Dispersion of nanosized ceramic powders in aqueous suspensions

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Abstract. Seven commercially available dispersants have been applied to produce high concentrated aqueous suspensions of the nanosized alumina and partially stabilized zirconia powders processed by the plasma technique. Simultaneously, the electrokinetic behaviour of powders has been investigated in diluted suspensions by microelectrophoresis method. Zeta potential measurements are used to estimate the influence of selected dispersants on the electrokinetic properties of the powder surface. On the basis of obtained data the correlation between the surface electrokinetic properties in dilute suspensions and reached maximal suspension concentration is discussed.

1. Introduction
The quality of ceramics produced by wet forming process is strongly influenced by the state of the powder dispersion [1]. A good stability, low viscosity and high solid loading are required to obtain high quality products [2].

Ceramic fine particles have the tendency of agglomeration in aqueous media. In general, aqueous suspensions can be stabilized by controlling the repulsive forces proceed from a charged electric double layer, surrounding the particle (electrostatic stabilization), or from non-charged or charged polymers, adsorbed on the surface (steric and electrosteric stabilization, respectively) [3].

Despite the good knowledge of stabilization mechanisms and the methods to make a well dispersed and stable slip, there is no general stabilization technique applicable for alumina and yttria-dopped zirconia powders. The powder properties, either chemical or physical, can vary significantly depending on powder processing methods [4]. In the present study nanosized alumina and partially stabilized zirconia powders obtained from the vapour phase in the radio-frequency plasma jet have been investigated.

The electrokinetic or zeta potential measurements are used to estimate the electrostatic effect, which is responsible for the repulsive forces between the particles and determines the suspension stability. Particle electrophoretic studies have proved to be useful in many practical situations where colloid stability is involved [5]. Electrophoresis techniques, however, can only be applied to extremely dilute powder dispersions [6]. In this work the attempt is made to correlate the electrokinetic properties determined in dilute suspensions and reached maximal solid loading. Seven commercially available organic surface-active agents are chosen as dispersants.

2. Experimental
Alumina is produced by evaporation of the mixture of commercially available alumina and aluminium powders in the thermal air radio-frequency plasma jet (5400 – 5600 K). Partially stabilized nanosized zirconia powder is produced by evaporation of the mixture of commercially available zirconia, yttria...
and alumina. The plasma processing technique developed at the Institute of Inorganic Chemistry of Riga Technical University is described in detail by Grabis et al. [7,8].

The synthesis products are characterized by X-ray diffraction studies using CuKα radiation. Alumina contains δ- and θ-phases, zirconia – tetragonal (90 %) and monoclinic (10 %) phases. Zirconia contains Y2O3 5.3 and Al2O3 0.3 wt. %.

The specific surface areas are determined by BET low-temperature argon adsorption - desorption method and are 50 and 30 m²/g, correspondingly.

The characteristics of used surfactants are shown in Table 1.

| Surfactant       | Producer     | Chemical characteristic                                                                 |
|------------------|--------------|-----------------------------------------------------------------------------------------|
| Tiron            | Aldrich, USA | a low molecular weight aromatic di-sulfonic acid, anion-active                           |
| Aluminon         | Aldrich, USA | a low molecular weight aromatic tri-carboxylic acid, anion-active                       |
| Tri-ammonium     | Merck, Germany | a low molecular weight aliphatic tri-carboxylic acid, anion-active                       |
| citrate          |              |                                                                                         |
| Atsurf 3315      | ICI, UK      | a modified polycarboxylic acid, anion-active                                             |
| Atsurf 3222      | ICI, UK      | polyalkylene amine derivative, cation-active                                            |
| PAA              | Aldrich, USA | polyacrylic acid, Mw 1200, polyelectrolyte, anion-active                                  |
| KD 7             | Uniqem, UK   | polyacrylic acid-based copolymer (PAA – polyethylenglycol), anion-active                 |

The zeta potential measurements are performed on the Malvern’s Zetamaster S. This instrument includes a heterodyne laser Doppler electrophoresis system to determine the sign and value of the electrokinetic potential.

The zeta potential – pH dependence has been determined by electrokinetic titration method using a computer-controlled system, which combines Malvern’s Zetamaster S, Mettler’s autotitrator DL21 and ultrasonic equipment.

The suspension was prepared by dispersing 500 mg of the powder in 50 ml of water applying the ultrasonic treatment and mechanical stirring simultaneously. After ageing for 72 hours, the sample was subjected to a short ultrasonic pretreatment and 2 ml of the suspension was placed into the titration vessel containing 200 ml of 0.01N KCl solution. Then titration was performed from pH 6 to 11 and 2 with 0.1 N KOH and HCl solution respectively. The isoelectric point (iep) was determined as an intersection point of the titration curve with abscissa.

Concentrated suspensions were prepared step by step by mechanical stirring under ultrasonic treatment and adding small amounts of the surfactant and powder.

3. Results and discussion

The investigated surfactants differently affect the electrokinetic behaviour of plasma-processed alumina and zirconia particles in aqueous suspensions. The changes in surface charge represented by the sign and value of zeta potential are demonstrated in Fig.1 and 2.
Fig.1. Zeta potential versus pH in alumina aqueous suspensions with and without surfactants.

The surface of alumina particles is positive over a wide range of pH. Aluminon and Tiron considerably enlarge the pH region where the surface of alumina is negative and create a high negative zeta potential (~50 mV) in the basic pH range, from pH 7 - 11. The $i_{ep}$ is shifted in the acidic pH region. The displacement of $i_{ep}$ is almost 7 units with Aluminon. The addition of citric acid results in the shift of $i_{ep}$ to pH 4.5, the zeta potential reaching the value of -30 mV at pH 8 - 11.

Atsurf 3315 reduces both the positive and negative value of alumina zeta potential. The reason for this may be the configuration of the polymer chain on the surface and small number of ionogenic groups in the chain segments.

Fig.2. Zeta potential versus pH in zirconia aqueous suspensions with and without surfactants.

The $i_{ep}$ of plasma-processed zirconia is located at pH 7.5 the zeta potential reaching +40 mV and -40 mV in the extremes of pH. In the presence of PAA and citrate the i.e.p. shifts far in the acidic pH range. Zirconia surface coated with citrate is negatively charged in the pH range from 2.5 to 11. PAA creates a high negative zeta potential in the basic pH range, from 6 to 11, the $i_{ep}$ located at pH 2.9.
The addition of KD7 and Atsurf 3222 to the suspension is less effective. It gives the shift of the *iep* to pH 5.5 and 6.0, respectively, and less negative value of the zeta potential.

Table 2 compares the effectiveness of surfactants on preparation of concentrated suspensions. The dispersion medium (pH) and surfactant exert an influence on the solid loading.

As for alumina, comparatively high solid content can be achieved in acidic medium without any surfactant. It correlates with the high zeta potential (+40 mV) and long-lasting stability observed for alumina suspensions in acidic pH range. Tiron (aromatic sulfonic acid) and Aluminon (aromatic carboxylic acid) both have high negative zeta potential in basic pH region, however, maximally attainable solid content differs quite a lot pointing that the molecular structure affects the powder loading. The small highly charged molecules of tri-ammonium citrate ensure the purely electrostatic stabilisation mechanism, while polymer Atsurf 3315 acts through steric stabilization and is less effective than Tiron acting through electrostatic stabilization.

**Table 2.** The maximum of powder loading in Al₂O₃ and ZrO₂ suspensions depending on dispersion medium and used surfactants (~2 wt.% on weight of solid)

| Powder/surfactant | Medium          |                |                |                |
|-------------------|-----------------|----------------|----------------|----------------|
|                   | 0.1 N CH₃COOH   | H₂O            | 0.1 N NH₄OH    | 1 N NH₄OH      |
| Al₂O₃/ -          | 77,1            | 71,0           | -              | 36,0           |
| Al₂O₃/citrate     | 63,4            | 67,9           | 63,5           | 75,3           |
| Al₂O₃/tiron       | -               | -              | -              | 79,2           |
| Al₂O₃/aluminon    | -               | -              | -              | 67,0           |
| Al₂O₃/atsurf 3315 | 73,6            | 74,0           | -              | -              |
| ZrO₂/citrate      | 48,1            | 55,7           | 62,5           | 69,3           |
| ZrO₂/atsurf 3222  | 66,3            | 72,7           | 72,2           | 52,6           |
| ZrO₂/PAA          | 48,6            | 61,4           | 41,9           | 67,5           |
| ZrO₂/KD 7         | 68,6            | 70,7           | 68,6           | -              |

In the case of zirconia the experiments are performed at the whole pH range. The tri-ammonium citrate is more effective in basic dispersion media – the highest powder loading of 69 wt. % is reached in 1 N NH₄OH solution. This result correlates with the zeta potential dependence on pH as presented in Fig. 2.

In the case of PAA the highest suspension concentration is achieved in 1 N NH₄OH solution, i.e., in strongly basic medium. About the same solid loading is recorded in water suspension –weakly acidic medium as zirconia in water suspensions creates pH 3-4 in the bulk solution most likely due to nitrogen oxides on the powder surface (the powder is synthesized in air plasma). The stability of the suspension in the basic medium can be explained by considering a high zeta potential value of the surface at basic conditions. Obviously, electrosteric stabilization takes place in this case while steric repulsion of PAA molecules may be responsible for the suspension stability in weakly acidic medium.
The highest solid contents in suspensions are achieved using Atsurf 3222 and KD 7 as dispersants. The solid content of 70 wt. % and more is reached in water (weakly acidic media) and in 0.1 N NH₄OH solution. The achieved high solid loading is little dependent on acidic or basic character of dispersion medium and anionic (KD7) or cationic (Atsurf 3222) character of the surfactant. It suggests that given surfactants stabilize the suspensions more by steric effect.

4. Conclusions

The results show that the optimal dispersion medium can be found for any surfactant investigated and high solid content can be achieved. The correlation between these results and measured zeta potential values is observed when the repulsion potential is based mainly on the electrostatic repulsion.

As for alumina, the comparatively high solid loading in the medium of acetic acid without a surfactant (77.1 wt.%) correlates with the high positive zeta potential of the particles and long-lasting stability of alumina suspension in acidic conditions. The high solid loading with Tiron in ammonium hydroxide medium (79.2 wt.%) correlates with the high negative zeta potential of the particles in basic conditions in the presence of Tiron.

The absence of correlation indicates that the high molecular weight polyelectrolytes stabilize the zirconia suspensions more by steric effect than by electrostatic repulsive forces. The highest concentrations (up to 70 wt.%) of nanosized partially stabilized zirconia powder in water suspensions can be reached using Atsurf 3222 and KD 7 as dispersants.

The molecular structure of the surfactant and the dispersity of the powder also exert an influence. Tiron gives the better result than Aluminon having alike electrokinetic characteristics. Likewise, the solid loading is dependent on the nature of powders. It is seen if compare reached different solid contents in zirconia and alumina suspensions though the repulsion potential is approximately the same in both cases.

In any case it is vital to have an information of the amount of surface charge present in diluted suspensions and the microelectrophoresis method is quick and reliable enough.

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