Journal of the European Ceramic Society 22 (2002) 2805–2812

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Temperature induced forming of zirconia from aqueous slurries: mechanism and rheology

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Received 8 August 2001; received in revised form 15 March 2002; accepted 24 March 2002

Abstract

Several near-net shape-forming techniques via colloidal process were received a great attention for manufacturing low cost and reliable advanced ceramics. Temperature induced forming is known as a suitable procedure that allows the solidification of aqueous suspension, which produce green parts, with interesting economics and environmental benefits. In the present work, well-dispersed zirconia suspensions in aqueous media were prepared using tri-ammonium citrate (TAC) as dispersant agent. Results of electrokinetics phenomena and rheological properties of the investigated system were used to optimize the content of TAC and to maximize the solid loading. Krieger–Dougherty's model was applied to describe the relation between relative viscosity of the dispersion and volume fraction of the solids in this system. Consolidation mechanism of the 40-vol.% zirconia suspensions in aqueous media was studied using temperature induced forming technique. The consolidation conditions were evaluated via measuring of viscoelastic functions of the sample, storage modulus (G′) and loss modulus (G″) as a function of temperature at frequency of 10 s^{-1}. To confirm the gel formation, the heights of the moulded samples were measured at different temperatures after keeping the mold in the oven for 14 h at the desired temperature. The obtained green body by this technique was characterized in terms of density and microstructure.

Keywords: Microstructure-prefiring; Rheology; Suspensions; Temperature induced forming; ZrO_2; Shaping

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1. Introduction

The manufacturing of advanced ceramics is a complex operation because it requires several steps with careful control to achieve its ultimate product performance. Advanced ceramic materials should have a microstructure characterized by a small defect size, and well distributed homogeneous grain boundary composition in order to obtain optimal performance and high reliability. In order for a product to attract the attention of manufactures with high productivity, advanced ceramic can be formed in a near-net shape. This eventually minimizes machining and surface finishing. For mass productions of advanced ceramics, high productivity with minimum cost must be fulfilled especially when shareholder value dictates the market. Forming technique impacts directly the productivity, the ultimate quality and cost of the manufactured products.

In recent years, the colloidal processing has been recognized as a technological important route of green shape forming for advanced ceramic powders.[1–4] Much progress has been introduced to produce all many types of engineering ceramics. The forming of ceramic green body via colloidal process as slip, tape and drain casting were reported.[1,3,5] The slip casting technique still requires much more times and needs improving the strength of the green body.[6,7] Because of the importance of the reliability, productivity, fabricatability and economy, several near-net shape forming techniques were recently developed and studied i.e. gel casting, direct coagulating methods, short-range steric force or salt induced plasticity and temperature induced forming.[1,8–14]

A successful colloidal process of the advanced ceramic powder requires an accurate control of both the rheological properties and colloidal stability. The objective

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0955-2219/02/$ - see front matter
PII: S0955-2219(02)00060-2

of this work is to study the rheology and consolidation mechanism of the zirconia suspensions in aqueous media using temperature induced forming.

2. Experimental procedure

2.1. Materials

Zirconia powder (Zirconia-TZ-3Y) used in this work was obtained from Tosoh Corporation (Tosoh Ceramics Division, NJ, USA). The powder contains 5 wt.% yttria for stabilization of the tetragonal phase. Chemical analysis of the powder (provided by supplier) is given in Table 1. The powder has a BET surface area of 15.4 m^2/g and a sinter density of 6.05 g/cm^3. Their particle size distribution is characterized by $D_{10} = 5$ μm, $D_{50} = 0.7$ μm and $D_{90} = 0.2$ μm (as measured with L.S. particle size analyzer). Tri-ammonium citrate (TAC) was used as dispersing agent (supplied by Aldrich).

2.2. ζ-Potential measurements

Electrokinetic studies were performed on two sets of zirconia suspensions (2 vol.%) prepared in ultra pure water and in a solution of TAC containing 0.4 mg/(g solids) of tri-ammonium citrate respectively. The pH of the first and second set of samples was adjusted to different values from 1.5 up to 9.5 using Fisher brand HCl and NaOH, respectively. Samples were prepared by planetary ball milling with high-purity zirconia grinding balls for 15 min at 150 rpm. Zeta potential measurements were carried out using an Acoustosizer^{TM} instrument. The sample was loaded into the cell of the instrument and multiple measurements of the zeta potential of the particles were made at room temperature (25 °C).

2.3. Rheological characterization

2.3.1. Rheological measurements

The rheological properties of the samples at different volume fraction of the particles were determined using a Paar Physica UDS 200 rheometer with a cone-and-plate geometry. Experiments were performed at different temperatures. The sample temperature was controlled within ±0.1 °C using water as the heat transfer fluid. In all experiments, a cone of radius 4.30 cm with a cone angle of 0.5° (a gap size of 25 μm) was used. The possibility of sedimentation of the particles and water evaporation from the samples during experiments were examined by performing viscosity measurements as a function of time at a fixed shear rate. Also a cone of radius 3.75 cm with a cone angle of 1.0° (a gap size of 50 μm) was used to check for other possible errors (e.g. inertial and secondary flows, edge effects, etc.). The results did not change over the time period of experiments and the viscosity values measured with two different cones agreed within experimental error (±3%).

The dependence of shear viscosity on dispersant dosage was studied using dispersions of 35 vol.% zirconia particles prepared over a range of TAC dosage from 3 mg/(g solids) to 10 mg/(g solids). Effect of solids loading on shear viscosity was studied using samples of volume fractions ranging from 5 to 45 vol.%. These samples were prepared at a pH of nearly 9 using 4 mg/(g solids) of TAC and then milled using the above mentioned procedure. Temperature dependent viscosity was measured with mechanical seals and an oil layer on top of the slurry to prevent evaporation.

2.3.2. Theoretical background

The mechanism of gel formation between cations and citric acid has been reported in the literature[15,16] to be a complex reaction. At high pH levels, protons will be released from the alcohol groups of citric acid, which causes coordination of CA with yttrium ions. By inducing temperature, CA-Y complex undergoes a gel-like structure and one of the advantages of this gel is that dehydration is not accompanied by crystallization.

Tri-ammonium citrate has been extensively used for dispersions of alumina in water.[9] However, its influence on stability and fluidity of zirconia suspensions has not received much attention. One of the objectives of this paper is to discuss the consolidation behavior of zirconia slurries by complexation of cations with the dispersing agent (TAC) as a novel method for temperature induced forming technique. The key point of this process is to have a better understanding of the rheological behavior of the slurry to be able to control stability and fluidity of the system particularly at high solids loading. Also, optimal conditions for gelation to consolidate the slurry needs to be identified. A number of factors such as molecular weight and molecular structure of the polymer, charging effect, ionic strength, adsorption density and thickness of the adsorbed layer have been realized to affect the rheological behavior of electrosterically stabilized colloidal dispersions.[17] To be able to fully control the stability and rheological properties,

Table 1
Chemical analysis of tosoh zirconia powder (TZ-3Y)

	ZrO_2	Y_2O_3	Al_2O_3	Fe_2O_3	SiO_2	Na_2O	L.O.I
Wt.%	Min. 94.117	5.17	Max. 0.005	Max. 0.002	Max. 0.005	0.021	0.680

proper evaluation of suspension stability was reported in earlier publications.[3,8] Rheological behavior of the system can give some insight into the interaction between particles, the polymer, and the media. Furthermore the strength of the interactions can be estimated with information at various shear rate conditions. In particular, if an appropriate model can represent the data, the evaluation may be more convenient and effective. Several models have been developed that can be applied to describe the relation between relative viscosity of the dispersion and volume fraction of solids in the system.[18,19] One of the well-known correlations is Krieger–Dougherty's model which can be written as

$$\eta_\mathrm{r} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta\,]\phi_\mathrm{m}} \tag{2}$$

where η_r is the relative viscosity of the suspension with respect to the suspending fluid at a given shear rate, ϕ is the volume fraction of solids, $[\eta]$ is the intrinsic viscosity of the suspension, and ϕ_m is the maximum packing fraction of solids.

In this work we can applied rheological characterizations to (1) identify the optimal concentration of the dispersing agent to maximize the solid loading, (2) estimate the maximum packing fraction by fitting the relative viscosity-volume fraction data to Krieger–Dougherty model, and (3) confirm temperature induced gelation through measurements of viscoelastic parameters of the slurry (storage modulus G′ and loss modulus G″) as a function of temperature.

2.4. Qualitative method for gelation test

The slurries after sonication and de-bubbling were cast into a nonporous PVC mould and then were covered by a layer of oil to prevent water evaporation. The samples were then placed in an oven at different temperatures ranging from 25 to 85 °C for 14 h at each temperature. The height of the sample was measured before and after demoulding.

The stability of the samples can be calculated from the height of the sample before and after demoulding using the following equation

$$\%\text{Height stability} = 100 - \left(\frac{h1 - h2}{h1}\right) \times 100 \tag{1}$$

where $h1$ and $h2$ are the height of the sample before and after demoulding, respectively.

2.5. Green body preparation

The forming process is described in Fig. 1. First, the zirconia powder and dispersant were added to deionized water, ball milled for 15 min. The slurry after sonification and degassing were cast into nonporous plastic or PVC mould, then covered by oil to prevent drying and placed into an oven. After keeping at 85 °C for 14 h, the sample was demoulded and the height of the wet green body was measured. After drying the samples, the density and SEM in term of fracture surface were characterized.

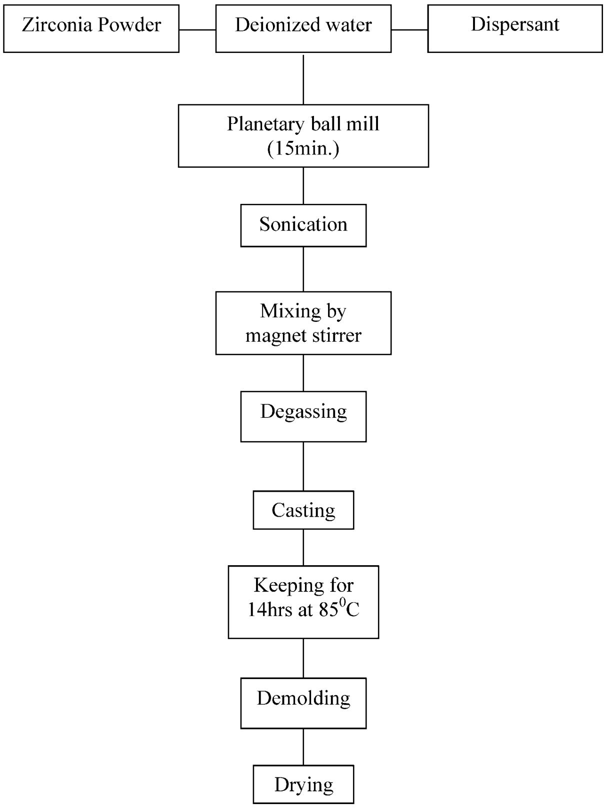

Fig. 1. Flow chart of shaping process.

3. Results and discussions

3.1. Electrokinetic studies

Well-dispersed aqueous dispersions can be achieved by dispersing the powder in an aqueous medium having a pH adjusted far away from the point of zero charge.[20] This should ensure sufficient electrostatic stabilization from the development of charge onto the surface of solids. The results reported here are for aqueous dispersions of zirconia particles using TAC as a dispersing agent. An interesting feature about this system is that the isoelectric point for zirconia (in the absence of dispersant) is in the pH range of 9–10. As the pH of the suspension is increased from a value of 3 to a value of 10, the surface charge of zirconia will change from a positive to a negative value. In this pH range, TAC will change from an effectively uncharged state to a highly negative charge, resulting conditions at which the polyelectrolyte and surface can either have an electrostatic attraction at low levels of pH or an electrostatic repulsion at high pH levels.

The variation of zeta potential of zirconia as a function of pH is shown in Fig. 2. It is clear that the ζ-potential of ZrO_2 in the absence of TAC did not exceed −5 mV in the pH range of 9–11 where the ζ-potential of ZrO_2 in the presence of TAC retained a high negative value of nearly −35 mV over a pH range of 7–10.8. It was also observed that the IEP shifts from a pH of 9.8 in the absence of TAC to a pH value of 4.9 in the presence of TAC. Stable aqueous colloidal dispersions of ceramic powders can be achieved through the generation of highly charged surfaces which can be achieved by adjusting the pH far away from the isoelectric point that will result in a strong double layer repulsion. In the case of zirconia suspensions with TAC as a dispersing agent, highly negative potential was achieved in the alkaline medium range and therefore, it is preferred to prepare the dispersions at higher pH levels.

3.2. Rheological behavior results

3.2.1. Variation of viscosity with TAC dosage

The effect of dispersant agent on the rheological properties of suspensions is attributed to the charges on the adsorbed polyelectrolyte molecules. The adsorbed polyelectrolyte molecules induce a combination of electrostatic and steric repulsive forces between the suspended particles and consequently affect the viscosity behavior of the system. The effect of dispersing agent dosage on the viscosity of zirconia suspensions of 35 vol.% is shown in Fig. 3 which presents plot of viscosity as a function of shear rate at different concentrations of the dispersant agent (25 °C and pH 9.3±0.2). It is observed from this figure that at all levels of TAC dosage, the sample exhibited a strong shear thinning behavior at intermediate shear rates followed by a tendency to Newtonian plateau at higher shear rates values.

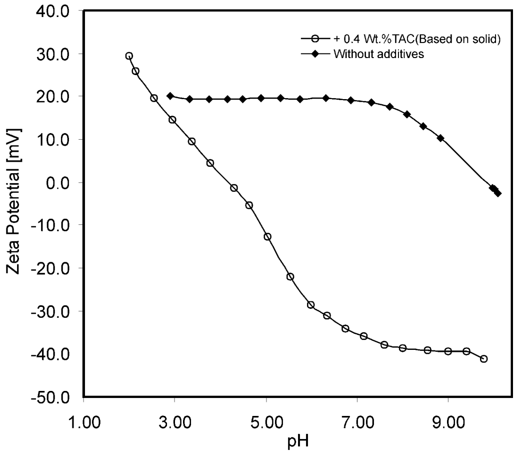

Fig. 2. The variation of zeta potential of zirconia suspension as a function of pH.

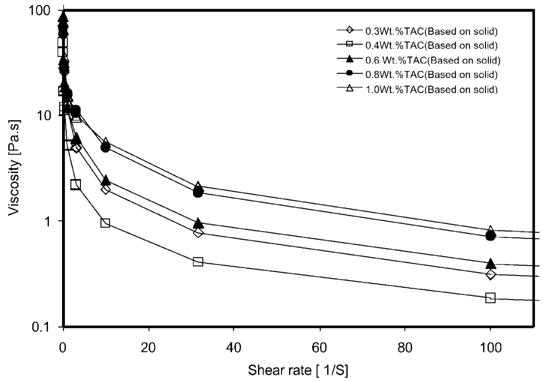

Fig. 3. Viscosity of zirconia suspension with different concentrations of TAC as a function of shear rate.

Fig. 4 represents the viscosity data as a function of the concentration of TAC at a shear rate level of 10 s^{-1} for suspensions of zirconia particles at 35 vol.%. As can be observed, there is an initial decrease in the viscosity of the dispersion with an increase in TAC concentration up to 0.4 wt.% (based on dry solids). The data presented in Fig. 4 indicate that the viscosity of the dispersion increases with further increase in TAC concentration. The higher viscosity of suspension can be explained in view of insufficient electrostatic repulsion forces to overcome the Van der Waal attraction force at lower concentrations of dispersant than 0.4 wt.%. As the surface coverage of adsorbant increases, the repulsion forces increases accordingly and eventually, attains a level that is strong enough to overcome the Van der Waal forces.[21] At this coverage level (0.4 wt.% TAC), the suspension is dominated by repulsive forces, thus it is stabilized, consequently the viscosity decreased. While the further addition of TAC leads to the increase of viscosity due to this excess amount of TAC, which does not adsorbed on the surface and therefore the high electrolyte content

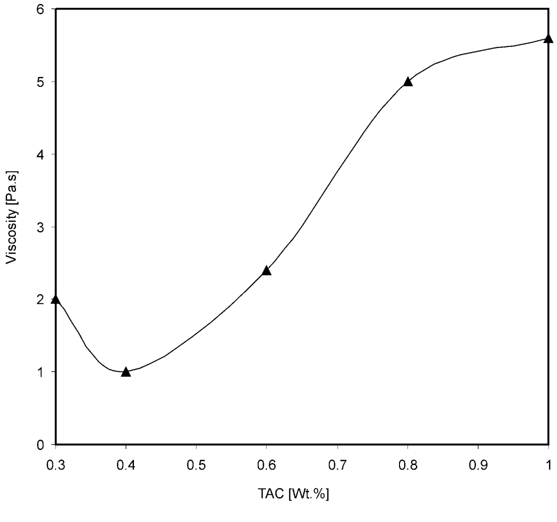

Fig. 4. Viscosity of zirconia suspension as a function of TAC concentration at shear rate 10 s^{-1}.

causing compression of the double layer and the surface-to-surface distance becomes smaller, consequently weaker repulsion obtained.[21]

According to the above results, the well-dispersed suspension can be prepared from the addition of 0.4 wt.% TAC.

3.2.2. *Effect of solid loading*

Using dispersions of higher solid loading in preparation of ceramic green body has a very important role on the quality of the ultimate products. The higher the solid loading, the lower the liquid content of the slurry which in fact will lead to a green body of higher packing factor or higher density which also minimizes the shrinkage of green body. This is only possible if the sample at high levels of solid loading maintain its stability against sedimentation and aggregation of the particles with acceptable viscosity for easy casting.[22]

Fig. 5 represents the viscosity as a function of shear rate and volume fraction of the particles for aqueous zirconia suspensions containing 0.4 wt.% (based on dry solids) dispersing agent. The viscosity shows changes with both shear rate and volume fraction of the particles. Newtonian behavior is observed for volume fractions of up to 20 vol.%. At higher volume fraction of the particles and moderate shear rates, the viscosity falls monotonically with increasing shear rate and does not appear to approach a final limiting value at high shear rates. There is at least three orders of magnitude change in viscosity as the solid loading is increased from 5 to 45 vol.%. It appears that the differences in viscosity at various volume fractions are more significant at low shear rates which is due to the fact that at low shear rates, the interparticle forces are dominant and control the viscosity of the suspension.

Relative viscosity (the viscosity with respect to the viscosity of the suspending fluid) of zirconia suspensions at two different shear rates, 10 and 1000 s^{-1}, are presented in Figs. 6 and 7 which are plots of relative viscosity as a function of volume fraction of the particles. Relative viscosities were defined as a function of volume fraction of the particles employing Krieger–Dougherty's equation. Using this model, relative viscosities at shear rates of 10 and 1000 s^{-1} can be expressed respectively as:

(a) at 10 s^{-1}:

$$\eta_r = \left(1 - \frac{\phi}{0.58}\right)^{(-11.045 \times 0.58)} \tag{3}$$

(b) 1000 s^{-1}:

$$\eta_r = \left(1 - \frac{\phi}{0.62}\right)^{(-7.466 \times 0.62)} \tag{4}$$

The behavior of the suspension changes from a liquid-like to a solid-like as ϕ approaches the maximum packing fraction. Different values have been reported in the literature for the maximum packing fraction of suspensions of monodisperse particles. These results indicate that the maximum packing fraction may change significantly with

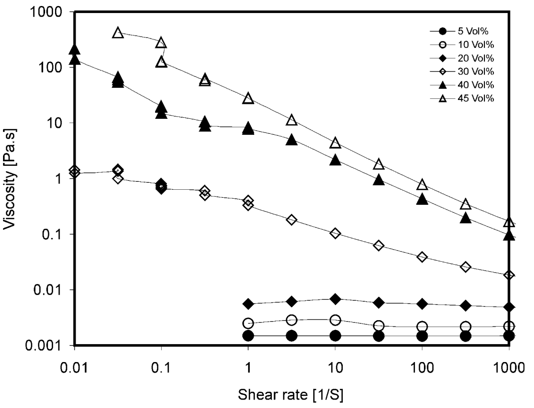

Fig. 5. Viscosity of different volume fraction of zirconia suspensions with 0.4 wt.% of TAC (based on solid) as a function of shear rate.

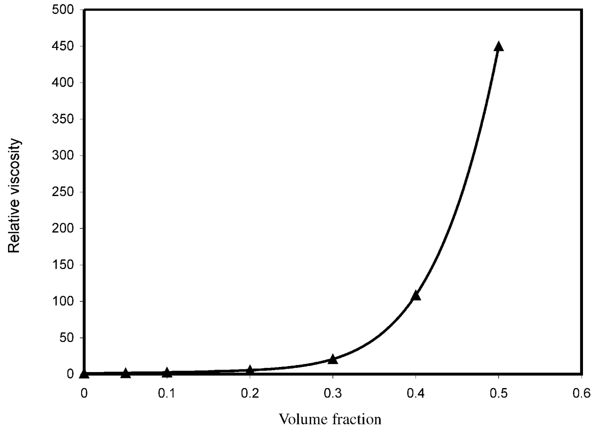

Fig. 6. Relative viscosity of zirconia suspension as a function of volume fraction at 1000 s^{-1}.

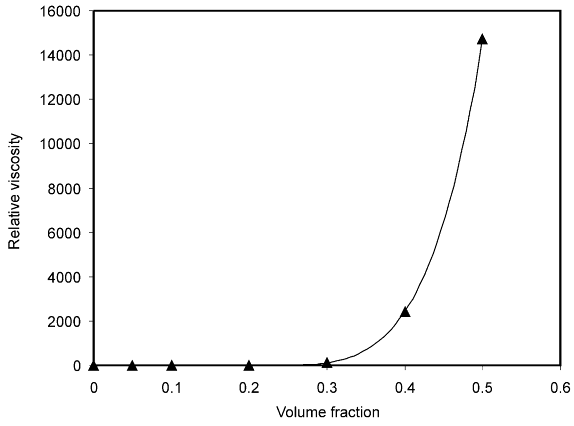

Fig. 7. Relative viscosity of zirconia suspension as a function of volume fraction at 10 s^{-1}.

purity, shape, relative monodispersity of the particles, and the level of accuracy of experiments. Even different models may predict different values for the maximum packing fraction of the same system. The maximum packing fraction, ϕ_m, appears to be shear-rate-dependent, and an increase in ϕ_m with increasing shear rate is due to the fact that particles pack more closely under shear.

The calculated values of $[\eta]$ for suspensions of zirconia particles using Krieger–Dougherty model gives much larger values than the theoretical one of $[\eta]$ for suspensions of spherical particles equals the value of 2.5. It is known that the intrinsic viscosity of suspensions is affected by the shape and surface roughness of the particles and since in our system, the zirconia particles are not exactly spherical, therefore we believe that this may be a reason for the high value of the intrinsic viscosity of the suspension. Additionally, the polydispersity of the samples as well as surface roughness may also be responsible for the high intrinsic viscosity. The data presented in Figs. 6 and 7 indicate that the effect of solids loading on relative viscosity of the system increases rapidly as the solids loading is increased above 40 vol.% meaning that preparation and handling of the suspension will be difficult at higher levels of volume fraction of the particles. Therefore, in this work it was decided to prepare the green body ceramic suspension at 40 vol.% to avoid difficulties associated with highly viscous samples.

3.3. Temperature induce gelation

The effect of temperature on shear viscosity of a 40 vol.% zirconia suspension at a shear rate of 10 s^{-1} is shown in Fig. 8. The data presented in this figure indicate that change in viscosity with temperature is not significant (slight increase) for temperatures up to 47 °C. However, there is a big jump in viscosity in the temperature range of 47–50 °C indicating changes in the structure of the suspension. Since a layer of oil was used to cover the samples around the cone and prevent evaporation of water from the sample, we do not believe that this structural change is due to possible increase in solid loading due to the loss of solvent at high temperature.

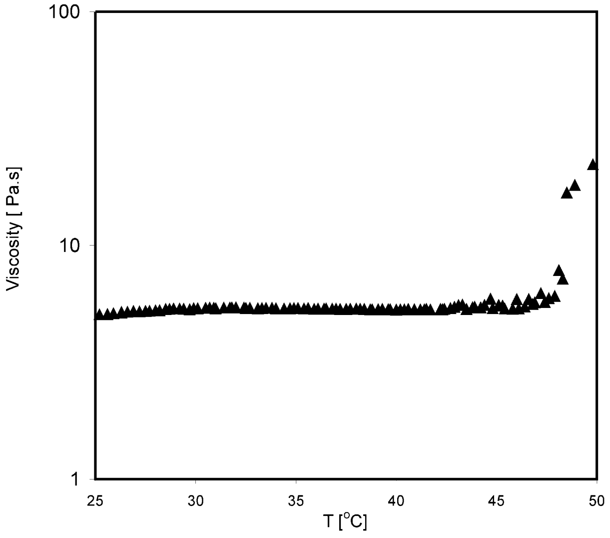

Fig. 8. Viscosity of 40 vol.% zirconia suspension as a function of temperature.

In order to come up with a possible explanation for this phenomenon, the viscoelastic functions of the sample, G′ (storage modulus) and G″, (loss modulus) were measured as a function of temperature at a frequency of 10 s^{-1}. These data are presented in Fig. 9 and as can be observed, the behavior is quite similar to the shear viscosity of the suspension. There is a change in the slope of G′ and G″ versus temperature confirming structural changes that was observed from shear viscosity measurements. The most possible explanation for increase in viscometric function of the suspension is temperature induced gelation causing network formation in the system which is accompanied with an increase in the shear viscosity and viscoelastic functions of the sample.

Another method that was employed to confirm the temperature induced gel formation in the sample was to measure the height of the moulded sample at different temperatures after leaving the mold in the oven for 14 h at a given temperature. The height stability of the samples of 40 vol.% as a function of temperature is presented in Fig. 10. It can be observed that the height stability of the samples is not significant as the temperature is raised up to 47 °C which is due to the low viscosity of the sample. Above this temperature the height stability increases with temperature reaching 100% at 85 °C. The results observed using this method with that obtained from rheological measurements confirm the temperature induced gel formation and can be applied to consolidate the zirconia suspension in aqueous media and in turn can be used to produce ceramic green parts.

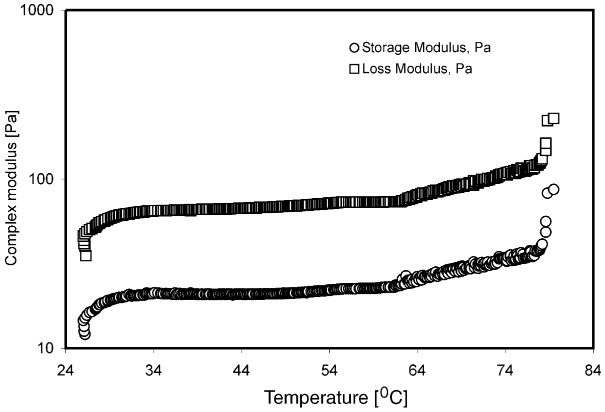

Fig. 9. Complex modulus of 40 vol.% of zirconia suspension as a function of temperature.

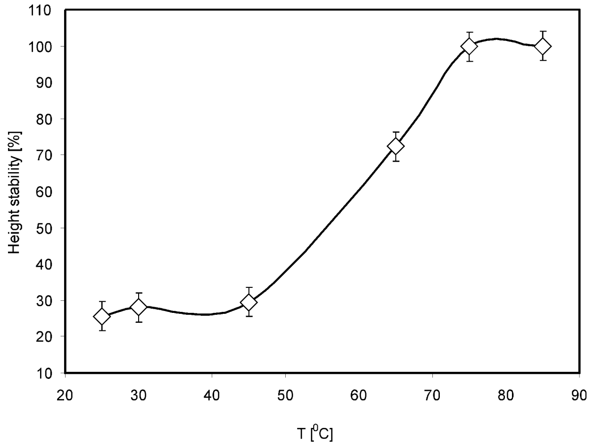

Fig. 10. Height stability percentage of 40 vol.% zirconia suspension in aqueous medium as function of temperature with soaking time 14 h.

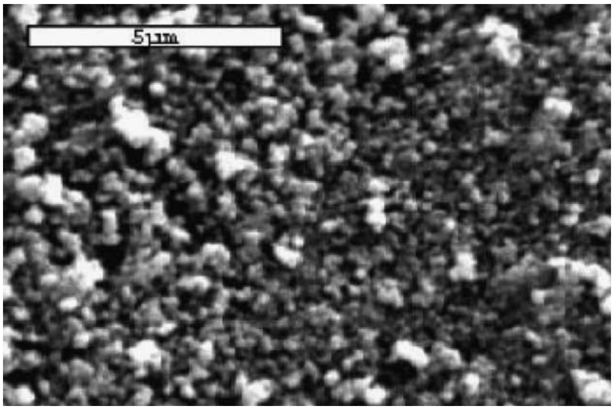

Fig. 11. SEM of fracture surface of green zirconia compact.

3.4. Characterization of the green body

The dry green body with high density (2.75 g/cm^3) was made in comparison with typical body produced by axial press (2.55 g/cm^3). The enhancement in density of this body produced via this technique is due to its high compaction and uniform without pores. The increasing in the density of the green body was confirmed by studying its morphology through SEM in term of fracture surface as shown in Fig. 11. The figure revealed high compaction and uniform body green without pores.

4. Conclusions

The present work proved that it is possible to obtain rather dense ceramic green parts from zirconia with homogeneous microstructure. This ceramic part was obtained via temperature induced forming from aqueous zirconia slurries. The obtained ceramic part by this technique has rather dense comparing with typical pellet produced by uniaxial pressing.

Studies of the electrokinetic phenomena and the rheological behavior of this system has allowed to determine the optimum content of dispersant (TAC), which gives well dispersed zirconia suspension in aqueous media. The optimum conditions were found to be 0.4 wt.% (based on solid) of TAC at 25 °C and at pH 9.3±0.2. The application of Krieger–Dougherty's model on the system illustrated that the maximum solid loading to prepare green ceramic parts to avoid difficulties associated with high viscous samples is 40 vol.%.

The optimum temperature to gel this system is 85 °C for 14 h. The consolidation mechanism is due to a temperature induced gelation causing network formation in the system that is accompanied by an increase of both the shear viscosity and viscoelastic functions of the suspension.

The density of the green zirconia parts made via this technique is as high as 2.75 g/cm^3, which are much higher than typical parts produced by axial press (2.55 g/cm^3). The higher density of the parts may be explained due to the high compaction and uniform body green without pores as revealed from SEM observations.

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