A novel prediction method for preparation and microstructure developing of zirconia ceramics by colloidal processing

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ABSTRACT

A novel prediction method for preparation and design of dense, homogeneous and high mechanical properties with microstructure developing of Zirconia nano-composites by colloidal processing was investigated and developed. Electroacoustic technique called "Electrokinetic Sonic Amplitude" (ESA) used to measuring stability and zeta potential of highly solids concentrated zirconia suspensions. The results gave good correlation between started powder characteristics, colloidal processing properties, stabilized rheological properties, pH and zeta potential of optimum cast slips with maximum solid loading of 77wt% with homogeneous and dense microstructure of zirconia nano-composites.

INTRODUCTION

Many recently developed ceramic processing techniques including spray drying, slip casting, pressure casting, tape casting and gel casting employ well-dispersed suspensions with very high levels of solid loading. For such type of forming processes, it is critical that the process engineer be able to increase the solid loading in the slurry to as high a level as possible. In addition, high solids loading reduce the shrinkage during drying and firing and increase the green strength. However, with increasing solid loading, processing of a suspension becomes increasingly difficult. Good dispersion at high solid loading is not only necessary but also pre-requisite for all slurry based forming processes. The dispersion quality of ceramic suspensions, prior to the forming process, therefore, must be controlled satisfactorily in order to maintain high standard of manufacturing and to obtain consistent/reproducible products. The dispersant screening process usually starts at low solids loading using either sedimentation or light scattering to determine the degree of dispersion of the particles in the solvent. However, studies need to be carried out at higher solid loading since it has been shown that a dispersant that provides the same at low solids concentration may not necessarily provide good dispersion at high solids concentration [1]. Many new techniques are now available to characterize the dispersion quality of suspensions. These include the rheological, sedimentation, adsorption, electrophoresis and charge quantity measurements. Rheology is perhaps the most frequently used probe to determine the agglomeration properties of concentrated ceramic powder suspensions. Rheology may also be used as an analytical tool for determining the optimum viscosity of suspensions. Usually this means the minimum viscosity for the maximum solids

loading. The improvement in properties is also greatly dependent on the elimination of heterogeneity in the green body that could create flaws, isolated pores, voids and residual stresses [1-5]. From this point of view, the preparation of high dense, homogeneous microstructure with high mechanical properties of zirconia ceramics by advanced colloidal processing i.e. slip casting is studied. In the case of rheology, optimizing the formulation of high concentrated suspensions requires a suitable method for measuring the particle charge, known as the zeta potential.

1. EXPERIMENTAL PROCEDURE

1.1. Rheology

In the present investigation, optimization of rheological properties by measuring viscosity of high concentrated suspensions containing nanometer-sized commercial 3mol.% yttria-tetragonal stabilized zirconia powder with high purity >99.5%; Bulk density 6.05(g/cm^3); Mean particle size (d_{50} <0.6 μm); Specific surface area (by BET)= 16.0 (13.0-19.0) (m^2/g), (labeled TZ-3Y by TOSOH Corp., Japan) up to 77 wt% solid loading were determined by using different amounts of a commercial dispersant which is an alkali-free, carboxylic acid (Dolapix CE64, Zschimmer & Schwartz, Germany) in the range of 0.9wt%-1.6wt% (based on solids)and then with deionized water mixed and blended thoroughly by ball milling (ZrO_2 balls) for 30min to obtain the highly optimum stabilized fluid slips and conditions for colloidal processing of dense ZrO_2 compacts. The rheology of suspensions was characterized and compared by the rotational viscometry (Viscometer Haake, RV1, Germany) based on viscosity. Stability prediction and monitoring and characterization of the electrokinetic behavior of high concentrated suspensions determined by using Electroacoustic (ESA) instrument (which avoids dilutation of suspensions) by measuring directly on the concentrated suspensions, has been studied with the aim of maximizing the solid loading by increasing overall charge on the system using dispersant, and the resulting increase in mutual repulsion.

1.2. 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. ZrO_2 suspensions were prepared at different solids loading from 74, 75, 76 and of 77 wt% with constant amount of 0.9 wt% dispersant. The results observed that the higher solids content has higher green density which in compare will minimize the shrinkage of green body. From this point of view, suspensions with high solids loading of 77 wt% selected and then different amounts of anionic polyelectrolyte from the range of 0.9-1.6 wt% used for a dispersant optimization study and to obtain highly optimum stabilized fluid slips and conditions for colloidal processing of dense zirconia compacts.

1.3. Effect of viscosity

Low viscosity (< 1 Pas) at high solids loading is an important feature of slurries for slip casting. The handling (mould filling) is easier and high stability is provided. Viscosity is strongly dependent on the solids content and the pH value of the suspension. The lower the viscosity at a constant solids content, the higher the stability of the dispersed system. For the slurries of high

solids content (77wt%), slurry viscosity depend on the dispersant concentration. The results observed based on lower viscosity obtained by suspension with 1.4wt% dispersant as an optimum which exhibited Pseudo-plastic (shear-thinning) behavior without thixotropy and compared with the non-optimal suspensions contained 1.0 wt% dispersant. (See Fig.1)

As can be observed, there is an initial decrease in the viscosity of the dispersion with an increase in Dolapix concentration up to 1.4 wt% (based on dry solids). Also the data presented in Fig. 1, indicate that the viscosity of the dispersion increases with further increase in Dolapix concentration. Very high slurry viscosity is observed for dispersant concentration 1.0 wt%. The higher viscosity of suspension can be explained in view of insufficient electrostatic repulsion forces to overcome the Van der Waals attraction force at lower concentrations of dispersant than 1.0wt%. In the region of dispersant concentration 1.3–1.4 wt%, lower viscosity is in the range of 150–200 mPa s at shear rate $\gamma = 50(s^{-1})$. As the surface coverage of adsorbant increases, the repulsion force increase accordingly and eventually attains a level that is strong enough to overcome the Van der Waal forces[7]. At this coverage level (1.4 wt% Dolapix), the suspension is dominated by repulsive forces, thus it is stabilized, consequently the viscosity decreased. While the further addition of Dolapix leads to the increase of viscosity due to this excess amount of Dolapix, which does not adsorbed on the surface and therefore the high electrolyte content causing compression of the double layer and the surface-to-surface distance becomes smaller, consequently weaker repulsion obtained. According to the above results, the well-dispersed suspension can be prepared from the addition of 1.4 wt% Dolapix. The result is consistent with the zeta potential analysis. 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.

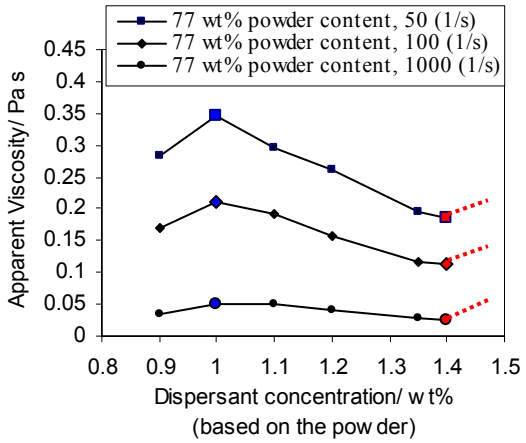

Figure 1. Viscosity of zirconia suspensions at 77 wt% solids loading as a function of Dolapix concentrations at different levels of 50,100, 1000 s^{-1}.

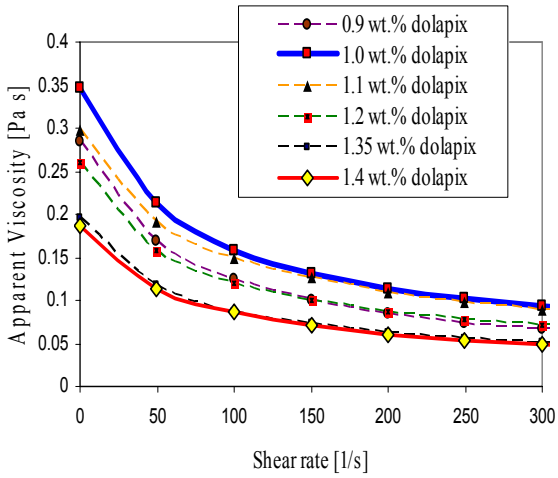

Figure 2. Viscosity of 77 wt% zirconia suspensions with different concentrations of dispersant (Dolapix CE 64), as a function of shear rate.

The effect of dispersing agent content on the viscosity of zirconia suspensions of 77 wt% is shown in Fig. 2, which presents plot of viscosity as a function of shear rate at different concentrations of the dispersant

agent (25 °C and pH 9.1±0.7). It is observed from this figure that at all levels of Dolapix contents, the sample exhibited a strong shear thinning behavior at intermediate shear rates followed by a tendency to Newtonian plateau at higher shear rates values. Two suspensions with maximum 77wt% solid content and different content of polyelectrolyte dispersant, one with (not-sufficient, agglomerate) 1.0wt% content of polyelectrolyte dispersant called suspension (TZ-1.0) and the other one with optimum content of polyelectrolyte dispersant 1.4wt% called suspension (TZ-1.4) were selected and compared by their rheological characteristics based on viscosity. (See Fig. 3, 4) The effect of addition of polyelectrolyte dispersant on the rheological properties of suspensions especially on their viscosity was measured. According to the previous established results by the author H. Sarraf et. al, suspension (TZ-1.0) observed high viscosity (>0.348 Pa s) at shear rate (50 s^{-1}) and exhibit Pseudo-plastic (shear-thinning) behavior with a slight hysteresis (i.e. thixotropy) and suspension (TZ-1.4) observed lowest viscosity (< 0.187 Pa s) at

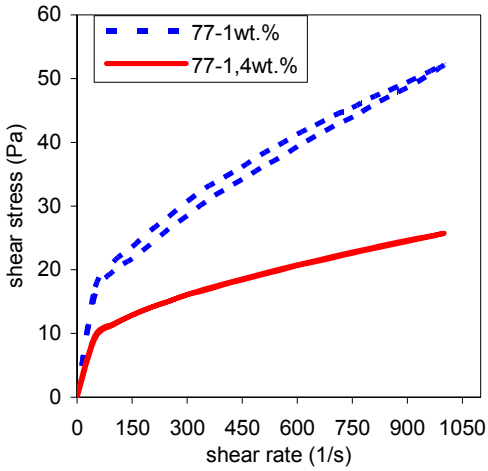

Figure.3. Comparison of Shear Stress (Pa) via Shear Rate (S^{-1})

shear rate (50 s^{-1}), by optimum 1.4wt.% content of polyelectrolyte dispersant exhibit Pseudo-plastic behavior without thixotropy and no-agglomerate. [Figures: 3&4]. The pH value of the slurries was adjusted between 9 and 10 depending on the addition of dispersant.

The flow curves (shear stress τ versus shear rate γ) can be fitted with ostwald-de waele's "Power Low":

$$\tau = K \gamma^{n}$$

Where, the consistency coefficient K attains values of 2.641 and n is 0.433 and 1.8 and 0.36 for the suspensions with 77-1.0 wt% and 77-1.4wt%, respectively.

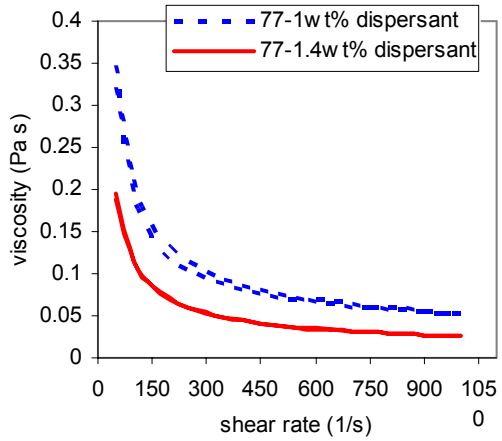

Figure.4. Comparison of Viscosity (Pa s) via Shear Rate (S^{-1})

2. A NOVEL METHOD FOR PREDICTION OF STABILITY

2.1. Electrokinetic studies

We have investigated a novel prediction method for characterization and monitoring of electrokinetic properties of high solid concentrated ZrO_2 suspensions using electrokinetic sonic amplitude (ESA) analyzer. Sarraf et al [6].

The ESA signal is proportional to zeta-potential, and provides a convenient method for determining the polarity and relative

magnitude of charge carried by particles in suspension. In this present work, firstly we have been predicted and decided to study the electrokinetic properties of suspensions at low solids (2vol%) concentrations with two different techniques such as Electroacoustic technique "ESA" applied at a nominal frequency of 1MHz (ESA-8000, Matec Applied Science, USA). The other method which used was laser light scattering technique by Zeta-sizer (Malvern Instrument, UK) and compared both of their results. In the first step, a low concentrated suspensions with 2 vol% solid content (equal to: 12.01 gram mass of powder) was prepared and tested and in the second step, measuring of high concentrated suspensions by 77 wt% solid content and to find out the trend which has influence to change the value of zeta-potential and pH from lower concentrate to high concentrate dispersed suspensions.

2.2. Electrokinetic properties of low concentrated suspensions

The Zeta potential of powder has an important effect on the state of particulate dispersion in suspensions during colloidal processing. A zero Zeta potential is defined as isoelectric point (I.E.P) which is the indicative of uncharged (electrical neutrality) particle surface (balancing of positive and negative sites) that leads to the flocculation of particles in suspension. Higher zeta potential value means a higher charge density on the particle surface which develops a good colloidal stability due to the generation of strongly electrical double-layer repulsive force between equally charged. Two sets of zirconia suspensions (2 vol%) were prepared at a solids concentration of 12.01 wt% in deionized water and containing 1.0 wt% and 1.4 wt% (based on solid content of powder) Dolapix respectively. Samples were mixed for a better dispersing by magnetic stirrer for a 30 min and sonicated for 3 min using a ultrasonic probe. To determine the Zeta potential as a function of pH for the first and second set of samples, the Merck brand 10^{-1} N HCl and 10^{-1} N NaOH solutions were used to adjust pH to the desired values from 2 up to 12 (see Fig 5) shows the Zeta potential of ZrO_2 particles at two different dispersant additions as a function of pH. In the case of ZrO_2 suspensions without dispersant addition, the I.E.P of ZrO_2 particles is at the pH of 9. As the pH of the suspension is increased from a value of 3 to a value of 11, the surface charge of zirconia will change from a positive to a negative value. In this pH range, Dolapix 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 introduction of dispersant results in a higher negative Zeta potential and shifts the I.E.P from 9.0 to 4.8 for suspension TZ-1.0 wt% of Dolapix and to 3.8 for suspension TZ-1.4 wt%. It seems that the changes of Zeta potentials and I.E.P of ZrO_2 particles are caused by the increasing of the charging density of particles which, in turn, is caused by the adsorption of negatively charged anion groups of dispersant on the surface of ZrO_2 particles. Therefore, it is expected that the optimum fluidity of ZrO_2 suspension will be achieved at pH 11. It is clear that the ζ-potential of ZrO_2 in the absence of Dolapix did not exceed −45 mV in the pH range of 10–11 where the ζ-potential of ZrO_2 in the presence of Dolapix retained a negative value of nearly −63 mV for suspension with 1.0 wt% Dolapix and a higher −68 mV for suspension with 1.4wt% Dolapix over a pH range of 7–11. Also the ZrO_2 specific surface area is big, 1.0wt% content of dispersant (Dolapix) was not enough to cover the ZrO_2 powder, and the surface charge of the ZrO_2 was not dominated by the polyelectrolyte but for optimum suspension 1.4 wt% dispersant was enough to cover ZrO_2 powder and the surface charge of the ZrO_2 was dominated by dispersant.

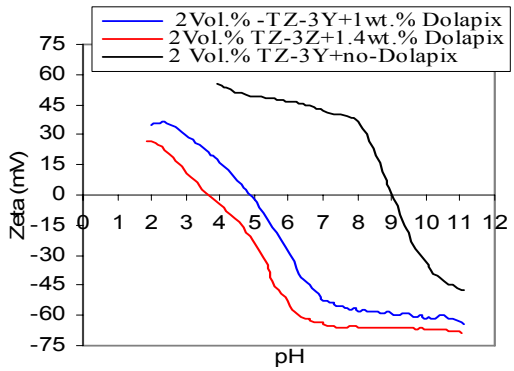

Figure 5. The variation of zeta potential of zirconia as a function of pH.

2.3. ESA Measurements

It is well known that the stability of suspensions increases with increasing ESA, e.g. with increasing surface charge. Therefore, ESA measurements were performed in order to determine the optimal zeta potential and pH conditions of zirconia slurries. As can be observed from Fig.[6] and table.1. ESA value increases by increasing dispersing stability from -5.34 (TZ-1.0) to –5.557 (TZ-1.4) for low concentrated (2vol%) suspensions. However the level changing is small but also by shifting the I.E.P of pure suspension to 3.61 of (TZ-1.4) suspension, dispersing stability is higher, which means increasing surface charge.

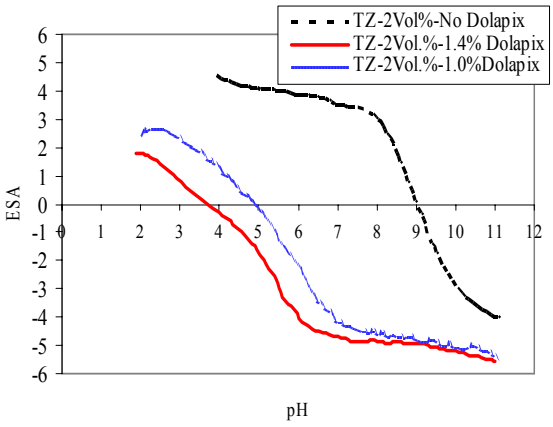

Figure.6. ESA versus pH of low solids concentrated of (2vol%) zirconia suspensions.

Parameters measured by ESA	ESA [m Pa^ V]	I.E.P
2vol%-no-dispersant	-4.028	9.06
2vol%-1.0wt% dispersant	-5.34	4.83
2vol%-1.4wt% dispersant	-5.557	3.61

Table 1. Electrokinetic properties of 2vol% zirconia suspensions based on ESA value and I.E.P.

2.4. Electrokinetic properties of high concentrated suspensions

The electrokinetic properties of high concentrated zirconia suspensions with different contents of dispersant (Dolapix) based on ESA value and zeta-potential have been investigated before by authors Sarraf et al.[6] as shown in tables 2 and 3 and figures 7 and 8. The result observed from ESA for high concentrated suspension with optimum dispersant (TZ-1.4) has higher ESA value and with pH-value = [9.27]. Also it shows that in optimum suspension particles have a high negative zeta potential and means are colloidally stable and provide better colloidal stability with consist of homogeneous structure that are likely to lead to dense and homogeneous slip-cast ceramics. However, as can be observed from results, suspensions prepared from out of this optimum are colloidally unstable and consist of the large agglomerates that are likely to lead porous slip-cast ceramics. All measurements were repeated to check for reproducibility and sample alignment.

77 wt.% solid content of TZ-3Y	**ESA**	**Zeta**
0.9wt.% of dispersant	-10.984	-6.6
1.0wt.% of dispersant	-11.348	-3.3
1.1wt.% of dispersant	-11.806	-7.1
1.2wt.% of dispersant	-11.464	-7.6
1.4wt.% of dispersant	-12.301	-8

Table 2. Electrokinetic properties of 77wt% zirconia suspensions with different concentrations of Dolapix by ESA.

Parameters measured By ESA	ESA [mPa^ V]	Zeta-potential [mV]	PH units
77-1.0 wt%	-11.348	-3.3	9.03
77-1.4wt%	-12.301	-8	9.27

Table. 3. Electrokinetic properties of optimum and non-optimum high concentrated zirconia suspensions with by ESA.

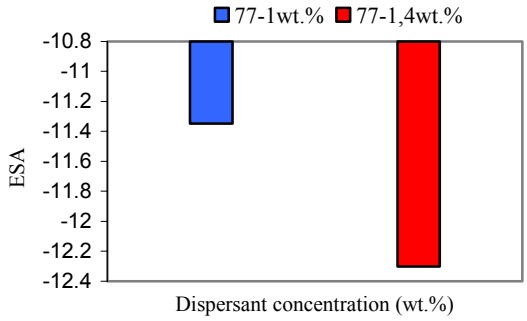

Figure 7. Effect of content of dispersant (wt%) on ESA value.

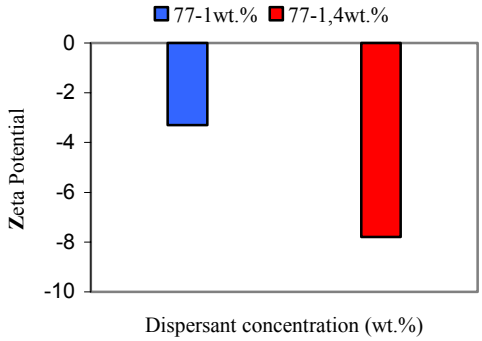

Figure 8. Effect of dispersant agent (wt%) on Zeta Potential by ESA.

3. CHARACTERIZATION OF GREEN BODY

The selective slurries: (TZA-1.0) AND (TZB-1.4) free from foam, applied for shaping of green cylindrical-shaped specimens (with 5x5x60 mm) cast into the plaster molds to achieve high green densities in combination with good homogeneity. The bodies were removed from the moulds and dried at ambient temperature in air for 48h. The relative green densities were measured by the Archimedes technique in Petrol and also were characterized by mercury porosimetry (Poresizer 9320, Micromeritics / USA). 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. 9 and 10. The figure 9 of TZ-1.4 as an optimum sample revealed high compaction and uniform body green without pores, also in comparison by morphology of non-optimum sample by heterogeneous Fig 10. The size and total number of pores in TZ-1.4 are smaller than in TZ-1.0, since the amount of porosity for TZ-1.4 cast sample is smaller (42.91vol%) than in TZ-1.0 (44.5vol%).

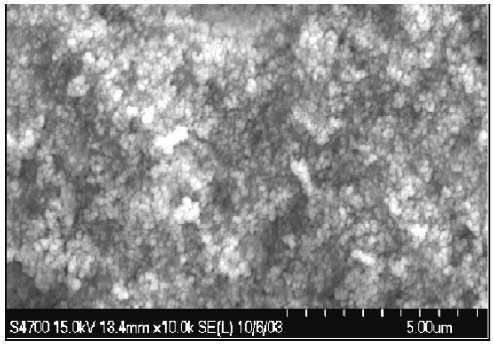

Figure 9. SEM micrograph of uniform, homogeneous green body (TZA-1.4) zirconia sample.

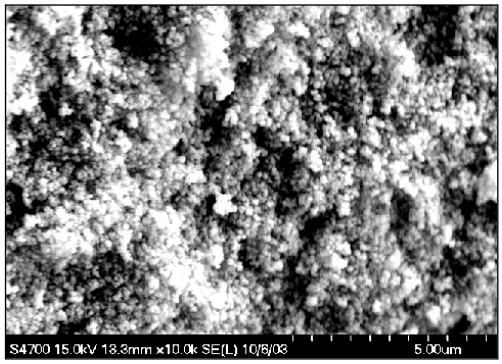

Figure 10. SEM micrograph of non-uniform green body of (TZA-1.0) zirconia sample.

The density of the optimum green zirconia parts (TZB-1.4) made is as high as 3.31 g/cm^3 which are much higher than green density 3.16 g/cm^3 of non-optimum

green zirconia parts (TZ-1.0). The higher density of the optimum sample may be explained due to the high compaction and uniform body green without pores as revealed from SEM observations. Although the relative green densities increased with increased solids content in the slurry, the maximum for suspension with 77 wt% solid content and 1.4wt% dispersant was observed 54.77 wt% of theoretical density, which was higher than the non-optimum suspension of 77 wt% - 1.0 wt% dispersant, about 52.2 wt% TD.

4.SINTERING AND MICROSTRUCTURE EVALUATION

Specimens were sintered at optimum temperature of 1490°c, respectively (by heating rate 2 °c/min, soaking time 120 min). Sintered specimens were then characterized via Archimedes measurements (bulk density) and SEM analysis. Fracture surface of sintered bodies was observed by using SEM (JSM-6301F Scanning Microscope, Japan) to estimate the microstructure uniformity and porosity of the specimens. As can be seen, by SEM micrographs, in the slip-cast TZP-1.4 sample, microstructure is homogeneous but in TZP-1.0 sample, it has heterogeneous microstructure and with grain growth and the formation of porosity.

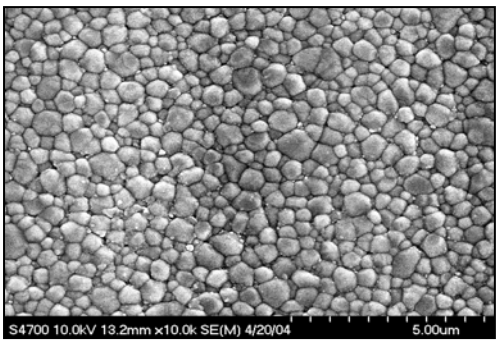

Figure 11. SEM micrographs of the thermally etched surfaces of TZB-1.4 sample sintered at 1490°c. - showing the uniform, dense microstructure, submicron grain size, which is homogeneous and less pronounced residue porosity and lower grains growth.

CONCLUSIONS

It has demonstrated experimentally that the zeta potential of nano-particle sized zirconia powders in highly concentrated aqueous suspensions as measured with the electrokinetic sonic amplitude (ESA) method is statistically identical with the streaming viscosity measured by rheological method. Optimum suspension characterized by rheological method and ESA method has followed the same characteristic and gave good correlation into one another, with reproducible experimental results, respectively. For 77 wt% suspensions, the precision of the measurements by ESA is high but precision of the measurements of zeta potential and pH values are slightly lower. A good agreement between rheology and electroacoustic tests is found which identifies lower viscosity, higher ESA value, optimum concentration of dispersant for promising dispersion. Both rheological (viscosity) measurement and ESA are effective ways to describe the existence state of ceramic powder in high concentrated aqueous suspension, particularly the directly measured pH which can give good evidence of the result of zeta.

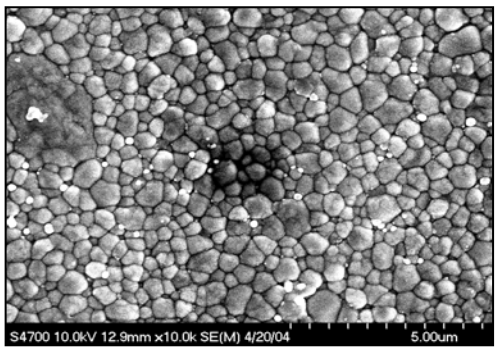

Figure 12. SEM micrographs of the thermally etched surfaces of TZA-1.0 sample sintered at 1490 °c, showing porosity and grains growth.

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