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Effect of dispersants on surface chemical properties of nano-zirconia suspensions

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Abstract

Surface charge and particle dispersion of zirconia in aqueous suspension with addition of different dispersants, such as ammonium polymethacrylic acid (Darvan C), polyethylene imine (PEI) and diammonium citrate (DAC) were investigated by measuring its zeta potential and particle size. It was found that the zero point of charges (zpc) of 3Y-TZP powder was determined to be $pH_{zpc} = 6$, surface charge of zirconia powder changed significantly and zpc shifted under different dispersion conditions. Zirconia particle was in monodispersed state far from zpc, while in a certain degree of agglomeration in the vicinity of zpc. The study illustrates how zeta potential and effective particle size can be utilized in the investigation and optimization of the properties of ceramic suspensions. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: C. Surface chemical properties; Dispersant; Nano-zirconia suspensions

1. Introduction

Fine-grained and uniform microstructures are desirable for most structural ceramic applications in producing a strong and reliable structural part; cheaper and more convenient methods of forming green bodies are of great interest. The concept of colloidal processing has been successfully applied to the field of structural ceramics and several studies have shown that the inhomogeneities could be minimized, and complex shaped and reliable ceramics have been produced by controlling and manipulating the interparticle forces in the suspension during processing and forming [1,2]. During colloidal processing, the state of dispersion (colloidal stable or flocculated) has a significant influence on the casting behavior and the resulting green-body properties [3]. Generally, colloidal stable suspensions are preferred since they usually produce higher average packing densities and a narrower pore size distribution compared with strongly flocculated suspensions.

Ceramic particles in solution are charged and may possibly become dispersed in a repulsive manner by forces developed on the surface of particles. The particles can be dispersed in an aqueous solution by either electrostatic, steric or electrosteric stabilization. However, it is difficult to obtain homogenous, well stabilized and dispersed high solid content suspension without dispersant. During processing of the suspension, the surface chemical properties of particles are influenced by many factors, such as the nature of the ceramic particles, particle size distribution, surface impurities, solvent, pH value, etc [4]. Surface chemical properties can be changed significantly due to minute changes of these factors.

Zirconia ceramics have been widely used for their excellent mechanical properties. Currently, colloidal processing has been of great interest in submicron powder forming method [5,6], however, the colloidal processing reports on nano-size zirconia powder are very few [7], in particular, the colloidal chemistry, surface chemical properties and the interactions of powders with dispersants are not very clear. As we know, the dispersion state of ceramic powders is very closely related to the adsorption state of the polymer on the powder surface [8]. So in this study, we have studied zeta potential and particle size distribution of nano-zirconia aqueous suspension with different dispersants in different pH condition so as to gain a more complete understanding of the interactions of dispersants with the oxide surface. The directly measured particle size may give a specific description on the dispersion state of ceramic powder.

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2. Experimental procedures

2.1. Materials

A polycrystalline, partially stabilized tetragonal zirconia powder Y-TZP, containing 3 mol% yttria was used in all studies. The powder was made by chemical coprecipitation method with an average particle size of 0.34 μm and a BET surface area of 34 m^2/g. The primary particle size was about 30 nm and Fig. 1 shows the TEM micrograph of zirconia powder used in this study.

Three dispersants were used, one was Darvan C, an ammonium salt of polymethacrylic acid, produced by the Vinderbilt company, with an average molecular weight of 10 000–16 000; the second was polyethylene imine (PEI, Aldrich), a cationic polymer with an average molecular weight of 50 000; the third was analytical reagents diammonium citrate (DAC). All HCl, NaOH, NaCl used in this experiment was of analytical grade.

2.2. Characterization

Surface chemical properties of zirconia powder were characterized by zeta potential measurement. The measurement of zeta potential as a function of pH were performed for 0.01 vol% zirconia suspensions using a zeteplus zeta potential analyzer (Brookhavan company, USA) by electrophoresis light scattering method. 10^{-4} M NaCl solution was used to adjust the ionic strength of the suspension, HCl and NaOH solution was employed to adjust the pH values.

The degree of dispersion of zirconia powder suspension was evaluated in terms of effective particle diameter as revealed by dynamic light scattering technique using the zetaplus analyzer. Suspensions containing 0.025 vol% of zirconia powder were prepared with various dispersants in aqueous solution.

In order to break agglomerates, all the suspensions were ultrasonicated for 10 min and a period of 24 h mechanical stirring was allowed to achieve chemical equilibrium between the powder surface and the deflocculant in the suspension. The experiments were carried out with and without deflocculant, respectively.

3. Results and discussion

3.1. Surface chemical properties of zirconia suspension

The stability of zirconia suspension is closely related to its electrophoresis properties in aqueous solution. Well-dispersed suspension can be obtained with high zeta potential value of the powder where there is sufficiently high surface charge density to generate a strongly repulsive double-layer force. The effect of pH on zeta potential of zirconia powder in aqueous solution is shown in Fig. 2. The zpc of zirconia powder used is approximately 6. As we know, oxide powder dispersed in water can adsorb water molecules and form a hydration layer, especially as the zirconia powder used in this experiment is nano-sized powder which can easily adsorb H^+ and OH^- ions on the powder surface for its huge specific surface area. The surface chemical properties of the powder are determined by the H^+ and OH^- ions adsorbed on the particle surface. Therefore, the H^+ and OH^- ions in aqueous suspension play a role of surface charge determining ions of oxide particles, the hydration reaction is as follows:

$$\mathrm{MeOH_2^+(Surface)} \leftarrow^{H^+} \mathrm{MeOH(Surface)}$$
$$\rightarrow^{OH^-} \mathrm{MeO^-(Surface)} + \mathrm{H_2O}$$

Where Me represents metal ion.

At zpc, the number of positive charge sites produced by zirconia powder adsorbed H^+ ions is equal to the negative charge sites of adsorption of OH^- ions, so the net charge equals zero, and the particle in the suspension can be easily agglomerated and flocculated. From

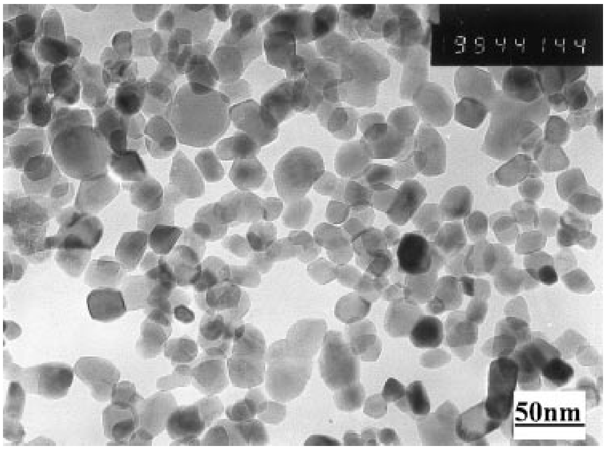


Fig. 1. TEM image of zirconia powder.

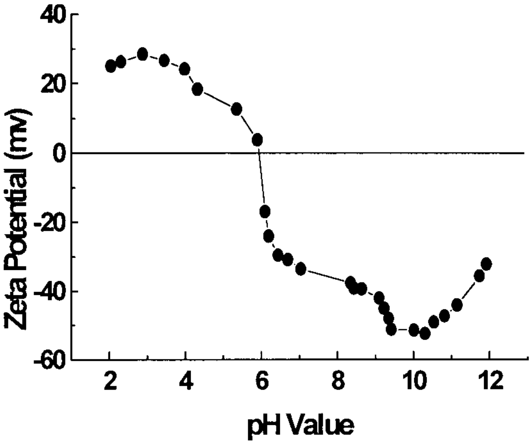


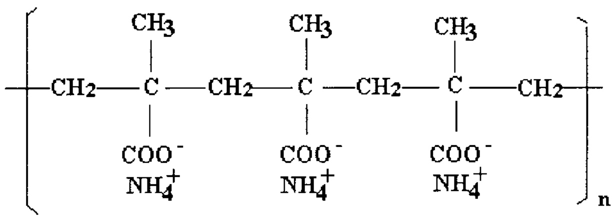
Fig. 2. Zeta potential curve of zirconia powder.

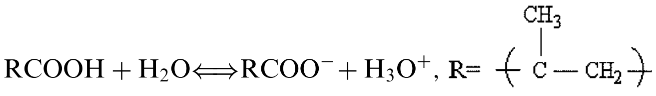
the zeta curve of zirconia powder we can see that under strong acidic conditions ($pH < 2$) and strong basic conditions $pH > 11$, zeta potential has a tendency to decrease, which can be explained by DLVO theory. Under both strong acidic and basic conditions, more HCl or NaOH are needed to adjust the pH values, the increased ionic strength in the suspension compresses the thickness of double electric layer and results in the decrease of zeta potential of the powder.

Fig. 3 shows particle size versus pH values of zirconia powder in aqueous suspension. It can be seen that particle size is about 300 nm with no obvious agglomeration under the condition of $pH < 7$ and $pH > 11$. However, particle diameter is larger at a pH range of 8 to 11 and 1000 nm can be reached at pH 9.5, which shows a partial agglomeration state. It is very interesting that this is not in agreement with the high zeta potential, the reason can be attributed to the surface chemical properties of zirconia powder in the suspension. Zirconia particle is negatively charged by adsorption of OH^- ions under basic conditions, the negatively charged zirconia particle could bond with the water molecules by hydrogen bond, which makes the zirconia particles interconnected with each other and consequently leads to the agglomeration, as demonstrated in Fig. 4.

3.2. Interaction of zirconia powder with Darvan C

In order to obtain well-dispersed and stabilized slurry, the polyelectrolytes are often used during the preparation of ceramic suspension, Darvan C is an effective dispersant. Fig. 5 shows the zeta potential curve of zirconia powder with addition of Darvan C. The zpc of zirconia powder shifts from pH 6 down to near pH 2.5. The surface which is negatively charged at a wide range of $pH > 2.5$ shows the significant charge changes on the zirconia particle surface as addition of Darvan C. The reason could be due to Darvan C, which is an anionic polyelectrolyte, its formula is:





$$RCOOH + H_2O \Longleftrightarrow RCOO^- + H_3O^+,\ R= \left(\overset{\overset{CH_3}{|}}{C} - CH_2 \right) \qquad (1)$$

The negatively charged carboxyl group dissociated from Darvan C is very easily adsorbed on the positive charged zirconia surface and consequently the powder is negatively charged [9–11]. When Darvan C is adsorbed on the surface of the particle, the hydroxyl groups will react with the carboxylic groups of Darvan C and this will result in a shift of the zpc to a lower value. The particle size curve of the powder with Darvan C is shown in Fig. 6, near zpc pH 2.5, particles are partially agglomerated while monodispersed at the range of $pH > 3.5$, this is in fair agreement with zeta potential curve. Double electric layer repulsive force is small near zpc and van der Waals attraction force makes particles

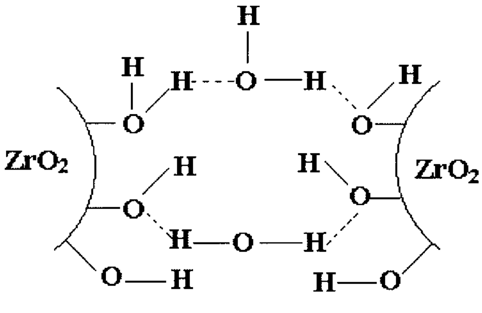


Fig. 4. Schematic illustration of bridging of zirconia particles with water by hydrogen bond.

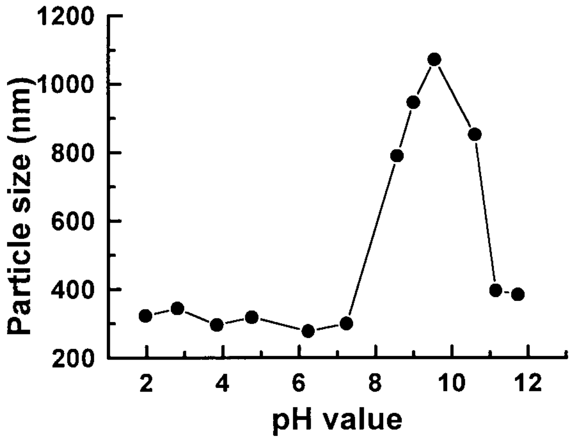


Fig. 3. Particle size of zirconia powder in different pH conditions.

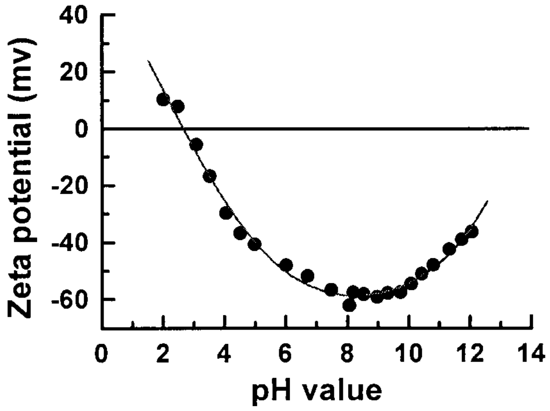


Fig. 5. Zeta potential curve of zirconia powder with addition of Darvan C.

adhere to each other and agglomerate while high zeta potential far from zpc separates the particles from each other. This differs from zirconia suspension without dispersant, where no agglomeration occurs near pH 9 because carboxylic groups are more easily adsorbed on the positive zirconia surface than OH^- ions and no hydrogen bond is formed.

3.3. Interaction of zirconia powder with PEI

Fig. 7 shows zeta potential curve of zirconia powder with addition of PEI. The zpc of zirconia powder shifts from pH 6 to 10.5 with PEI, the zirconia surface charge is significantly changed and is positively charged at a wide range of pH < 10.5. This could be due to PEI which is a cationic polyelectrolyte and has a formula as follows:

$$-(CH_2-CH_2-NH-)_n$$

The addition of a strong acid to a solution of PEI neutralizes −NH− basic groups and then confers a positive charge on the polymer skeleton according to the reaction [12]:

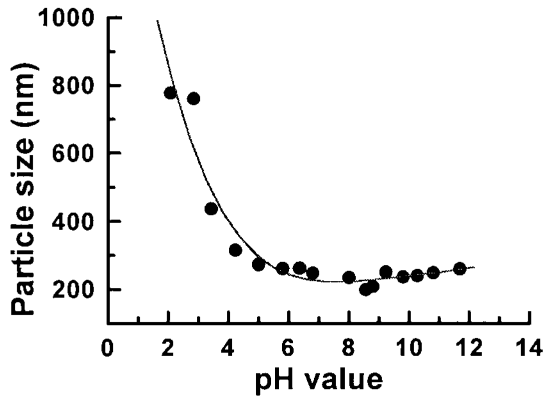


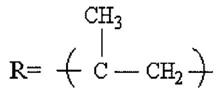
Fig. 6. Particle size of zirconia powder with addition of Darvan C.

$$\begin{aligned}&-(CH_2-CH_2-NH-)_n+H_3O^+\rightarrow\\&-(CH_2-CH_2-NH_2^+-)_n+H_2O\end{aligned}\tag{2}$$

The positively charged $-NH_2{}^+$ groups of PEI produced by adsorbing H^+ ions in aqueous solution can be easily adsorbed on the negatively charged zirconia particle surface which results in a shift of zpc to more alkaline pH. The corresponding dispersion experiment (Fig. 8) indicated that the particle is in a monodispersed state at the range of pH < 10 and somewhat slightly agglomerated near zpc at pH > 10, this corresponds well with the zeta potential curve. So zeta potential measurement is an effective way to reflect particle existence state in aqueous suspension.

3.4. Interaction of zirconia powder with DAC

DAC is seldom used as dispersant in ceramic processing, but the investigation found that carboxylic group containing agents could be good dispersants in deflocculate alumina suspension [13]. Here DAC was studied for its dispersability on zirconia suspension, its formula is:



$$R=\left(\begin{matrix}CH_3\\ |\\ C\end{matrix}-CH_2\right)$$

Zeta potential curve with addition of DAC shows that the zpc zirconia powder obviously shifts to approximately pH 2 (Fig. 9). Zirconia particle surface is negatively charged at all measured pH ranges. The tendency to influence zirconia suspension is similar to Darvan C due to containing easily adsorbed carboxylic groups on the surface of the zirconia powder. Zirconia particle surface has higher charge density and can be well dispersed in suspension at pH between 4 to 12. Fig. 10 shows the particle size versus pH value with addition of DAC, the zirconia particle is in a partially agglomerated state at pH < 3 while monodispersed at pH > 3, indicating

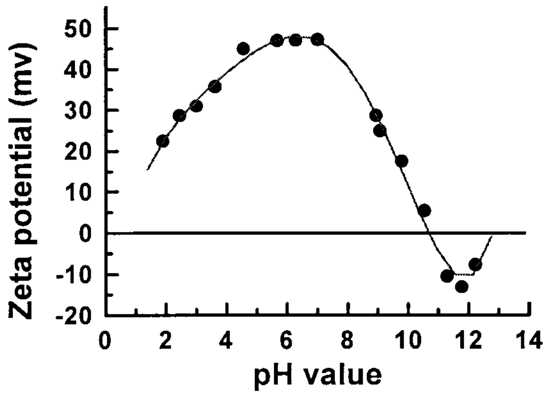


Fig. 7. Zeta potential curve of zirconia powder with addition of PEI.

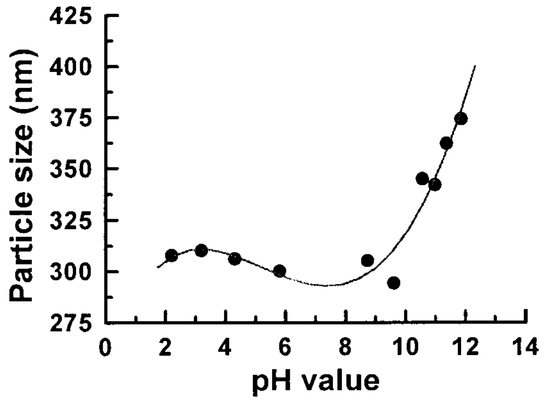


Fig. 8. Particle size of zirconia powder with addition of PEI.

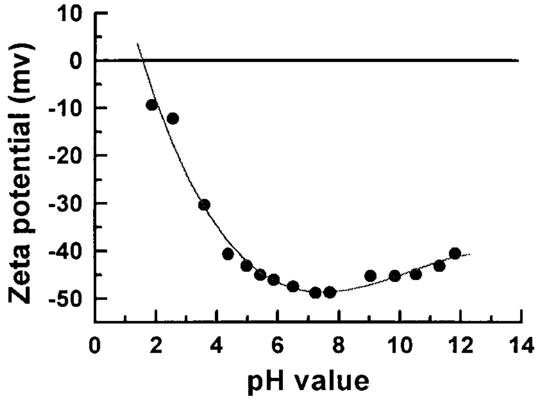


Fig. 9. Zeta potential curve of zirconia powder with addition of DAC.

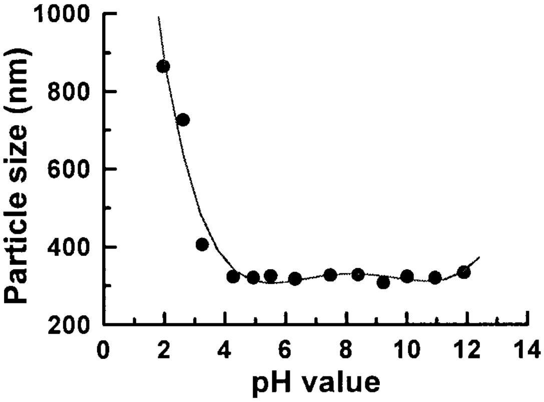


Fig. 10. Particle size of zirconia powder with addition of DAC.

that DAC is a good dispersant for zirconia powder. DAC as a dispersant of the influence of rheological and green body behavior of zirconia suspension will be discussed in detail elsewhere.

4. Conclusions

Both particle size measurement and zeta potential are effective ways to describe the existence state of ceramic powder in aqueous suspension, particularly the directly measured particle size which can give good evidence of the result of zeta potential. The zpc of zirconia powder without dispersant is near pH 6, zeta potential has a tendency to decrease under both strong acidic and basic conditions because of increased ionic strength compressing the thickness of the double electric layer. Zirconia particles can be connected with each other by hydrogen bond and lead to agglomeration at pH 8 to 11. The zpc of zirconia powder shifts to more acidic pH with addition of anionic polyelectrolyte, but shifts to more alkaline pH with addition of cationic polyelectrolyte, both the anionic and cationic polyelectrolyte can change the surface charge condition significantly.

Zirconia particle in aqueous suspension is partially agglomerated near zpc while monodispersed far from zpc with addition of dispersants.

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References

[1] F.F. Lange, Powder processing science and technology for increased reliability, J. Am. Ceram. Soc. 72 (1989) 3–15.

[2] E. Carlstrom, Surface and colloid chemistry in ceramics: an overview, in: R.J. Pugh, L. Bergstrom (Eds.), Surface and Colloid Chemistry in Advanced Ceramic Processing, Marcel Dekker, New York, 1994, pp. 1–28.

[3] L.B. Velamakanni, J.C. Chang, F.F. Lange, D.S. Pearson, New method for efficient colloidal particle packing via modulation of repulsive lubricating hydratin forces, Langmuir 6 (1990) 1323–1325.

[4] R.G. Horn, Surface forces and their action in ceramic materials, J. Am. Ceram. Soc. 73 (1990) 1117–1135.

[5] J. Cesarano III., I.A. Aksay, Stability of aqueous α-Al_2O_3 suspensions with poly(methacrylic acid) polyelectrolytes, J. Am. Ceram. Soc. 71 (1988) 250–255.

[6] J. Cesarano III., I.A. Aksay, Processing of highly concentrated aqueous α-alumina suspension stabilized with polyeletrolytes, J. Am. Ceram. Soc. 71 (1988) 1062–1067.

[7] R. Greenwood, L. Bergstrom, Electroacoustic and rheological properties of aqueous Ce-ZrO_2 (Ce-TZP) suspensions, J. Eur. Ceram. Soc. 17 (1997) 537–548.

[8] D.H. Lee, R.A. Condrate, J.S. Reed, Infrared spectral investigatin of polyacrylate adsorption on alumina, J. Mat. Sci. 31 (1996) 471–478.

[9] P.R.S. Pradip, S.G. Malghan, Electrokinetic behavior and dispersion characteristics of ceramic powders with cationic and anionic polyelectrolytes, Bull. Mat. Sci. 17 (1994) 911–920.

[10] M. Hashiba, H. Okamoto, Y. Nurishi, K. Hiramasu, Dispersion of ZrO_2 particles in aqueous suspensions by ammonium polyacrylate, J. Mat. Sci. 24 (1989) 873–876.

[11] R.J. Pugh, Dispersion and stability of ceramic powders in liquids, in: R.J. Pugh, L. Bergstrom (Eds.), Surface and Colloid Chemistry in Advanced Ceramic Processing, Marcel Dekker, New York, 1994, pp. 127–192.

[12] S. Baklouki, C. Pagnoux, T. Chartier et al., Processing of aqueous α-Al_2O_3, α-SiO_2, α-SiC suspensions with polyelectrolytes, J. Eur. Ceram. Soc. 17 (1997) 1387–1392.

[13] P.C. Hidber, T.J. Graule, L.J. Gauckler, Influence of the dispersant structure on properties of electrostatically stabilized aqueous alumina suspension, J. Eur. Ceram. Soc. 17 (1997) 239–249.