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Plastic clay-like flow stress of saturated advanced ceramic powder compacts

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Abstract

The flow stresses of saturated, consolidated alumina powder compacts and a commercial throwing clay were measured and compared. The flow stresses of certain saturated alumina powder compacts formed by consolidating salt coagulated slurries were found to be almost identical to the flow stress of the commercial throwing clay. The effect of volume fraction of particles, particle size, interparticle attraction, and consolidation pressure on the flow stress were systematically investigated. Plastic behavior and flow stresses, controlled by changing the forces between the particles, may be useful in developing low cost plastic forming processes for the production of advanced ceramic components.

Keywords: Al_2O_3; Clays; Colloidal processing; Plastic flow; Shaping

1. Introduction

Colloidal processing of advanced ceramic powders is important in removing strength limiting flaws from high performance ceramic components, by passing the powder, formulated as a dispersed slurry through a filter prior to further processing.[1–3] Since the diamond machining of ceramic components is expensive, it is economically advantageous to produce objects that do not require machining subsequent to firing. Forming techniques that produce green bodies that are very close to the desired final shape (and shrink uniformly during firing) are referred to as near-net-shape processes. These processes only require a minimal machining. Plastic forming processes that are compatible with the removal of flaws by filtration will allow the economical production of near-net-shape ceramic components of high strength and reliability. Traditional clay forming processes are well developed and inexpensive. If the plastic behavior of wet advanced ceramic powder compacts can be controlled to match that of clay, inexpensive plastic forming methods can to be used to produce high strength complex shaped ceramic components. Such a process has the potential to economically produce reliable, high performance ceramics.

Although the plastic properties of clay have been the subject of much research, there is still no general agreement to the mechanism responsible for plasticity.[4–6] Interpenetrating strong and weak particle networks, hydration repulsion and relative densities far from the maximum packing density probably contribute to this phenomena. On the other hand, as reported below, the development of plasticity for advanced powders such as alumina, zirconia and silicon nitride, has stemmed from the basic understanding relating interparticle pair potentials to the rheological behavior of particle networks. This basic understanding has directly lead to clay-like rheology and new near-net-shape forming processes.

The production of a plastic powder compact that can be used for net-shape forming requires two processing steps. The first step is formulating a slurry (powder + liquid mixture). The slurry must first be formulated such that particles are highly repulsive to allow the strength degrading inclusions to be removed by filtration.[1] As detailed below, after the flaws are removed from the powder, the slurry needs to be reformulated to cause the particle to be weakly attractive. Weakly attractive particle networks are needed to develop plastic behavior.

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Repulsive and attractive particle networks produce a wide variety of rheological properties that are controlled by changing the surface chemistry of the particles through changes that include pH, salt and polymer concentration.[3,7,8] Other parameters such as particle volume fraction, size and shape can also affect the rheology of slurries. It will be shown that the preferred interparticle pair potential required for a shape forming operation is one in which the particles form a weakly attractive network.[3,8] The weakly attractive network is created when the slurry is formulated to produce a short range repulsive potential. When combined with the pervasive van der Waals attractive potential, the short-range repulsive potential prevents attractive particles from coming into contact. Instead, the particle 'sit' in a potential well separated by an equilibrium distance. Particles in the weakly attractive network must be pulled apart to induce flow. The force needed to pull the particle apart and the number of particle per unit volume will control the flow stress.

The second processing step to form a plastic powder compact is called consolidation, namely, a process that increases the volume fraction of powder. Consolidation is generally performed by forcing the liquid within the slurry through a filter while retaining the particles on the filter in the form of a 'cake' that is saturated with the liquid. This method of consolidation is generally known as either pressure filtration or de-watering. During consolidation, the particle network supports the applied pressure. Particles that are separated by either a short- or a long-range repulsive potential can be pushed into touching contact during consolidation.[9] The applied pressure is not equally shared by all particles, thus, a fraction of the particles within the network are the first to be pushed into touching contact during consolidation. After consolidation, the particles that have been pushed into contact form a much stronger network that interpenetrates a much weaker particle network that existed within the slurry. The much stronger particle network can act as a skeleton that supports the much weaker network. Higher consolidation pressures cause a greater fraction of particle to be pushed into contact. The strong particle network causes the consolidated body to initially exhibit an elastic stress/strain behaviour during mechanical testing. The elastic regime occurs until a peak stress is observed where the strong network is broken apart.[9] The peak stress increases with the consolidation pressure, i.e. increases with the fraction of particles that are forced into contact during consolidation. For bodies consolidated below a critical pressure, further deformation causes flow at a flow stress. As detailed below, the flow stress depends on the nature of the interparticle pair potential that existed in the slurry, the particle size, and the volume fraction of powder within the saturated, powder compact. When the body is loaded a second time no peak stress is observed since the strong network is already broken apart. Bodies consolidated above a critical pressure are elastic and fracture before they flow, i.e. their yield stress exceeds their flow stress. In, the stress/stain data is generally reported for the second time the body is loaded. These data will exclude the peak stress because it is not observed once the strong network is broken apart during the first loading period.

This paper systematically explores the parameters which control the flow stress of plastic, saturated powder compacts. By way of reviewing the recent literature, a complete picture is presented of how each parameter effects the flow stress. These parameters include the volume fraction of the particles, the average size of the particles, the magnitude of attraction between the particles, and the consolidation pressure. It will be seen that saturated, consolidated powder compacts formed from advanced ceramic powders can be produced with a flow stress that is identical to that of a commercial throwing clay.

2. Experimental procedure

Alpha-alumina powder (AKP-50 and AKP-15, Sumitomo Chemical Company, approx. 0.23 microns and 0.59 microns average diameter, respectively) was prepared as aqueous slurries containing 0.20 volume fraction of solids. After dispersing the aqueous slurry at either pH 4.0 or 12, it was then either coagulated with additions of NH_4Cl, LiCl, NaCl, KCl, CsCl, or tetraethyl ammonuim (TEA) chloride (Fisher Chemical, Fair Lawn, NJ, USA, analytical grade) to create either a weakly attractive network or flocculated to create a strongly attractive network by changing the pH to 9 (the isoelectric point of this powder where very strong attraction exists between the particles). The pH was adjusted (± 0.1 pH units) with analytical grade HCl or the hydroxide corresponding to the salt cation.

The slurries were consolidated by pressure filtration. A predetermined volume of slurry was poured into a pressure filtration cavity, to consolidate cylindrical bodies (1.9 cm dia. by $\approx$2.9 cm high) within the pressure range of 2.5 to 100 MPA. The relative density of the consolidated bodies was determined using the weight difference method described previously.[10]

A commercial throwing clay (WSO throwing clay, Laguna Clay Co., Laguna, CA, USA) was obtained with solids composition approximately 40 wt.% kaolin, 25 wt.% ball clay, 20 wt.% silica sand, and 15 wt.% feldspar, according to the manufacturer. The clay was formed into cylinders by hand packing into a cylindrical die cavity and pressing at 10 MPa with a piece of parafilm wax paper in place of the filter paper. In this way a cylindrical body, suitable for mechanical testing, was formed without either increasing the relative density of the clay or applying a pressure to the powder network (since the applied pressure is transmitted hydrostatically through the pore fluid). Other clay specimens were consolidated by pressure filtration with a paper filter in place as described above. The weight difference method of calculating volume fraction solids was used with the assumption that the average density of the solids in the clay body was 2.56 g/cc and that all weight loss was due only to water. The average density of 2.56 g/cc was calculated from the weight fractions and densities of each solid component, (kaolin, ball clay, silica, and feldspar).

Load–displacement measurements were performed using a screw driven (Instron model 8562, Canton, MA, USA) mechanical test machine. The saturated cylindrical bodies (contained within a sealed plastic bag to prevent drying) were loaded in unconstrained, uniaxial compression as described previously.[9] Each experiment consisted of initially deforming the body at 1 mm/min displacement rate to reach a constant flow stress beyond the peak stress prior to unloading. (As described by Franks and Lange,[9] the peak stress is due to particles being forced into a strong touching network during pressure consolidation. The initial deformation step performed in this work ensures that this strong network is broken down before the flow stress is measured. Such a process is analogous to the potter kneading the clay before throwing the pot.) The body was then reloaded at a displacement rate of 1 mm/min. The engineering strain was calculated as the displacement divided by the initial height of the cylinder. The area during deformation was calculated by assuming the body uniformly deformed as a right cylinder while conserving its volume. The nominal stress was calculated by dividing the load by the calculated area. All stress–strain curves are presented in the form of nominal stress versus engineering strain.

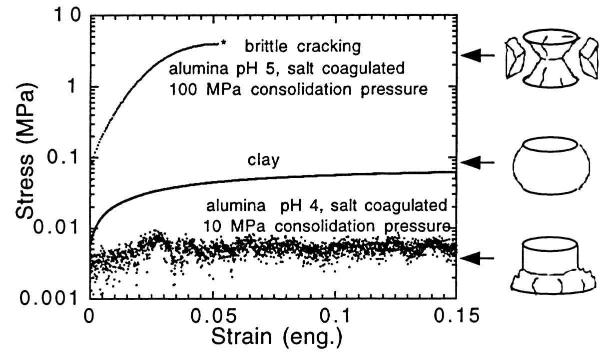

Fig. 1. Comparison of clay mechanical behavior with the wide variety of behavior possible for AKP-50 alumina. [The data for the WSO throwing clay (Laguna Clay Co.) is from the initial loading of the body. The brittle alumina body was formulated at pH 5, with 1.0M NH_4Cl, consolidated at 100 MPa, and is the data for the initial loading of the body. The alumina body that liquified was formulated at pH 4, with 0.5M NH_4Cl, consolidated at 10 MPa, and had a peak stress of about 0.06 MPa during the initial (approx. 7% strain) loading (not shown). The second loading (without peak stress) is shown here. The peak stress is described in the text and Ref. 9].

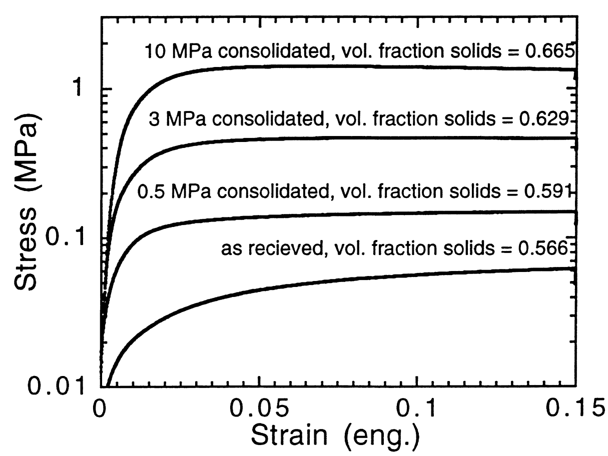

Fig. 2. Stress–strain behavior and relative densities (as labelled) of clay consolidated (at various pressures as labelled) by pressure filtration (dewatering). The data shown are for the initial loading of the body (adapted from Ref. 11).

3. Results and discussion

3.1. Clay behavior

The typical stress–strain behavior of the commercial throwing clay investigated is shown in Figs. 1 and 2. The clay bodies usually exhibited uniform deformation with a minimal amount of barrelling. The flow stress at a strain of 0.15 is ≈0.06 MPa. Also, as illustrated in Fig. 1, the behavior of alumina powder compacts, saturated with water, may vary from elastic to plastic to liquification with the flow stresses varying by several orders of magnitude for the same powder. The aim of this work is to understand and control the parameters that affect the mechanical behavior of saturated advanced ceramic powder compacts so that the clay behavior may be matched. The volume fraction of solids in the as-received clay was 0.566. Dewatering the clay by pressure filtration increased its the relative density and flow stress as illustrated in Fig. 2. The maximum volume fraction of solids was 0.736 when the clay was consolidated by pressure filtration at 100 MPa. The high relative density that could be achieved by pressure filtration is more than likely due to the extended size distribution of the different particles, which includes coarse silica sand (>20 micron) and fine ball clay (<1 micron). Such bimodal mixtures result in high packing densities.[12,13] Since no peak stress was observed in the stress–strain behavior of the clay, it may be concluded that the particles are not pushed into a deeper minimum during consolidation. Such behavior is not unexpected since even in the slurry state the particles prefer to be in a deep attractive minimum due to the difference in sign of the surface charge on the edges and the faces of the plate-like clay particles. The increase in flow stress that occurs when the clay is dewatered is due primarily to the increase in relative density of the material as discussed next.

3.2. Alumina behavior, effect of volume fraction

Increasing volume fraction is known to have a very strong effect on increasing the rheological behavior of suspensions.[14–19] As shown in Fig. 2 for clay bodies and Fig. 3 for alumina bodies the flow stress increases with volume fraction of powder for saturated consolidated bodies as well. The flow stress (and yield stress) of an attractive particle network depends upon the number of interparticle bonds which must be broken per unit volume and the force needed to break each bond. The effect of increasing the volume fraction is to increase the number of interparticle bonds per unit volume. As shown in Fig. 3, the behavior of strongly attractive particles (such as bodies prepared from slurries formulated at the isoelectric point) changes from plastic to elastic with increasing volume fraction. Elastic bodies fracture prior to plastic flow because their yield stress exceeds the fracture strength of the body.

3.3. Alumina behavior, effect of particle size

Fig. 4 shows two examples of how smaller particles produce higher flow stresses when other parameters such as volume fraction and slurry formulation are held constant. The exact size dependence of the yield stress and flow stresses of attractive particle systems is not completely understood. According to theory[10,12,21–23] an inverse size dependence is predicted for most rheological behavior but in practice[12,16,23] an inverse square or cube size dependence is often observed. In general the effect of particle size is that smaller particles produce a greater number of particle–particle bonds per unit volume which must be broken to produce flow, which results in a greater flow stress for the powder compacts made of smaller particles.[12]

3.4. Alumina behavior, effect of interparticle attraction

It is well known that the interparticle pair potential can be manipulated by controlling the formulation of the slurry including changing the pH and salt and polymer concentration, etc.[3,7,8] Usually, either the electrical double layer method (which uses pH and salt concentration control) or the steric method (which used polymers or surfactants adsorbed or bonded to the particle surface) are used to produce the weakly attractive interparticle pair potential required for plastic forming. The magnitude of the interparticle attraction has a significant effect on the rheological behavior of

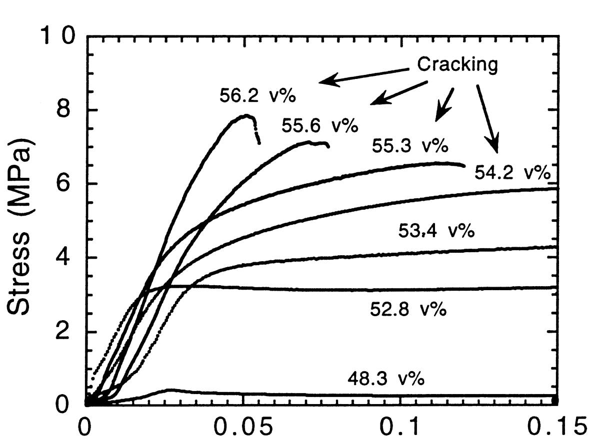

Fig. 3. Effect of increasing volume fraction on the mechanical behavior of AKP-50 alumina flocculated at the iep (pH 9 where a strongly attractive touching particle network is formed). The data shown are for the initial loading of the body (adapted from Ref. 20).

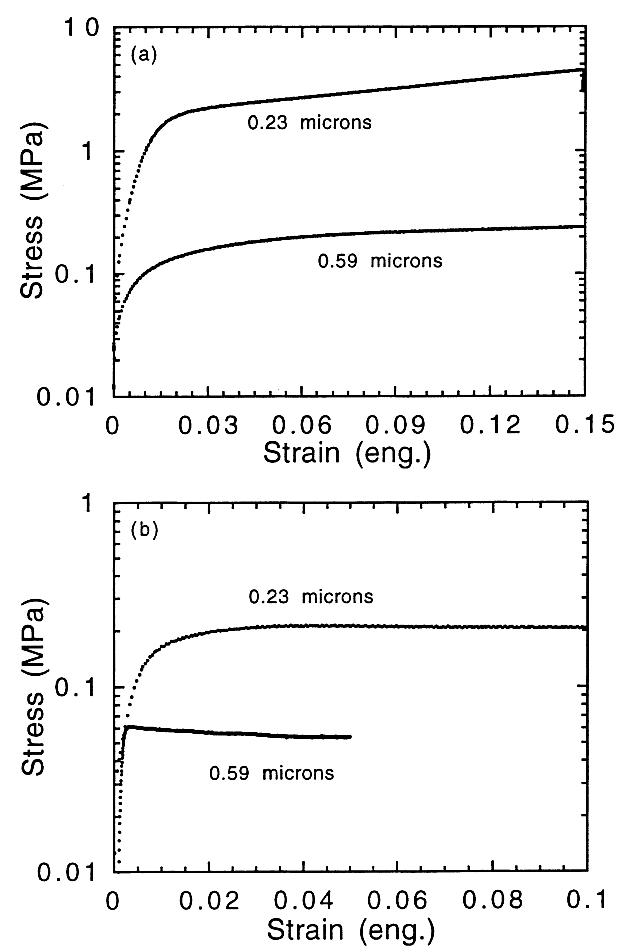

Fig. 4. Comparison of mechanical behavior of 0.23 micron average size alumina (AKP-50) with 0.59 micron average size alumina (AKP-15) at; (a) pH 5.0 with 1.0M NH_4Cl at 55 vol.% solids; and (b) pH 6.0 with 0.5M NH_4Cl at 54 vol.% solids. The data shown are for the second loading of each body (after about 7% strain preworking).

slurries[14,16–19] and saturated consolidated bodies.[24,25] Fig. 5 illustrates that a larger flow stress results with increasing interparticle attraction. For this example, the magnitude of the attraction is controlled by using different salts to coagulate the slurries. The counterion associated with each salt changes the depth of the potential well in which the particles "sit", and thus, changes the force needed to pull the particles apart. For the data shown in Fig. 5, Li^+ counterions produce the deepest potential well and the greatest force needed to separate the particles. In addition, the relative density achieved during consolidation also changed with the different counterions, ranging from 0.532 for LiCl to 0.565 for CsCl. As evident by the higher flow stress, the slight decrease in volume fraction (and thus number of particle-particle bonds per unit volume) for the body containing the Li^+ conterions was not enough to counteract the increase in attractive force. When the consolidated body is produced from a slurry formulated at the isoelectric point, the particles are strongly attractive and form a touching particle network that is even stronger than the networks produced when salt is used to produce a weakly attractive network. In comparing Fig. 5 to the data in Fig. 3 (flocced at the iep), it can be seen that bodies with similar volume fractions have a greater flow stress when formulated at the isoelectric point.

3.5. Alumina behavior, effect of consolidation pressure

When the particles form a touching particle network because the slurry is formulated at the isoelectric point, the primary effect of increasing the applied consolidation pressure is an increase in the volume fraction of solids of the consolidated body.[9,10] This results in a corresponding increase in flow stress as demonstrated in Section 3.2. On the other hand, when the particles from a weakly attractive network via dispersed slurries formulated with added salt, the particles in the consolidated body are still separated by a small distance unless they are pushed into contact above a critical consolidation pressure. This effect of consolidation pressure on the plastic or elastic behavior is illustrated in Fig. 6, where the volume fraction of powder in all of the bodies is within a narrow range (from 58.3 to 59.0 vol.%), i.e. the number of particle-particle bonds is similar. At low consolidation pressures, the bodies have plastic behavior with low flow stresses. Above a critical consolidation pressure (between 17.5 and 25 MPa for the conditions shown in Fig. 6), the bodies exhibit an elastic behavior and fracture before they flow. This transition pressure is explained as follows.[9] When slurries are formulated to produce a weakly attractive particle network, the short range repulsion prevents the particles from coming into contact. At low consolidation pressures, nearly all the particles remain in the weakly attractive minimum after consolidation and thus have a low yield and flow stress. At higher consolidation pressures, the applied force between some particle pairs is greater than the short range repulsive force and these particles are pushed together into touching contact. Above the critical transition pressure, a sufficient fraction of particles have been pushed together by the applied pressure to produce a very strongly attractive percolating touching particle network. The bond between each of these touching particles is very strong and it becomes difficult to pull these particles apart and allow flow to occur before the body fractures. The magnitude of the consolidation pressure which produces elastic (brittle) behavior depends upon the type of short range repulsion[9,20] and the size[10] of the particles. It is

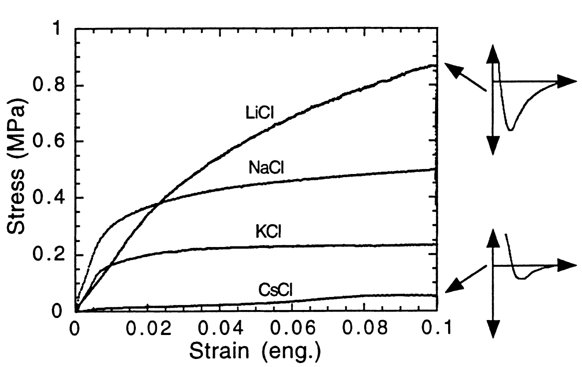

Fig. 5. Mechanical behavior of bodies with differing magnitude of interparticle attraction. The LiCl containing bodies have the greatest attraction between particles while the CsCl containing bodies have the least attraction. The bodies were formulated at pH 12 with 0.5M of salt (as indicated) and consolidated at 10 MPa. The data shown are for the second loading of the body (after about 20% strain preworking.) (adapted from Ref. 24).

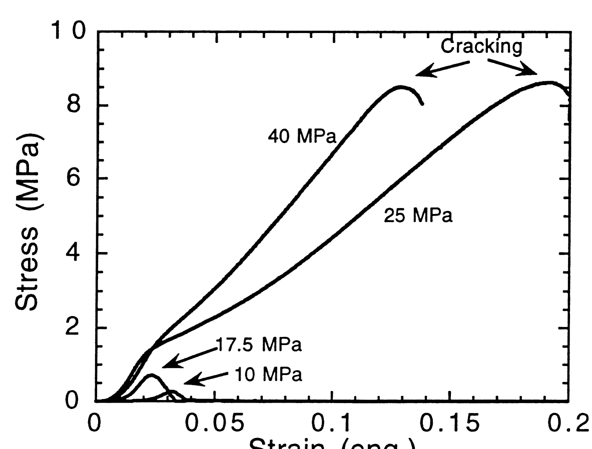

Fig. 6. Effect of increasing consolidation pressure on the mechanical behavior of particles interacting initially with a weak interparticle attraction. The volume fractions of the samples shown are within the narrow range of between 58.3 and 59.0 vol.% solids. The solution conditions are pH 12 with 0.5M tetraethyl ammonium chloride added for all the samples. The data shown is from the initial loading (adapted from Ref. 20).

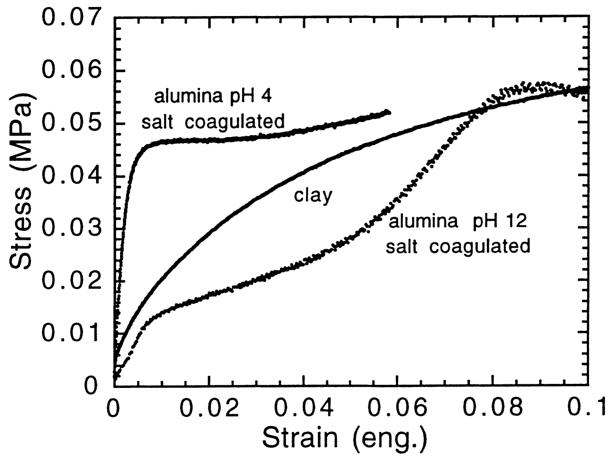

Fig. 7. Stress–strain behavior of clay compared to saturated alumina powder compacts. The pH 4 alumina was coagulated with 3.0M NH_4Cl and consolidated at 5 MPa to produce a body with relative density about 0.55. The pH 12 alumina was coagulated with 0.5M CsCl and consolidated at 10 MPa to produce a body with relative density about 0.55. The data shown for the alumina bodies is from the second loading (adapted from Ref. 11).

important to formulate the slurry to produce a high transition pressure in order to achieve a high relative density.

3.6. Clay-like behavior of alumina

By carefully controlling the parameters discussed above it has been possible to nearly match the plastic behavior of the saturated alumina powder compacts to the commercial throwing clay. Fig. 7 compares the flow stresses of some of the alumina bodies (after initial pre-working beyond 7% strain) to the measured clay behavior. Although it is clear that the mechanical behavior is not identical, the close match is recognized when one looks at Fig. 1 and sees the wide range of mechanical behavior that can be achieved, ranging from flow at less than 0.005 MPa to brittle fracture at over 10 MPa. Although no specific shapes were formed with the plastic alumina bodies, the bodies could be worked by hand and appeared to have the same consistency as the throwing clay. Although the results presented in this paper focus on alumina, it should be noted that plastic bodies with clay-like flow stresses are achievable with zirconia[26,27] and silicon nitride.[28,29]

4. Conclusion

The results presented here show that clay-like plastic behavior is achievable for high performance ceramic powder compacts by prudent choice of the interparticle pair potential formulated in the slurry state, consolidation pressure, volume fraction and particle size. In general, higher flow stresses result from higher volume fractions of particles, smaller particles, greater interparticle attraction and higher consolidation pressures. The clay-like flow stress now achievable in advanced ceramics can be exploited for the plastic forming of complicated shapes using relatively low cost traditional clay processing techniques.

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