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Preparation of concentrated aqueous suspensions from nanosized plasma-processed zirconia powder

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Abstract. Four commercially available dispersants have been compared for their ability to produce high-concentrated suspensions of the partially stabilized nanosized zirconia powder, processed by the plasma technique. Zeta potential measurements are used to study the influence of these dispersants on the electrokinetic properties of the powder surface. The highest solid loading (up to 70 wt%) is achieved using Atsurf 3222 and KD7 as dispersants. The optimal amounts of the dispersant (2–3 wt% of the dry mass of the solid) have been determined by adsorption and viscosity measurements. On the basis of obtained data, the correlation between the surface electrokinetic properties and maximal suspension concentration reached is discussed.

Key words: zeta potential, adsorption, surfaces, surfactants, concentrated suspensions, nanosized zirconia.

1. INTRODUCTION

Slip casting is one of the most common forming techniques, used in fabrication of ceramics. The quality of slip casting products is strongly influenced by the state of powder dispersions [1]. Among other specific characteristics, the powder dispersions have to possess good stability, low viscosity and high solid loadings. The stability of water-based systems depends on the net interaction forces between particles. 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) [2]. The electrosteric stabilization with polyelectrolytes as dispersants is a very effective method, widely applied for the preparation of stable suspensions [3–5].

In the present study the optimal conditions for preparation of high-concentrated suspensions of nanosized partially stabilized zirconia powder, manufactured by the plasma technique, were investigated. Some commercial surface-active agents of high molecular weight were tested as dispersants. The zeta potential of the powder surface was employed to estimate the electrostatic effect, which was responsible for the repulsive forces between the particles and the stability of the suspension. The adsorption isotherms have been determined to find the optimal amount of the surfactant. The same investigations have been performed earlier with plasma-produced alumina [6].

2. EXPERIMENTAL

Partially stabilized nanosized zirconia powder is produced by evaporation of the mixture of commercially available zirconia, yttria and alumina at high temperature (5000–6000 K) gaseous flow. The plasma apparatus for producing fine powders of refractory compounds is described in detail in [7]. Characteristics of the used zirconia powder are shown in Table 1.

The following surfactants are tested: tri-ammonium citrate (a low molecular weight organic compound) and three polyelectrolytes – polyacrylic acid PAA (Aldrich, USA), polyoxyalkylene amine derivative ATSURF 3222 (ICI, UK) and copolymer polyacrylic acid – polyethylenglycol KD7 (Uniqem, UK).

The zeta potential – pH dependence has been determined by electrokinetic titration method using a computer-controlled system, which combines the Malvern Zetamaster S, Mettler DL21 autotitrator 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 h, 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 0.01 N KCl solution. Then titration was performed with pH from 6 to 11 and 2, for 0.1 N KOH and HCl solution, respectively. The isoelectric point (IEP) was determined as an intersection point of the titration curve with the abscissa.

Table 1. Characteristics of the used zirconia powder

Powder characteristic	Value
Content of yttria, wt%	5.3 ± 0.3
Content of alumina, wt%	0.3 ± 0.1
Specific surface area, measured by the BET low-temperature argon adsorption-desorption method, m^2/g	30 ± 2
The average particle size, calculated from the specific surface area, nm	30
Crystallographic phases, determined by XRD analysis	Monoclinic – 10% Tetragonal – 90%

Experiments, concerning the adsorption of dispersants were performed by adding 1.1 g of the powder to 10 ml of the solution with given amount of the dispersant. The pH adjustments were made using KOH and HCl solutions. The suspension was deagglomerated by applying the ultrasonic treatment during 10 min in the vessel, provided with a water jacket. The pH was readjusted again and the sample was put onto a gentle mechanical shaker for 24 h to reach the equilibrium. Then the suspension was filtered through a membrane filter and the concentration of the dispersant in the filtrate was determined by UV spectroscopy (at wavelength of 240 nm for Atsurf and 257 nm for KD7). The adsorption was calculated from the difference between the amount of dispersant added and that remaining in the solution. All surfactant concentrations are given in wt% with respect to the dry powder mass (dmb).

Concentrated suspensions were prepared step by step by mechanical stirring under ultrasonic treatment and adding small amounts of the surfactant and powder. Effectiveness of investigated surfactants was checked by fixing the maximal powder loading in various pH regions. The viscosity measurements were used to optimize the surfactant content. The viscosity was measured using a RHEOTEST 2.1 rotational viscosimeter (cylinder-cylinder working unit).

3. RESULTS AND DISCUSSION

3.1. Elektrokinetic properties

Figure 1 demonstrates the changes in zeta potential with pH for the bare and surfactant-coated zirconia particles. The IEP of zirconia is located at pH 7.5. Over a wide range of pH (2.0–7.5) the surface charge of zirconia particles, represented by the sign and value of zeta potential, is positive. The increase of the pH value above 7.5 creates a negative charge on the particle surface.

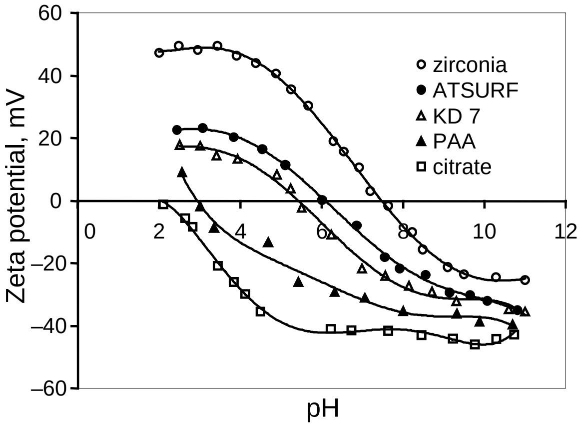

Fig. 1. Zeta potential versus pH in zirconia aqueous suspensions with and without surfactants.

As can be seen in Fig. 1, the investigated surfactants considerably affect the electrokinetic behaviour of plasma-prepared zirconia in aqueous suspensions. Zirconia surface, coated with tri-ammonium citrate, is negatively charged in the pH range from 2 to 11, the IEP is located at pH 2.1. The displacement of the IEP is almost 6 units. PAA creates a high negative zeta potential in the basic pH range, from 6 to 11; the IEP is shifted to pH 2.9. The addition of KD7 and Atsurf to the suspension is less effective. It resulted in the shift of the IEP to pH 5.5 and 6.0, respectively, and in the less negative value of the zeta potential at pH 10–11.

3.2. Adsorption isotherms

Atsurf and KD7 are chosen for the adsorption measurements as the highest solid loading is achieved using these dispersants (Table 2). The adsorption of KD7 on zirconia is displayed in Fig. 2. The adsorption isotherms represent the equilibrium state at pH 3.5 and 9. For both pH values investigated, the adsorbed amount increases with increasing copolymer concentration, followed by a weakly increasing isotherm (pH 3) or plateau (pH 9) at elevated copolymer concentrations. Acid-base potentiometric titration shows that the copolymer is almost uncharged at pH 3 and almost fully ionized at pH 9. However, the maximal amount of KD7 adsorbed is nearly the same at both pH (2.0 and 2.5% of the weight of oxide) while the affinity between the surface and surfactant is different. The isotherm at pH 9 shows high-affinity, which is evidenced by the sharp increase of the adsorbed amount at low copolymer concentration. The isotherm at pH 3 is of a low affinity since a definite amount of copolymer remains

Table 2. The maximum of powder loading in suspensions depending on the dispersion medium and used surfactants. Surfactant content is 2 wt% on a dry mass of solid

Surfactant	Dispersion medium	Powder loading	
		wt%	vol%
Amonium citrate	0.1 N CH_3COOH	48.1	13.4
	H_2O	55.7	17.3
	0.1 N NH_4OH	62.5	21.7
	1 N NH_4OH	69.3	27.4
Polyacrylic acid	0.1 N CH_3COOH	48.6	13.6
	H_2O	61.4	21.0
	0.1 N NH_4OH	41.9	10.7
	1 N NH_4OH	67.5	25.7
Atsurf 3222	0.1 N CH_3COOH	66.3	24.7
	H_2O	72.7	30.8
	0.1 N NH_4OH	72.2	30.2
	1 N NH_4OH	52.6	15.6
KD7	0.1 N CH_3COOH	68.6	26.7
	H_2O	70.7	28.6
	0.1 N NH_4OH	68.6	26.7

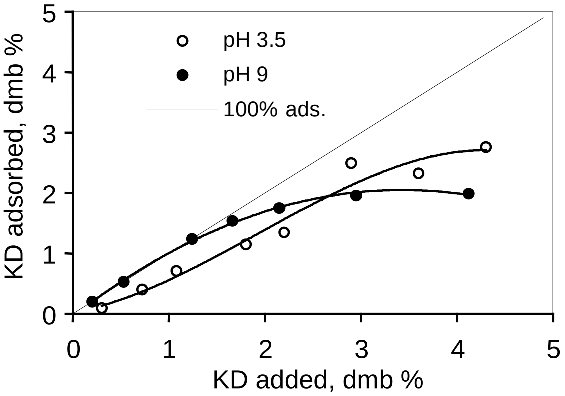

Fig. 2. Adsorption isotherms of KD7 on zirconia in 10 wt% aqueous suspension at pH 3.5 and 9.

unabsorbed even at low initial copolymer concentration. Zirconia surface is positively charged at pH 3 and negatively charged at pH 9 (Fig. 1). Considering this fact, one can conclude that the adsorption of the copolymer is controlled mainly by non-electrostatic affinity. At pH 3, undissociated carboxylgroups can be responsible for the copolymer adsorption on the zirconia surface, interacting through hydrogen bounds [8]. Adsorption of anionic polyelectrolytes at high pH, where pH > pH_{IEP}, is dictated by the balance of the specific (non-electrostatic) affinity between segments of the surfactant molecule and powder surface, and the electrostatic repulsion between the negatively charged solid/liquid interface and the strongly negatively charged polyelectrolyte chains. The fact that anionic polyelectrolytes adsorb at pH > pH_{IEP} implies that the specific segment – surface interactions are of significant magnitude [9].

At pH 9, Atsurf (Fig. 3) exhibits high-affinity adsorption at the beginning of the isotherm. The plateau is close to 6 wt% (on a dry mass of solid) of added surfactant, which is a higher value than for KD7.

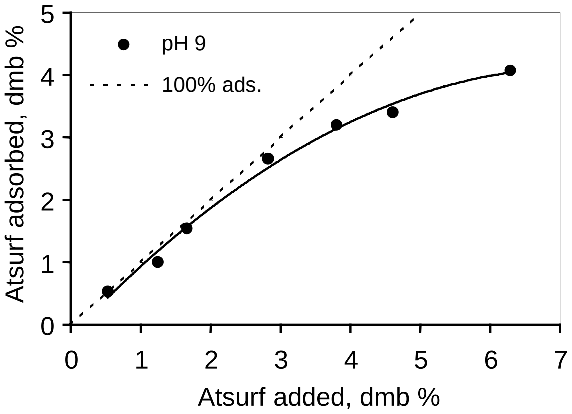

Fig. 3. Adsorption isotherms of ATSURF on zirconia in 10 wt% aqueous suspension at pH 9.

3.3. Concentrated zirconia suspensions

Table 2 compares the effectiveness of surfactants by preparation of concentrated suspensions. The results show that the optimal dispersion medium can be found for any surfactant investigated and high solid content can be achieved. However, there is no direct correlation between these results and measured zeta potential values of the coated and uncoated zirconia surfaces in diluted suspensions.

The tri-ammonium citrate is more effective in the basic dispersion media – the highest powder loading of 69 wt% is reached in the 1 N NH_4OH solution. This result correlates with the zeta potential dependence on pH as presented in Fig. 1. Tri-ammonium citrate creates a high negative zeta potential on the zirconia surface due to the presence of three carboxylic groups in the molecule, which dissociate in the basic pH region. It causes electrostatic stabilization of the suspension.

In the case of PAA, the highest suspension concentrations are achieved in water and 1 N NH_4OH solution, i.e., in strongly basic and weakly acidic medium. Zirconia in water suspensions creates pH 3–4 in the bulk solution most likely due to nitrogen oxides on the powder surface as the powder is synthesized in air plasma. The stability of the suspension in the basic medium can be explained by considering the high zeta potential value of the surface at these 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 and KD7 as dispersants. The solid content of 70 wt% and more is reached in water (weakly acidic media) and in 0.1 N NH_4OH solution. The achieved high solid loading depends weakly on the acidic or basic character of the dispersion medium and on the anionic (KD7) or cationic (Atsurf) character of the surfactant. It suggests that given surfactants stabilize the suspensions more by the steric effect.

The performed viscosity measurements in concentrated zirconia suspensions allow to optimize the surfactant content. Figure 4 shows that the optimal content of tri-ammonium citrate is 1.0–1.5 wt% on the dry mass of the solid. Comparing the viscosity curves in Fig. 5, one can conclude that the suspension with KD7 content of 3.0 wt% on the dry mass of the solid has the lowest value of viscosity, especially at lower shear rate values. It means that the suspensions, prepared using KD7, could be more suitable for technological application. According to the adsorption data, plotted in Fig. 2, the optimal surfactant concentration approximately corresponds to the saturation of the particle surface.

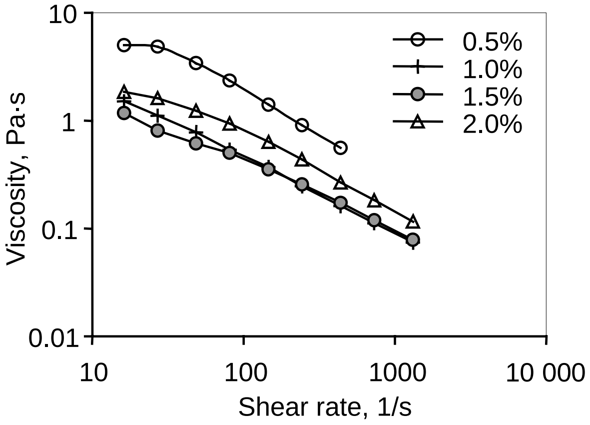

Fig. 4. Viscosity versus shear rate for ZrO_2 (25 vol%) suspension in 1 N NH_4OH depending on the ammonium citrate content (wt% of the dry mass of the solid).

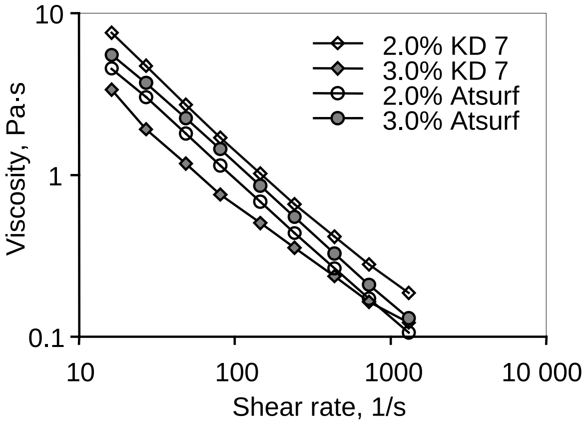

Fig. 5. Viscosity versus shear rate for ZrO_2 (27 vol%) suspension in water depending on the Atsurf 3222 and KD7 content (wt% of the dry mass of the solid).

4. CONCLUSIONS

The highest concentrations (up to 70 wt% or 27 vol%) of nanosized partially stabilized zirconia powder in water suspensions can be reached using Atsurf 3222 and KD7 as dispersants. These high molecular weight polyelectrolytes stabilize the suspensions more by steric effect than by electrostatic repulsive forces.

Tri-ammonium citrate can be successfully used for preparation of concentrated suspensions of zirconia in basic dispersion medium (1 N NH_4OH solution). Low molecular weight surfactant creates a high negative zeta potential on the zirconia surface that leads to the electrostatic stabilization of the suspension.

REFERENCES

1. Michael, J. R. Optimized processing of advanced ceramics. *Ceram. Eng. Sci. Proc.*, 1993, **14**, 288–297.
2. Hunter, R. J. *Foundations of Colloid Science*. Oxford Science, Oxford, 1991.
3. Kelso, J. F. and Ferrazzoli, T. A. Effect of powder surface chemistry on the stability of concentrated aqueous dispersions of alumina. *J. Am. Ceram. Soc.*, 1989, **72**, 625–627.
4. Briscoe, B. J., Khan, A. U. and Luckham, P. F. Optimizing the dispersion of alumina using commercial polyvalent electrolyte dispersants. *J. Eur. Ceram. Soc.*, 1998, **18**, 2141–2147.
5. Boufi, S., Baklouti, S., Pagnoux, C. and Baumard, J. F. Interaction of cationic and anionic polyelectrolyte with silica and alumina powders. *J. Eur. Ceram. Soc.*, 2002, **22**, 1493–1500.
6. Chera, L., Palcevskis, E., Berzins, M. and Lipe, A. The influence of some surfactants on obtaining concentrated aqueous suspensions of plasma processed fine alumina. In *Proc X-th International Baltic Conference "Materials Engineering BALTTRIB 2001"*. Jurmala, 2001, 22–26.
7. Grabis, J., Kuzjukevics, A. and Rasmane, D. Preparation of nanocrystalline YSZ powders by the plasma technique. *J. Mater. Sci.*, 1998, **33**, 723–728.
8. Vinogradov, S. N. and Linnel, R. H. *Hydrogen Bonding*. Van Nostrand Reinhold, New York, 1971.
9. Laarz, E. The effect of anionic polyelectrolytes on the properties of aqueous silicon nitride suspensions. *J. Eur. Ceram. Soc.*, 2000, **20**, 431–440.

Kõrge kontsentratsiooniga happesuspensioonide valmistamine plasmatehnoloogiaga saadud nanosuurusega tsirkooniumpulbrist

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Plasmatehnoloogiaga saadud nanosuurusega osaliselt stabiliseeritud tsirkooniumpulbrist valmistatud kõrge kontsentratsiooniga suspensioone on võrreldud nelja dispergaatoriga. Zeta potentsiaali mõõtmise abil on uuritud nende dispergaatorite mõju pulberpinna elektrokineetilistele omadustele. Kõrgeim kontsentratsioon (kuni 70 massiprotsenti) on saavutatud, kasutades dispergaatoreid Atsurf 3222 ja KD7. Optimaalne dispergaatori kogus (2–3 massiprotsenti) on määratud absorptsiooni ja viskoossuse mõõtmisega. Nende andmete põhjal on analüüsitud pinna elektrokineetiliste omaduste ja suspensiooni maksimaalse kontsentratsiooni korrelatsiooni.