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Optimisation of performance of dispersants in aqueous plasma dissociated zircon suspension

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Abstract

Plasma dissociated zircon (PDZ) is a unique product obtained during in-flight dissociation of zircon sand in a plasma reactor. In PDZ, submicron zirconia crystallites are intimately mixed with glassy silica. This paper describes the selection and optimisation of dispersants in controlling stability of an aqueous suspension of PDZ. It has been observed that inorganic dispersants and organic additives give clearly distinct behaviour. In both cases, optimum dispersant dosages can be obtained from the streaming potential characteristics. It is shown that there is a critical concentration of each dispersants, which gives the highest streaming-potential/surface charge and hence optimum performance. Studies showed that the isoelectric point of PDZ particulate is at pH 2.8. Additions of dispersant increase the charge in magnitude and modified the surface to have more negative charge in the pH range 2.8–9.4. An assessment of particle/additive interactions, overall stability, and optimised chemical additive required to obtain homogeneous, well-stabilized suspension can be derived from the streaming potential characteristics. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Plasma dissociated zircon, Streaming potential, Dispersants, Optimisation

1. Introduction

Zircon i.e. zirconium silicate is an inert and refractory material having very high melting point (2550 °C) and hence to prepare dense zircon based refractories it is required to sinter the body at very high temperature for a long duration. However, one can start with thermally split zircon, which is basically a mixture of zirconia and silica in 1:1 molar ratio. This material can be used as starting material to form green ceramic bodies, which during sintering reassociate to form zircon. In this particular study, we have used thermally split zircon, which has been dissociated in-flight in a plasma reactor [1], and referred as plasma dissociated zircon (PDZ).

It is well established that the control of the microstructure and the tailoring of related physical properties such as mechanical strength, fracture, toughness as well as thermal shock and wear resistance are of crucial importance for a successful application of advanced ceramic materials. Mostly in the manufacturing process of ceramic bodies, either directly during shaping or milling or blending step, the ceramic powder is dispersed in a liquid phase. With the increasing trend to use finer powders having a higher surface area, the surface charges play an important role in stabilizing this type of slurry. There are number of inter-particle forces that play an important role in stabilizing the ceramic suspension. Among those, the dominating force is the van der Waals force, which is attractive in nature between the like particles and exhibits power law distance dependence. The strength of this force depends on the dielectric properties of ceramic particles and intervening medium. To mitigate this long-range attractive force so as to achieve the desired degree of suspension stability, one approach is to generate like charges of sufficient magnitude on the surface of suspended particles. This causes strong electrostatic repulsion between the suspended particles and, thereby, deflocculates the suspension. Hence, measurement and control of charge on the particles may be used to control the properties of the suspension. This can be achieved by adding different surface-active agents. In the present investigation different organic and inorganic dispersants were used to study the stability of the PDZ suspension.

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In this context, it is wise to explain the concept of the point of zero charge (pzc) of particulate system, which is used as reference as how suspension will behave in aqueous media. Each material has a unique point of zero charge unless contaminated by impurities [2]. Since impurities are difficult to eliminate completely it is common to find a range in the pzc. Point of zero charge (pzc) of a material is defined as the condition of the system where the surface appears to carry zero charge. The pzc of oxide materials are determined by potential determining ions (PDI) i.e. H^+ and OH^- ions. The isoelectric point (iep) is the pH dependent point of zero charge of the surface only in the presence of any specifically adsorbed ions. Consequently, at this pH, the repulsion between adjacent particles is at a minimum permitting flocculation. For all practical purposes pzc and iep is treated as same but literally it is not true. At pH below the iep, the surface charge of most metallic oxides is positive which is attributed to the protonation of the surface hydroxyl group. The surface charge is negative at pH above iep. The iep reported for zirconia varies from pH 4 to 7 and that of amorphous silica 2 to 3 [3].

In the current study, the application of the recently developed 'streaming potential' measurement technique (PCD 03 pH) is used to measure potential characteristics of the suspension. The optimum dispersed condition and dispersant amount can be derived from the potential characteristics by titrating a particle suspension of defined solids content with the dispersant solution.

In this study, we propose a selection and optimisation criteria of dispersant for suspension of PDZ by using the PCD technique. On the whole this paper describes the process of optimisation of PDZ ceramic aqueous suspension by using different commercially available inorganic as well as organic dispersants.

2. Experimental

2.1. Materials

The material used in this study was PDZ, which is a mixture of ZrO_2 and SiO_2. A scanning electron micrograph of PDZ is given in Fig. 1, which shows tiny crystallites of zirconia embedded in a glassy silica matrix. The size of the crystallites are 0.1–0.2 μm, but can be varied from submicron to nanometer, depending on the quenching rate employed during the cooling of the dissociated product. Also high thermal stress generated in PDZ during cooling makes the silica highly reactive. This product is highly sensitive towards re-association of zirconia and silica to form zircon. The furnace product has a particle size of $-250+100$ μm and density of 3.8 g/cc. The product is ground in a ball mill for 10 h and particle size distribution and the surface area are shown in Table 1.

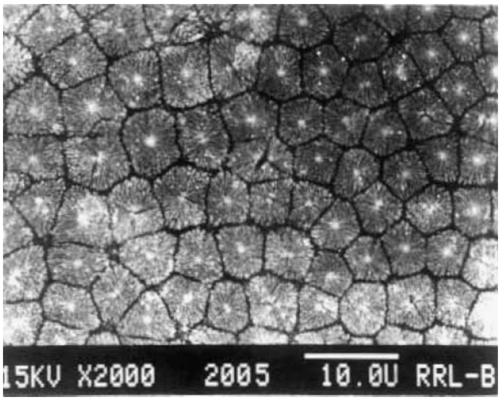

Fig. 1. Scanning electron micrograph of plasma dissociated zircon (PDZ).

Table 1
Size distribution of PDZ used for the study

Sample	Particle size distribution, μm			Specific surface area (m^2/cc)
	d_{10}	d_{50}	d_{90}	
PDZ	0.70	1.22	6.57	4.9976

Two different classes of dispersants, inorganic and organic are selected for this study, which are commercially available reagents. They were used as received. A complete list, along with their molecular weight, ionicity are given in Table 2. Among the organic dispersants, dispex N-40 is a proprietary anionic dispersant which is basically a salt of acrylic acid, acquired from Allied Colloids, UK, Lignosulfonate is a commercially available sugarated sodium salt of lignosulfonic acid. Initially, 0.1% solution (w/v) was prepared and a different concentration was used from the original one. Doubly distilled water was used as dispersing medium in all the experiments. HCl and NaOH were used to adjust the pH. All other reagents are of analytical grade and were used without purification.

2.2. PCD-potential measurement

The potential characteristics (in mV) were measured with a particle charge detector (PCD 03 pH) apparatus (Make: Mutek, Germany). A cylindrical test cell fitted with a displacement piston constitutes the centrepiece of the PCD apparatus [4]. If an aqueous sample is filled into the measuring cell, colloidally dissolved substances and solid particles in water will adsorb at the plastic surface of the piston and on the cell walls, under the action of van der Waals forces. The counter-ions remain comparatively free. A definite narrow gap is kept between the test cell and displacement piston for their movement. The plastic displacement piston oscillates with a constant frequency within the plastic cylindrical test cell, which contains the sample in an aqueous medium. The oscillating

Table 2
List of dispersants along with their molecular weight and ionicity

Organic dispersant	Ionicity	Molecular weight	Inorganic dispersant	Ionicity	Molecular weight
Citric acid	A[a]	210.1	Sodium silicate	A	284.2
Dibasic ammonium citrate	A	226.2	Sodium hexametaphosphate	A	672.0
Sodium alginate	A	48×10^3–186×10^3	Sodium tripolyphosphate	A	336.0
Lignosulphonate	A	54×10^3			
Polyethylene sodium sulfonate	A	218×10^2			
Dispex N-40	A	–			

[a] A = anionic.

movement of the piston forces a flow of the liquid phase of the sample between the piston and the wall of the cell. As a result, the diffuse cloud of counter ions of electrical double layer is partially separated from (sheared off) the colloidal particles and other reagents present in the liquid. This partial separation of charges induces the so called 'streaming potential' which can be measured directly (in terms of mV). When the measured streaming potential is 0 mV, the particle suspension is in a neutral state called the isoelectric point (iep) or the point of zero charge (pzc). When a measurable streaming potential exists, then the particle is either negatively or positively charged depending on the sign of the potential displayed. The quantitative estimation of the overall charge of the system can be made by titrating the sample with a standard polyelectrolyte of opposite charge until neutralisation. The PCD apparatus has been used together with a compatible standard automatic titrator (702 SM Titrino). On reaching the zero streaming potential, it stops automatically and the exact volume of titrant consumed is read directly from the display. The specific surface charge, q in (eq/g) is calculated using the following formula.

$$q = \frac{V.c.1000}{w} \tag{1}$$

where V is volume of titrant consumed (ml), c is titrant concentration (=0.001 N), 1000 is the calculation factor for the charge density, and w is the weight of the sample (in g).

The total charge quantity (in C/g can be obtained by multiplying the specific charge (in eq/g) with the Faraday's constant (=96485 C/eq).

3. Results and discussion

3.1. Origin of surface charge on ceramic particle dispersion

The origin of surface charges may be due to three principal types: (a) presence of ionizable functional groups such as –OH, –COOH, on the solid ceramic surfaces, (b) lattice imperfections at the surface or isomorphous lattice replacements, and (c) adsorption of ions on the surface [5]. Immersing a ceramic powder in water, usually results in the building up of a charge at the solid/liquid interface. The interfacial charge is due to adsorption or desorption of ionic species in solution i.e. by proton transfer reactions with the surface hydroxyl groups or by adsorption of specifically adsorbed ions. The dissociation reactions of oxides (MO) may be written as:

$$\mathrm{MOH} \Longleftrightarrow \mathrm{MO}^- + \mathrm{H}^+ \tag{2}$$

$$\mathrm{MOH}_2^+ \Longleftrightarrow \mathrm{MOH} + \mathrm{H}^+ \tag{3}$$

The net charge is dependent on the pH of the slurry. The point of zero charge (pzc) is the pH value where surface concentration of $[\mathrm{MO}^-]$ and $[\mathrm{MOH}_2^+]$ are equal. The surface charge is negative at $\mathrm{pH} > \mathrm{pH}_{\mathrm{pzc}}$ and positive at $\mathrm{pH} < \mathrm{pH}_{\mathrm{pzc}}$. Ions of opposite charge (counterions) are attracted to the charged interface and form a diffuse ion cloud adjacent to the particle surface. The thickness of this electrical double layer is a very important parameter because it controls the range of the double layer repulsion. The double layer thickness can be controlled by the concentration and valence of ions in solution. A high concentration of ions (high ionic strength) results in a compression of the diffuse layer leading to reduction in thickness of the double layer. The double layer compression consequently decreases the surface charge and zeta potential which in turn decreases the stability of the system.

The interaction between two charged particles in a polar media is related to the osmotic pressure created by an increase in ion concentration between the particles whose electrical double layer overlap [6]. The PDZ slurry under this investigation has a natural pH of 6.6 in distilled water. In the absence of any dispersant, it exhibits a net negative specific charge of −0.1264 C/g.

3.2. Isoelectric point of PDZ

The isoelectric point (iep) of the suspension was measured by measuring PCD-potential. Fig. 2 shows the

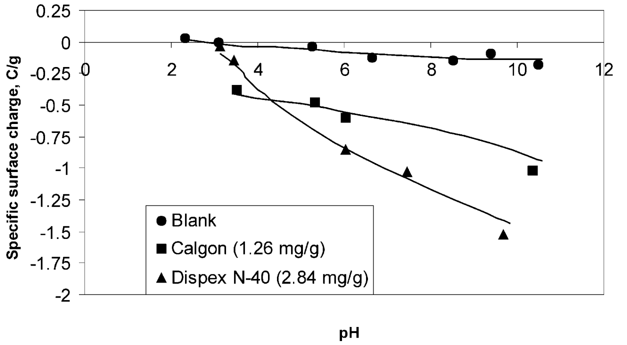

Fig. 2. Variation of specific surface charge of 5% (w/v) PDZ slurry with pH.

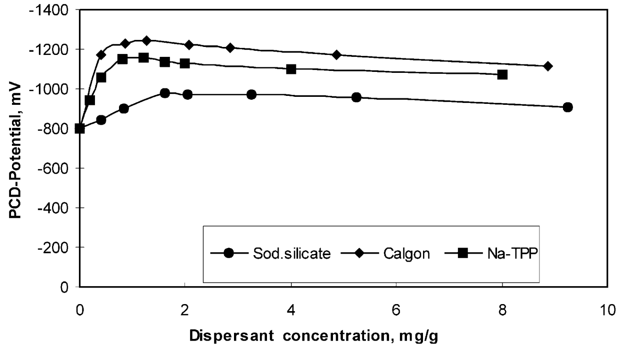

Fig. 3. Effect of inorganic dispersants concentration on PCD-potential of 5% (w/v) PDZ slurry.

variation of surface charge (C/g) of PDZ with pH. The PCD-potential and (surface charge) changes from +46.8 mV (+0.0345, C/g) at pH 2.32 to −846.9 mV (−0.924, C/g) at pH 2.8. Plasma dissociated zirconia is a mixture of zirconia (iep 4–9) and silica (iep 2–3) [3], but resultant iep is shifted to 2.8 which is closer to the iep of silica. This may be due to the fact that the zirconia particulates are embedded in silica matrix and silica surface is exposed to the aqueous environment. At pH below 2.8, the PDZ is positively charged and above 2.8 it is negatively charged. The magnitude of the negative PCD-potential and hence the surface charge increases with increasing pH. These results suggest that the PDZ suspensions should experience progressive deflocculation with increasing pH. Fig. 2 also depicts the variation of surface charge of PDZ slurry with one inorganic (calgon) and one organic (Dispex N-40) additives. It shows that the presence of Calgon make the PCD-potential more negative and shift the iep of the system to low pH values whereas with organic additive Dispex N-40, sthepecific charge becomes more negative at higher pH but did not change the iep appreciably. It shows that ionisable groups on Dispex N-40 are pH dependent [7].

3.3. Determination of stability maxima and optimum dispersant dosages

Fig. 3 shows variation of PCD-potential with different dosages of inorganic dispersants such as Calgon (sodium hexameta phosphate), sodium poly phosphate and sodium silicate. All three polyelectrolytes are highly negatively charged. Initially, it shows an increase in PCD potential with increasing concentration of dispersant, and then remains almost constant after reaching the plateau value. It indicates that at low concentration region, the adsorption of negatively charged species of dispersants on the ceramic particles render and increase the magnitude of negative surface charge on it. Any amount of the dispersant above optimum concentration, remains in the aqueous phase, which may affect the viscosity of the solution. All the three dispersants show similar behaviour, and the pH of the solution increases with the increasing addition of the dispersants. The dispersive power of the above dispersants were in the following order: Calgon > sodium poly triphosphate > sodium silicate. These data are further corroborated with visual observation of the settling behaviour of the suspension in the presence of the above dispersants. A distinctly optimum dispersion condition and dispersant amount can be determined from the potential characteristics obtained from the PCD and the results can be readily used for practical purposes. Fig. 4 shows the relationship between PCD-potential with concentration of various organic dispersants. In this case, dispersants employed were citric acid, dibasic ammonium citrate, lignosulphonate, polyethylene sodium sulphonate, sodium alginate and Dispex N-40. Increasing the dosage of Dispex N-40, sodium alginate and dibasic ammonium citrate increases the PCD-potential and hence the specific charge because of their high negative charge density, while the other three show an overall decrease in PCD-potential. The decrease in overall PCD-potential may be explained on the basis of ionisation characteristics of the polyelectrolyte with pH. In aqueous systems, the dissociation behaviour of polyelectrolyte and, consequently, the total charge of the polymer are considered to be pH dependent. At low pH values the polyelectrolyte is not in a completely ionised state resulting in a decrease in the charge density of the polymer, whereas the content of dissociated acid groups increases at high pH values. Addition of citric acid, polyethylene sodium sulphonate and lingnosulphonate decreases pH of the solution, and thus are in a less ionised state. The adsorption of these less ionised state polyelectrolytes do not decrease the magnitude of negative charge on the surface. The effect is most pronounced in the case of lignosulphonate. On the other hand, addition of Dispex N-40, sodium sulphonate and dibasic ammonium citrate increase the pH towards alkaline region leading to their ionisation. The adsorption of these ions on the PDZ surface increase the negative charge substantially. The maximum increase in negative PCD potential (and thus the surface charge) was observed for Dispex N-40. The dispersing ability in terms of PCD potential was found to be in the following

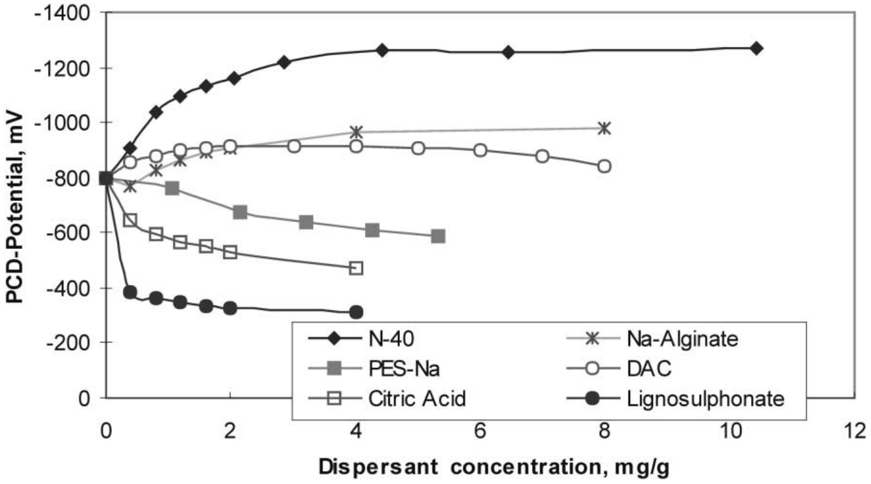

Fig. 4. Effect of organic dispersants concentration on PCD-potential of 5% (w/v) PDZ slurry.

Table 3
Summary of optimum concentration of dispersants and the PCD potential

Dispersant	Optimum dispersant concentration, mg/g of PDZ	PCD potential, mV
Dispex N-40	2.84	−1280
Dibasic ammonium citrate (DAC)	2.0	−1193
Sodium alginate	1.60	−890
Polyethylene sodium sulphonate	1.07	−760
Citric acid	0.4	−645
Lignosulphonate	0.4	−383

order: Dispex N-40 > dibasic ammonium citrate > sodium alginate > polyethylene sodium sulphonate > citric acid- > lignosulphonate. A summary of optimum concentration and PCD potential in presence of different dispersants are presented in Table 3. Therefore, one can easily measure the optimum condition of dispersion and amount of dispersant by knowing the PCD potential characteristics of various dispersants.

4. Conclusions

Based on this investigation following conclusions are drawn:

1. The PCD technique provides a convenient and reliable method of rapidly determining the dispersion condition and optimum dispersant dosages.
2. This technique allows measurement of the minimum amount of dispersant required to have best condition for dispersion for different class of dispersant.
3. Among the dispersants investigated for PDZ, the dispersive power of inorganic dispersant were found to be in the order of Calgon > sodium poly phosphate > sodium silicate and while for organic dispersants, it is Dispex N-40 > dibasic ammonium citrate > sodium alginate > polyethylene sodium sulphonate > citric acid > lignosulphonate respectively.

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