failure strain of a strong fiber is generally much larger than the surround matrix, crack extension initiates within the matrix. In terms of crack extension, one requirement for notch insensitivity is that the fibers must be isolated from the very high stress field of a matrix crack. A fiber within a good CMC is only expected to fail when the applied stress exceeds its strength.

The processing of porous matrix CMCs starts by packing a powder around the fibers within a perform, e.g., stacked sheets of cloth, a woven or knitted fabric, etc. and ends with a step that makes the powder matrix stiffer and strong. Haslam *et al*¹³ have introduced a rapid method to pack powder around the fibers called VibraIntrusion. VibraIntrusion also utilizes a consolidated body that can be fluidized as described above. The slurry containing the weakly attractive particle network is first consolidated by pressure filtration and then packed around the fibers by vibration-assisted intrusion. As described above it requires a slurry formulated with a special interparticle pair potential and knowledge of how this potential is affected by the consolidation pressure. With this special interparticle potential, a consolidated body can be formed with a high particle packing density with the rheological properties of a fluid. To prevent evaporative drying, the fluidized body is rolled between sheets of plastic to form a thin layer, frozen to aid handling, placed between two layers of ceramic cloth, and vibrated between the fibers after it thaws. Since the fluidized body exhibits shear-rate thinning, the vibration reduces the viscosity and allows rapid intrusion of the particles into the fiber perform. This process can be repeated, with intermediate freezing of the previously intruded cloth layers, to quickly fabricate a multi-layered CMC. The intermediate freezing is needed to aid in handling thin layer of fluidized body. Since the thawed CMC is flexible, it can be bent, cut and formed, similar to a thawed, epoxy/fiber prepreg used to fabricate wings on an airplane. After shaping, the liquid within the powder matrix is removed by evaporation, and the matrix is made strong by one of a number of methods described elsewhere.¹⁴

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Discussion

L. Hench: The high volume fraction of particles and low shrinkage suggests your system would be ideal for rapid microwave densification. Please comment.

F.F. Lange: 1. Since there is no shrinkage during water removal, rapid heating is possible.

L. Hench: What is in your opinion the possibility of achieving ceramics with a Weibull modulus of near infinity, i.e., a predictable, uniform failure strength?

F.F. Lange: I only believe in achieving a threshold strength, not a $m = \infty$ material.