Temperature Induced Bridge Flocculation of Aqueous Zirconia Suspensions in the Presence of Polyacrylic Acid

Emad EWAISS, Abbas ZAMAN* and Wolfgang SIGMUND**

Central Metallurgical Research and Development Institute (CMRDI), P. O. Box 87, Helwan, 11421 Cairo, Egypt
*Department of Chemical Engineering and Engineering Research Center for Particle Science and Technology, University of Florida, 311MAE, Gainesville, FL 32611-6905, USA
**Department of Materials Science and Engineering, University of Florida, 225, Rhines Hall, Gainesville, FL 32611-6400, USA

Temperature-induced bridge flocculation of aqueous zirconia suspensions in the presence of polyacrylic acid (PAA) has been studied. The viscosity (20 vol%) of zirconia suspensions with different concentrations of PAA as a function of temperature was measured. The results showed that the viscosity of the suspension in the absence of PAA suddenly increased with increasing temperature above 35°C due to the depletion of zirconium and yttrium cations. In contrast, heating the suspension over 45°C in the presence of PAA led to a sudden increase in viscosity, which can be rationalized by considering the increase in the ionic strength of the suspension as a result of leaching of both yttrium and zirconium cations and also the extent of adsorption of the PAA on the suspension particles. To confirm the bridge flocculation or gelation of the zirconia suspensions in the presence of PAA, viscoelastic measurements in terms of complex, storage and loss moduli (G” and G’ and G”, respectively) as a function of temperature were studied. Preliminary tests on temperature-induced bridge flocculation of high solid suspension (40 vol%) in the presence of PAA were also carried out. It was found that with increasing the temperature up to 85°C, the height stability of the samples reached to an optimum level and no deformation was detected. To reach the optimum stability for the samples at lower temperatures, the polymer dosage must be increased. G”, G’ and G” of high solid suspensions (40 vol%) were measured to evaluate the gel formation. The abrupt changes of G’ and G” values from <50 kPa to about 300 kPa were taken to indicate the formation of gel-like stable solids. (Received July 13, 2001; Accepted March 25, 2002)

Key-words: Zirconia, Temperature-induced bridge flocculation, Polyacrylic acid (PAA), Rheology, Height stability

1. Introduction

Advanced ceramic materials have become, in recent years, one of the main materials for integrating parts of different industries, such as automotive, electronic, defense and machining industries. They have a greater degree of resistance to corrosion and wear than do traditional materials.

Different stages of production of the ceramic objects must be controlled and developed. Forming, as one of the most important stages of production, has a significant impact on the productivity and economics of the ultimate product specifications. The main aim of developing forming techniques is to maximize the bulk density of the green body and to produce near-net shape parts.

Direct casting and solid free fabrication (SFF) were introduced as a useful approach for ceramic green body forming processes via a colloidal suspension. Different mechanisms depend on how the dispersed powder can be stabilized. Electrostatic or steric mechanisms were often used for dispersion stabilization. Aqueous ceramic suspension using water-soluble polyelectrolytes has received much attention for many years in colloidal processing for fine ceramics not only to due to the advantages in dispersion control but also because of ecological requirements.

Studies performed on different mechanisms of gelation of aqueous ceramic suspensions revealed their dependence on the methods of stabilization. Temperature-induced forming (TIF) as a well-known mechanism for gelation of the well-stabilized dispersed suspension has been successfully applied to alumina suspension. This mechanism depends on the variation of material stability with temperature to initiate gelation. A recent work revealed that the dispersion with a low molecular weight polymer is effective at room temperature. However, increasing the temperature necessitates the addition of a high molecular weight polymer to replace the low molecular weight one. The polymer concentration is maintained below the necessary level for stabilization and the gelation will occur through bridging flocculation.

The aim of this work is to evaluate the temperature-induced bridge flocculation of an aqueous zirconia suspension in the presence of PAA.

2. Experimental procedure

An aqueous suspension containing 40 vol% powder with 0.4 mass% (on powder basis) tri ammonium citrate (TAC, Aldrich) was prepared. The quantity of the dispersant was deemed to be sufficient to reach a well-dispersed medium and high solids loading (40 vol%) based on our previous work.

The zirconia powder (zirconia-TZ-3Y) was supplied by Tosoh Corporation (Tosoh Ceramic Division, NJ, USA). Chemical analysis of the supplied powder (provided by supplier) revealed the following (mass%): min. 94.117 ZrO2, 5.17 Y2O3, Max. 0.005 Al2O3, Max. 0.002 Fe2O3, Max. 0.005 SiO2, 0.021 Na2O and 0.68 ignition loss. The powder contains 5 mass% yttria for stabilization of the tetragonal phase. The powder has a BET surface area of 15.4 m²/g and sinter density of 6.05 g/cm³. The particle size distribution is characterized by D₅₀ = 0.2 μm, D₉₀ = 0.7 μm, and D₅₀ = 5 μm (as measured using the L.S. particle size analyzer). The suspension was prepared by mixing de-ionized water, TAC, and zirconia powder by agitation in a planetary ball mill with a high-purity zirconia grinding ball for a period of 15 min at 15 rpm. The pH of the slurry after preparation was measured as 8.7.

The polyacrylic acid (PAA, Aldrich) used in this experi-
ment has a molecular weight of 50000. For the gelation experiment, the desired amount of PAA was added as a 25 mass% solution in water at pH 9.3. The PAA was dispersed in the slurry by sonification and mixing by strong shaking. The prepared slurries had almost an identical pH of 9.3±0.2. De-airing was performed using a vacuum chamber with slurry under agitation created by a magnetic stir bar.

Rheological measurements of the suspension in terms of viscosity-temperature and viscoelastic behavior were conducted using a Dynamic Stress Rheometer (DSR) and sensor. The flow curve was automatically recorded via a built-in program. The measurements of viscosity as a function of temperature were carried out at a low volume fraction (20 vol%) to avoid the evaporation of water which leads to an inaccurate result. The effects of temperature on the suspension viscosity were determined in the temperature range from 20 to 80°C at a shear rate of 10 s⁻¹. Viscoelastic measurements were performed using a rheometer (boller CVO 120 HR) with a concentric, coaxial cylinder sensor system (C25 mm DIN standard). Complex (G*) storage (G’) and loss (G”) moduli were determined using the oscillatory measurement technique where the frequency and strain were set to be 1 Hz and 0.001, respectively. Preliminary tests for gelation were also carried out as in the previous study.8) The slurries were kept for 9 h, after debubbling, casting in non-porous poly vinyl chloride (PVC) mould and covering by a layer of oil to prevent water evaporation, in an oven at temperatures ranging from 25 to 85°C. The height stability of the samples was recorded as a function of PAA concentration at various temperatures. Its values can be calculated from the height of the sample before and after demoulding using the following equation;

\[
\% \text{Height Stability} = 100 - \left( \frac{h_1 - h_2}{h_1} \right) \times 100
\]

Where \( h_1 \) and \( h_2 \) are the height of the sample before and after demoulding, respectively.

The green body was prepared under the same condition as in the preliminary tests but the slurry was kept constant at 85°C for 9 h (Fig. 1). It was demolded and dried in an oven at 100°C in an electric furnace for 2 h (heating rate: 100°C/h, holding time at 1400°C : 2 h). Density measurement and scanning electron microscopy (SEM) were used to characterize the fracture surface of the green and sintered body.

3. Results and discussion

Colloidal processing has been recognized as a technologically important step in green shape forming techniques for advanced ceramic powders.1)-4) Colloidal systems involving slip, tape and drain casting techniques have been extensively studied.1)-4) The slip casting technique is time consuming and needs much more work to improve its green body strength.10),11) Therefore, a forming technique which contributes toward saving time, the manufacture of a strong and dense near-net shaped green body and enabling the mould to be used several times will be very important from an economic point of view and receive much attention. A key point for forming of the powder via a colloidal process is to make a stable colloidal system with a solid content as high as possible with low viscosity. A mechanism to change the stable colloidal system to gel form is also required. In our previous work,8) a stable aqueous suspension containing 40 vol% powder with 0.4 mass% (on powder basis) tri ammonium citrate was prepared.

Temperature-induced flocculation (TIF) has been identified as one of the mechanisms that has been applied to solidify an alumina suspension.6),7) TIF depends on the variation of material stability with temperature to initiate gelation. At room temperature, the dispersion with a low molecular weight polymer is stabilized while the dissolution with increasing the temperature exchanges the low molecular weight dispersion by high molecular polymer dispersion.

On the other hand, it is well known that dispersing yttrium stabilized zirconia powders in water results in a characteristic shift in the pH of slurry. This is due to the leaching of yttrium and zirconium ions from the solid surface both in acidic and basic medium ranges.12),13) Increased leaching at higher temperatures was reported.14) Therefore, we expect that the use of these properties will help in the solidification of zirconia suspension. In this work, temperature-induced bridge flocculation of aqueous zirconia suspensions in the presence of PAA will be investigated.

The viscosity of zirconia suspension in the presence of PAA as a function of temperature is shown in Fig. 2. It is clear from the figure that the viscosity of the suspension in the absence of PAA decreases slightly with an increase in the temperature from 25 to 35°C due to the decrease in the water viscosity. Above 35°C, it suddenly increases with increase of the temperature. The increase of temperature causes several reactions in the system. Among these, the depletion of zirconium and yttrium cations increases. The concentrations of these cations reached 40 and 170 mg/l, respectively.12),13) This causes the formation of hydroxides.14),15) On the other hand, the temperature also affects the equilibrium concentrations of the species present, which in turn creates a driving force for dissolution of the depleted cations. Thus, the adsorbed citrate molecules must temporarily be removed from the surface. These removed
molecules may form stable complexes with the depleted cations leading to an increase in the ionic strength of the suspension that contributes to raising the viscosity. In addition, the formed stable complexes tend to kinetically accelerate the desorption of citrate. Consequently, the repulsion forces decrease, which in turn increases the viscosity. The figure also illustrates that the presence of the high molecular weights PAA leads to a constancy of the viscosity of the suspension with increasing the temperature up to 45°C. The PAA will adsorb to the surface instead of the desorbed surface citrate molecules. At the pH of the suspension, the polymer coils at the zirconia surface will become progressively more charged leading to intrachain segment-segment repulsions. In addition, the surface-segment binding affinity will decrease as the electrostatic repulsion between the polymer and surface increases. Both effects will cause a chain expansion and the adoption of the "loops and tails" type conformation at the surface leading to the development of an (electro) steric barrier that leads to steric stabilization for the suspension.16) By increasing the temperature of the suspension above 45°C, the chain of the high molecular weight PAA will extend far into the solution. These extend molecules may form a bridged network. Such a network will constrain the solvent and increases the viscosity. In addition, the leaching of both yttrium and zirconium cations can form a stable and insoluble complex as colorless hydrogels, which contribute to the increasing of the suspension viscosity.17),18)

To prove that the mechanism of the flocculation or gelation in the presence of PAA was not solely due to the increase of the viscosity but also due to the bridge or network formation between the suspension particles, the flocculation of the suspension was studied by measuring complex, storage and loss moduli (G*, G' and G'' respectively) of 20 vol% of zirconia suspension with 0.02 mass% PAA (based on solids) as a function of temperature, if there was no difference between G' and G'' of the suspension. This means the suspension did not form a network or bridge between the particles. The results are shown in Fig. 3 illustrates that there is no significant change between G* and G' with increasing temperature up to 45°C. However G* and G' are gradually increased with increasing the temperature from 45 to 80°C while the increasing in G' in the same temperature range did not occur. The increase in G' means that the system behaves elastically with increasing temperature. This indicates and confirms that a bridge or network was formed with increasing temperature and the system behaves like a gel.

The viscosity and viscoelastic measurements as a function of temperature were performed on a low solid loading suspension to minimize the evaporation effect of water. From the above results, the flocculation or gelation of suspension was confirmed but there is no clear way of judging from the rheological point of view whether the gel formed is strong enough or not in particular for a high solid suspension. The preliminary tests for temperature-induced bridge flocculation of a high solid suspension (40 vol%) in the presence of PAA were carried out as described before in the experimental procedure. The dimension of the sample height was taken as a criterion for stability and deformation as shown in Fig. 4. This concept was used in the evaluation of the gel formation and its strength for a high solid suspension.

The correlation of the height stability of the samples and the dosage of PAA at all tested temperatures shows a linear relationship with approximately the same slope in the polymer dosage range from 0 to 0.01 mass% PAA (based on solids), as shown in Fig. 4. However with increasing the temperature up to 85°C, the height stability of the samples reached the optimum stability and no deformation appeared. For the optimum stability of the samples at lower temperatures, the polymer dosage has to be increased. The gel formation should be induced at the minimum content of the polymer dosage to minimize the pore content and enhance the sinterability of the body. Therefore, the temperatures
Temperature Induced Bridge Flocculation of Aqueous Zirconia Suspensions in the Presence of Polyacrylic Acid

play an important role in this case because they contribute to the gel formation.

On the other hand, the viscoelastic behavior of a high solid loading suspension (40 vol%) with 0.02 mass% PAA (based on the solid) in terms of $G^*$, $G'$ and $G''$ was measured as shown in Fig. 5. Because of the preliminary tests described in Fig. 4, the slurry (40 vol%) containing 0.02 mass% PAA (based on solids) was flocculated and had an optimum stability at temperatures above 70°C. Consequently, the presence of rheological values can be used to express the gel stability and its strength. The result shown in Fig. 5 illustrates that there are no significant differences between $G^*$ and $G'$ up to 50°C. However, with further increasing of temperature up to ~55°C, $G^*$ and $G'$ were close to each other but there was a gradual change between the combination of both ($G^* + G'$) and $G''$. With a further increase of temperature abrupt changes of $G^*$ and $G'$ occurred and the differences between their combination and $G''$ become huge where $G^*$ and $G'$ changed from less than 50 kPa to about 300 kPa and $G''$ was less than 50 kPa. The large differences between the combined terms ($G^* + G'$) and $G''$ indicate that the slurry behaves like a solid.

In the present work, a slurry of zirconia with solid loading of 40 vol% was dispersed with 0.4 mass% TAC (based on the solid) and allowed to bridge flocculate with inducing temperature in the presence of 0.02 mass% PAA (based on the solid). The object is easily demolded and is strong enough to be handled. The transition of the fluid slurry to a rigid body does not involve any evaporation of the solvent, as the oil layer prevented it. The development of a rigid body relates to the flocculation of particles by PAA as seen in the reaching of the optimum stability and the increase of the viscosity, $G^*$ and $G'$ with temperature. The dry green body with a high density (3.2 g/cm$^3$) was formed as compared with a typical body produced by Tosoh Corporation using an axial press (2.55 g/cm$^3$) where a sample of 25 g is put uniformly into the cavity of the mold and pressed under 70 MPa pressure and held at the pressure for a period of 30 s.

The fractured surfaces of the green and sintered bodies were characterized using a scanning electron microscope (Figs. 6(a) and (b), respectively). These figures revealed the uniform microstructures without large pores body for green or sintered zirconia compacts.

Figure 7 shows simple perfect-sintered parts formed via the TIBF process. The sintered density of these bodies at 1400°C was nearly the same (6.03 g/cm$^3$) as that of a typical body produced by Tosoh Corporation using an axial press (6.05 g/cm$^3$) which was sintered at a high temperature (heating rate: 100°C/h, holding time at 1500°C: 2h).
There was no cracking or distortion. In addition, the surfaces are very smooth and the objects need not be subjected to any machinability operations.

4. Conclusions

It was concluded from the study of temperature induced bridge flocculation of aqueous zirconia suspensions in the presence of PAA that:

1. Bridge flocculation of the slurry can be achieved by raising the temperature of the slurry above 45°C. This flocculation was found to be affected by two factors:
   1. The leaching of both zirconium and yttrium cations.
   2. The adsorption of the PAA on the suspension particles.

2. The different moduli (G*, G', and G") in competition with preliminary tests can be used as a criterion for the evaluation of gel formation and determine if it is strong enough or not. The range of the change in the values of both G* and G' combined (from 50 kPa to about 300 kPa) with remaining constant G" (<50 kPa), can be taken to indicate the formation of gel like stable solids.

3. This phenomenon can be applied to a novel near-net shape technique; temperature-induced bridge flocculation casting (TIBF) where it succeeded in achieving a green body with high density and homogenous microstructure.

References