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Effects of dispersants and soluble counter-ions on aqueous dispersibility of nano-sized zirconia powder

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Abstract

The effect of different dispersants and water leaching on aqueous dispersibility of zirconia powder was studied. Zeta potentials of aqueous solutions containing nano-sized zirconia powder and different dispersants, such as ammonium polyacrylic acid (PAA-NH_4) and tetramethyl ammonium hydroxide (TMAH) and water leaching were characterized. Better dispersion of nano-sized zirconia powder in aqueous solutions was achieved with the addition of dispersant and water leaching.

Keywords: Nano-sized zirconia powder; Aqueous dispersibility; Dispersant; Soluble counter-ion; pH value

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1. Introduction

Tetragonal zirconia ceramics have been widely used as an advanced structural material for their excellent mechanical properties [1–3]. For many applications, it is desirable to obtain a fine grain microstructure and to fabricate components with complex shapes. This can be accomplished by using ultrafine powders combined with shaping by colloidal processing. In colloidal processing techniques such as direct coagulation casting (DCC), gelcasting, slip casting, tape casting and centrifugal casting, it is imperative to have a slurry with good dispersion and a desirable rheological behavior because the quality of dispersion controls the casting behavior and the resulting green-body properties [4]. Powder dispersion in water relies on the adjustment of surface charge of ceramic particles by dispersant and elimination of the soluble counter-ions (especially the high-valence counter-ions).

Colloidal processing has attracted great interests in forming green bodies containing submicron powder, but it has not been successful applied to the nano-sized zirconia system [5–8]. It is known that the dispersion of ceramic particles is closely related to the role of the dispersant on the particle surface and the soluble counter-ions. In this study the effect of dispersant on a nano-sized ZrO_2 powder was investigated in order to achieve good dispersion of the powder in water. In addition, the soluble counter-ions of the powder were analyzed and their effect on the rheological behavior of the system was investigated after their elimination by water leaching.

2. Experimental procedure

The as-received nano-sized zirconia powder (3 mol% Y_2O_3–ZrO_2) was provided by Jingdezhen Advanced Ceramics Company in China. The average particle size of the powder analyzed by a particle analyzer (Model BI-XDC, Brookhaven Instruments Corp., Holtsville, NY) was about 50 nm (Fig. 1). Fig. 2 shows the TEM micrograph of the zirconia powder obtained by a Model H-800 TEM (Hitachi Instrument Corporation, Japan).

To prepare zirconia suspensions, deionized water was used as a liquid medium, and a 10 wt.% water solution of tetramethyl ammonium hydroxide ($(CH_3)_4NOH$, TMAH) and ammonium polyacrylic acid (PAA-NH_4) were added as a dispersant, respectively. An electromagnetic stirrer was used for the initial dispersion of the powder in the slurry. Then the slurry underwent ball milling at a rate of 630 rad/min for 24 h in a nylon resin

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coated jar with zirconia balls as a milling media for further dispersion.

Zeta potentials of the as-received powders were measured by a laser-light-scattering electrophoretic technique (Model ZetaPlus, Brookhaven Instruments). For the zeta potential measurement, dilute suspensions containing 100 mg/l solids were prepared in a 0.001 mol/l KCl solution by ultrasonic treatment, and their pH was adjusted using diluted NaOH and HCl solutions.

The analysis of rheological properties of slurries was accomplished with a rotary rheometer (MCR-300, Physica Instrument Corporation, Germany). A cylinder with a volume about 23 ml was used. The measurements of static rheological property were performed in the shear rate range of 0.1–250 s^{-1} at a constant temperature of 25 °C.

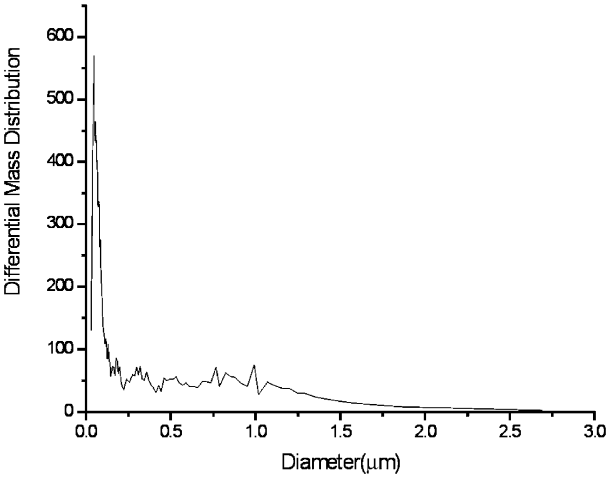

Fig. 1. The particle size distribution of ZrO_2 powder.

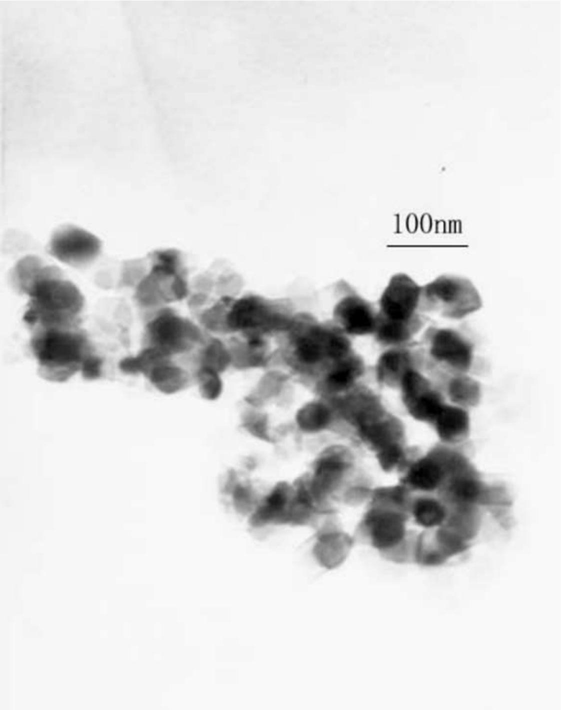

Fig. 2. TEM micrograph of ZrO_2 powder.

To study the soluble counter-ions in the powder, a suspension with 50 g of the ZrO_2 powder in 200 ml of deionized water was stirred intensively for 60 min and then centrifuged at a rate of 3000 rotations per minute for 10 min; the supernatant was used to measure anion and cation concentrations and ion conductivity. The above water leaching process was repeated. Then, pH value of the suspension was adjusted to about 5 with a HCl solution and the suspension went through water leaching again. A Na^+ ion exchange resin was used for elimination of high-valence cations in the suspensions (the mass ratio of powder and resin is 3:1) after 24 h ball-milling with ZrO_2 balls. The suspension was centrifuged and the powder was obtained when the resin and ZrO_2 ball were removed. The obtained powder was calcinated at 600 °C for 1 h to remove the residual resin, after which water leaching was carried out again and final powder was obtained. The supernatants obtained at different stages of water leaching were used in the measurements of the anion and cation concentrations, pH value and the ion conductivity. Both an ion chromatographic analyzer (Model HIC-6A, Shimadzu Corp., Kyoto, Japan) and a digital conductivity gauge (Model DDS-11AT, Shanghai Rex Instruments Factory, Shanghai, China) were used for this investigation.

3. Results and discussion

3.1. *Effect of dispersants on aqueous dispersibility of the powder*

The effect of dispersant on the dispersibility of the nano ZrO_2 powder was investigated by measuring the viscosity and the zeta potential of the suspension. In general, the dispersion of ceramic powders in suspensions can be improved when the absolute value of the zeta potential is increased after an addition of dispersant. The higher the absolute value of the zeta potential, the higher the charge density is on surface of powders and the larger the repulsion among particles. Fig. 3 shows the zeta potential vs. pH of ZrO_2 powder with and without dispersants in water. It was found that the isoelectrical point of as-received ZrO_2 powder in deionized water is about pH 8.0. When the pH value is below and above 8.0, the charge on the surface of ZrO_2 particles is positive and negative, respectively. Oxide powder dispersed in water can adsorb water molecules and form a hydration layer. Depending on the concentration of H^+ and OH^- ions in aqueous suspensions, the hydration reactions can take place as follows [9]:

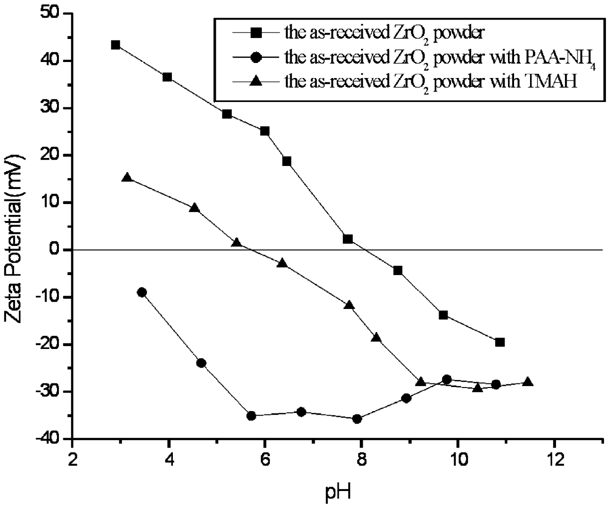

Fig. 3. Zeta potential versus pH of the as-received ZrO_2 powder with different dispersants.

$$MOH^+_{2(Surface)} \xleftarrow{H^+} MOH_{(Surface)} \xrightarrow{OH^-} MO^-_{(Surface)} + H_2O \tag{1}$$

where M represents the metal ion.

At the isoelectrical point the number of the positive charge sites presented by zirconia powder adsorbed H^+ ions is equal to the negative charge site of adsorption of OH^- ions, so the net charge equals zero, and the particles in the suspension can be easily agglomerated. Under strong acidic and basic conditions when more HCl or NaOH are introduced, the increased ionic strength in the suspension compresses the thickness of the double electric layer, resulting in the increase of the absolute value of zeta potential of the powder.

It can be seen that after addition of TMAH and PAA-NH_4 the isoelectrical point of zirconia powder shifted from pH 8.0 down to about pH 5.3 and 3.0, respectively. PAA-NH_4 is an anionic polyelectrolyte and can dissolve in aqueous solution, producing negatively charged carboxyl groups [shown in Eq. (2)], which are very easily adsorbed on the positively charged zirconia surface. Consequently the powder is negatively charged and this results in a shift of the isoelectrical point to a lower value. The dissociation of TMAH and PAA-NH_4 in water can be described as follows [10]:

$$RCOONH_4 \rightarrow RCOO^- + NH_4^+ \tag{2}$$

$$(CH_3)_4NOH \rightarrow (CH_3)_4N^+ + OH^- \tag{3}$$

The results in Fig. 3 indicate that PAA-NH_4 is a more effective dispersant for the nano zirconia powder than TMAH.

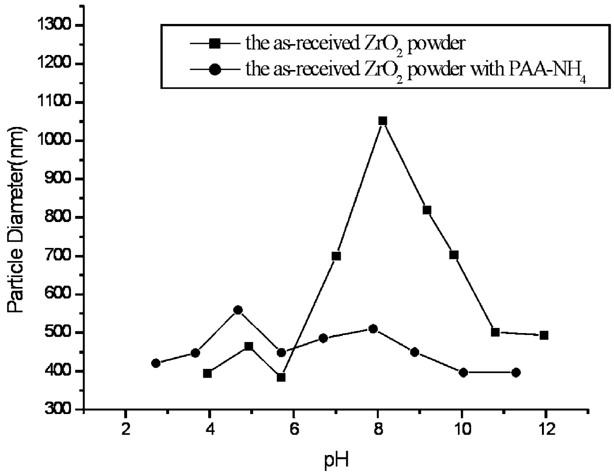

Fig. 4. Agglomerate size of the as-received ZrO_2 powder without and with PAA-NH4 at different pH values.

The size of zirconia agglomerates versus pH of aqueous suspensions was shown in Fig. 4. The agglomerate size was about 400 nm under the condition of $pH < 6$ or $pH > 10$ for the as-received zirconia powder. However, the agglomerate size reached 1050 nm at near pH 8, which shows a partial agglomeration state. Also, it can be seen that a relatively uniform size of about 500 nm was achieved in the wide pH range of 3 to 11 in the water leached zirconia powder with addition of PAA-NH_4. Compared to the particle size of the as-received zirconia powder, the agglomerate size appeared to have decreased after addition of the dispersant.

Fig. 5 presents the rheological property of the 50 wt.% zirconia suspension with different dispersants. A viscosity peak is seen for the suspensions without dispersant and with TMAH as a dispersant when shear rate was increased from 0 to 25 s^{-1}, which suggested that the suspensions were not well dispersed and had agglomeration. With the increase in the shear rate there are the obvious increase in the agglomeration role in the low shear rate area and the agglomeration was gradually

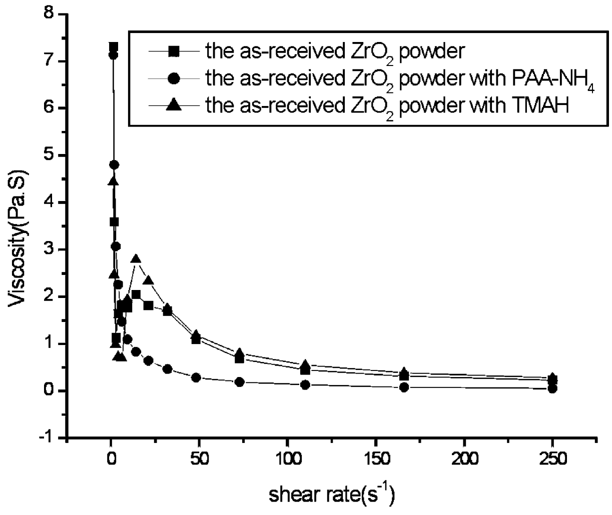

Fig. 5. The rheological property of the 50wt.% ZrO_2 suspension with different dispersants.

Table 1
Concentration of soluble ions of the ZrO_2 powder

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-
Supernatant of as-received powder	117.7	*	10.1	5.5	18.7	259
Water leaching supernatant	10.3	4.4	6.1	ND	8.5	63.6
Final supernatant	3.9	1.9	1.5	ND	1.8	17.1

Note: ND = Not Detected.
* NH_4^+ is covered by Na^+.

broken when shear rate was further increased. Then the viscosity decreased slowly and eventually showed a constant value at very high shear rates. TMAH appears not a good dispersant for the zirconia powder as little change was made in the viscosity behavior of the suspension containing TMAH. However, no viscosity peak was found in the suspension with addition of PAA-NH_4 and a constant low viscosity was reached when the shear rate was higher than 25 s^{-1}. The rheological study also indicates PAA-NH_4 to be an effective dispersant for the zirconia powder, which is in accordance with the data of zeta potential.

3.2. Effect of soluble counter-ions on aqueous dispersibility of the powder

The concentration of soluble ions of the as-received ZrO_2 powder and ZrO_2 powder with different water leaching process is shown in Table 1. The major soluble negative ion impurity is chlorine ion (Cl^-) in the as-received powder, which was introduced during the powder preparation process of chemical co-deposition. The major soluble positive ion impurity is Na^+ in the as-received powder, in addition to very lower concentrations of NH_4^+, K^+, Mg^{2+} and Ca^{2+}. The concentrations of Cl^-, Na^+, K^+, Mg^{2+} and Ca^{2+} ions decreased after water and weak-acid leaching which could eventually eliminate most of the positive and negative ions on the surface of zirconia powder.

Table 2 shows ion conductivity and pH value of the ZrO_2 powder at different stage of water leaching. The continuous decrease in ion conductivity after each water leaching indicated the gradual reduction in soluble impurity ions. There was an increase in ion conductivity of the supernatant after ion exchange because the high-valency positive ions on the surface of zirconia powder were replaced by Na^+ and released into the supernatant. Finally, there was almost no change in the ion conductivity. In addition, it can be seen that the pH value of the as-received powder in water was about 4.95, and it became about 6.8 after water and weak-acid leaching.

Table 2
Ion conductivity and pH value of the ZrO_2 powder

Supernatants	pH value	Ion conductivity (µs/cm)
Water leaching first time	4.95	855
Water leaching second time	5.23	351
Acid leaching	4.73	340
Water leaching third time	4.87	260
After ion exchange	6.37	560
Water leaching fourth time after calcination	6.31	281
Water leaching fifth time	7.94	92
Final supernatant	6.80	63.2

Fig. 6 illustrates the zeta potential versus pH of the leached ZrO_2 powder without and with the two dispersants in water. Compared to Fig. 3, the isoelectrical point of the powder after water leaching shifted from about pH 8 to about pH 3.5. Zeta potential did not change with pH value when the pH value is greater than 7. This may be attributed to the saturation of the charge adsorbed on the surface of powder. The addition of both TMAH and PAA-NH_4 has larger influence on the zeta potential under acid condition ($pH < 6$) compared to under basic condition ($pH > 7$). It can be seen that the isoelectrical point shifted to the acid region in both TMAH and PAA-NH_4 containing system compared to the data in Fig. 3. The absolute value of zeta potential of water-leached powder with addition of dispersant was increased from 30 to 50 mV under basic condition, which was responsible to a large extent the improve-

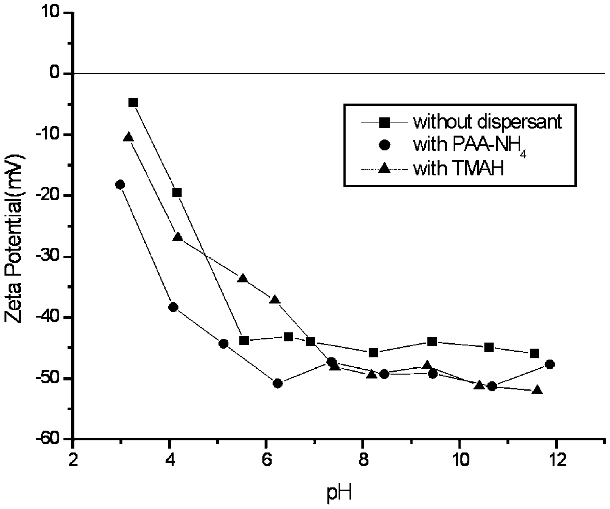

Fig. 6. Zeta potential versus pH of the ZrO_2 powder after water leaching (how many times?).

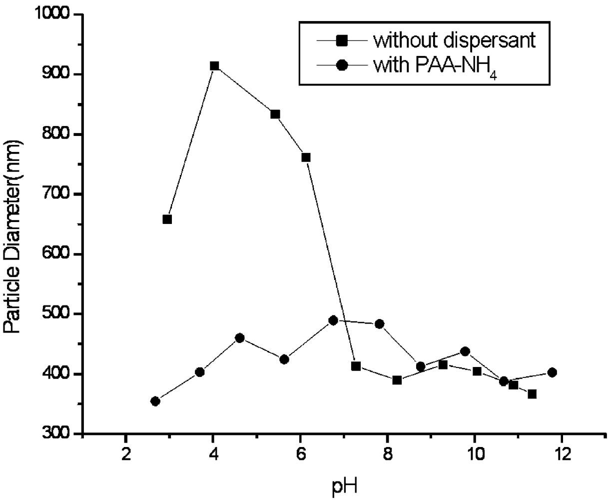

Fig. 7. Size versus pH value of ZrO_2 powder without and with PAA-NH4 after water leaching.

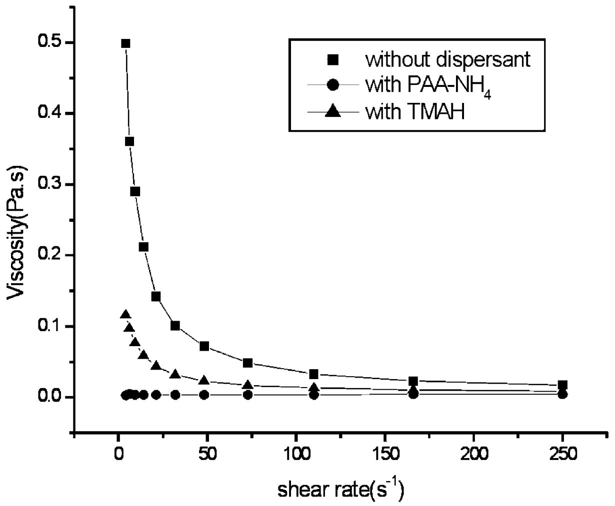

Fig. 8. The rheological property of the suspension prepared by the ZrO_2 powder after water-leaching.

ment of powder dispersion under basic condition. Therefore, it is thought that a basic condition would be suitable for the preparation of higher solid volume loading ZrO_2 suspensions.

Fig. 7 shows the correlation between size and pH of the water-leached zirconia powder in aqueous suspensions. Compared to the particle size of as-received zirconia powder, there was an obvious decrease in the particle size after water leaching, possibly due to the reason that particle size became lower is probably the agglomeration state of particles was broken when the soluble counter-ions was leached. It can be seen that the particle size is between 400 and 500 nm for a wide range of pH values in the dispersant-containing suspension after water leaching. However, a larger agglomerate size of 900 nm was formed in a pH range of 3–7 for the system without a dispersant.

Fig. 8 shows the rheological property of a 50 wt.% zirconia suspension without and with the two dispersants after water leaching. Compared to the curves of Fig. 5, there was an obvious decrease in viscosity for the water-leached suspensions under the same condition and no viscosity peak was seen with the increase in shear rate for the dispersant-free suspension, indicating little agglomeration and good dispersion for the water-leached powder compared to the as-received powder. Both suspensions without dispersant and with TMAH exhibited a shear thinning behavior at a wide range of shear rate. The viscosity of the suspension with an addition of PAA-NH_4 trends to a Newtonian liquid. The decrease in the viscosity illustrates adequately that the dispersant is easily adsorbed on the surface of particles, resulting in good particle dispersion after the elimination of soluble counter-ions on the surface of particles.

4. Conclusions

Both the addition of dispersant and elimination of soluble counter-ions are effective ways to improve the dispersion of nano-sized zirconia powder in deionized water. The dispersion of zirconia powder was described by measuring zeta potential, agglomerate particle size and rheological property of suspensions. The isoelectrical point of the zirconia powder in deionized water without a dispersant is near pH 8.0, and zeta potential decreases under both strong acidic and basic conditions. However, the isoelectrical point of zirconia powder shifts to a more acidic condition with the addition of both TMAH and PAA-NH_4 dispersants, and this shift is especially significant for the systems after elimination of soluble counter-ions and addition of PAA-NH_4.

PAA-NH_4 is a good dispersant for the nano-sized zirconia powder in deionized water and has significant effects on the zeta potential, agglomerate size and rheological property of the suspensions. To obtain a high solid volume loading of nano-sized zirconia suspension, it is necessary to take combined measures of eliminating the soluble counter-ions and introducing a proper dispersant.

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