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Effect of pH Value and Dispersant on Dispersibility of Silica Ceramic Slurry†

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In present work, the effect of pH value and the dosage of the dispersing agent on stability and dispersibility were evaluated. Sodium polycarboxylic acid was used as a dispersing medium for silica porous ceramic slurry. The stabilization mechanism of this kind of anion polymer polyelectrolyte in the slurries is attributable to the enhanced the effect of the electrostatic repulsion and the stereo hindrance and the zeta potential can get the highest value of 42.5 mV in addition of 0.06 % at pH = 9 in the silica ceramic slurry.

Keywords: Porous ceramic, Dispersant, pH value, Zeta potential, Anion polymer polyelectrolyte.

INTRODUCTION

In recent years, many methods have been successfully applied to fabricate porous ceramic such as polymeric sponge impregnation[1], gel-casting[2], extrusion[3], tape casting[4] and freeze casting process[5], *etc*. In the process of fabricating porous ceramics, energy consumption accounts for a substantial proportion of the production cost and an appreciable majority of this consumption is in the dry process. This is greatly interrelated with the forming method. Therefore, concentrated suspension with high solid loading, low viscosity and good stability is required during this forming processing. Preparation of high solid content slurry can increase the drying rate and removing the defects such as cracking, warping, bending and the other malformations. It is also one of the most efficient ways to improve the density and the yield of the sample.

The ceramic slurry is a complex mixture system of ceramic powder, solvent, binder, dispersant and other agents. The raw material component that is dispersed adequately is considered to be the most important factor affecting the quality and the processing properties of the ceramic products. Generally, pH value and the amount of dispersing agent in a slurry system can significantly improve the rheological properties of ceramic slurry, including viscosity, thixotropy and Newtonian fluid performance, *etc*.

Choosing a suitable dispersing agent at a certain pH value is very important to the large-scale commercial production of silica porous ceramics. In this study, we analyze the effect of pH value and the content of dispersant on the silica-based ceramic slurry.

EXPERIMENTAL

The starting powder consists of a mixture of 90 wt. % SiO_2, 5 wt. % $CaCO_3$, 4 wt. % Al_2O_3 and 1 wt. % MgO. The ceramic powders are mixed with 40 % solution of absolute ethyl alcohol and mill for 5 h at 400 rpm. After being dried at 80 ºC in an oven, the powders are granulated by mixing with poly(vinyl acetate). Thereafter, they were sintered for 1 h at 950 ºC using a high temperature furnace. After screening the mixed powders, the samples are obtained for analysis.

The slurry is carried out by including each of the components into 0.1 g samples of 100 mL deionized water. There after, pH values of the slurries are adjusted in the range from 2 to 13 using dilute HCl and dilute NaOH. We prepare various slurries with different dispersant concentrations (0.00, 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.30, 0.40 and 0.50 wt %) at pH = 9. The dispersion mechanism is analyzed by testing zeta potential of the suspensions and the testing is carried out according to JS94H Micro plasma electrophoresis apparatus.

RESULTS AND DISCUSSION

Influence of pH value: The dispersion and stability of the ceramic slurry correlates closely with its electric characteristics. Fig. 1(a) shows the effect of pH value of the slurry on zeta potential. The zeta potential increases first and then decreases with the increment of pH value.

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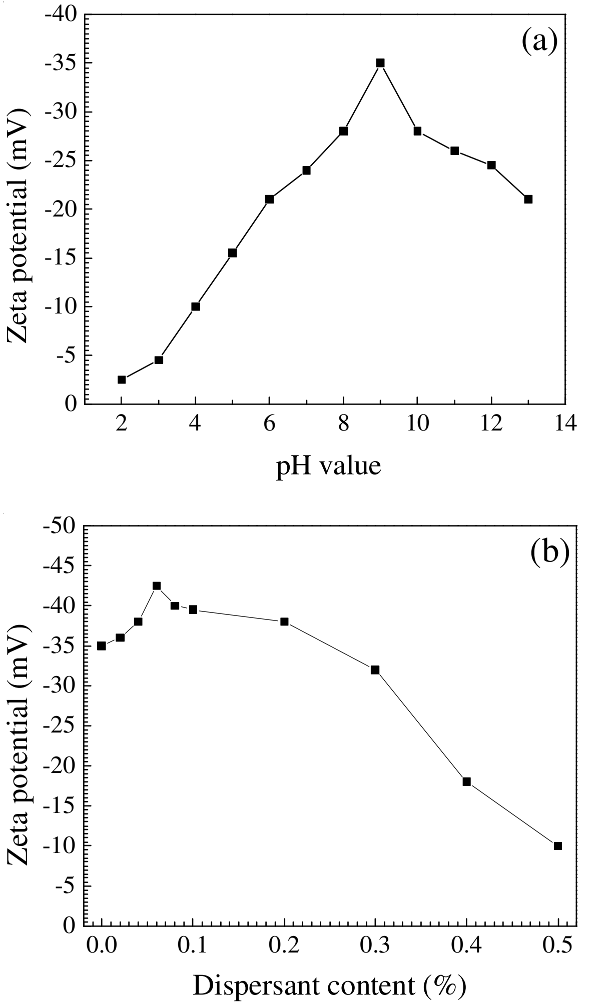

Fig. 1. Zeta potential of silica ceramic slurry in different pH value (a) and different dosage of dispersing agent (b)

It gets the highest zeta potential with the pH maintained at 9. This curve reflects that the slurry can obtain better dispersibility in alkaline conditions, while under acid conditions the dispersion of the slurry is poor. In aqueous dispersion, an important factor that affects its dispersion stability is pH value.

It is well known that zeta potential can reflect the surface charge of charged particles in the system. The greater the potential absolute value is, the thicker the double-layer is. This gives rise to the increase of the electrostatic repulsion between charged particles and the dispersions tend to stability. On the contrary, as zeta potential approaches zero, sedimentation of the particles will be much more obvious[6].

In the experimental pH value range of 2-13, the grains surface zeta potential is a negative value. This is due to the fact that silica powders can easily react with water and air to form silanol groups and the ionization of this kind of functional group can make the particle with electric charge. The sign of the charge and the charge density is determined by the pH value in medium. The reaction is given as follow:

$$\equiv Si-OH_2^+ \underset{}{\overset{H^+}{\rightleftharpoons}} \equiv Si-OH \overset{OH^-}{\rightleftharpoons} Si-O^- + H_2O \quad (1)$$

When pH value increased, more and more OH^- adsorb onto the particle surface, which make the double electrode layer thicken and the absolute value of zeta potential increase. At this point, electrostatic repulsion of charged ion gets stronger, which is advantageous to ensure the stability of the aquatic-solid systems.

However, when the pH value of the solution is higher than 9, there was a decreasing trend for zeta potential on SiO_2 particle surface. It is the consequence of excessive base solution introduce in inducing the increase of salt ionic concentration in solution. Thus, there is electrostatic repulsion between this newly admitted counter ion Na^+ and the original counter ion in the diffusion layer and a part of the original counter ion are squeezed into adsorption layer which cause a thinning of the diffusion layer and compress the electronic double layer thickness. Therefore, it led to the decrease of the absolute value of zeta potential.

Influence of dispersant: To generate ceramic suspension with high solid content, dispersing agent is introduced to the ceramic suspension[7,8]. Fig. 1(b) shows the effect of zeta potential with various contents of anionic polymer dispersant agent at the pH of 9. The result indicates that sodium poly-carboxylic acid dispersant has an optimum concentration range when the dosage of it ranges from 0.06 to 0.20 %. The absolute value of zeta potential increases up to -42.5 mV when the dosage is 0.06 %. However, when it is more than 0.20 %, the absolute value of zeta potential is lower and lower.

It is known that the poly-carboxylic acid type dispersant is a kind of anion polymer polyelectrolyte and the dissociation of these groups on their molecular chains can be the causal factor that makes the dispersant with negative charge. This type of dispersant with anchoring group which can tightly adsorb on the surface of ceramic particles through ionic bond, covalent bond, hydrogen bond and van der Waals force. And the solvent chain can fully extend in medium to form steric hindrance layer (Fig. 2(a)).

Sodium poly-carboxylic acid dispersant has the most excellent dispersing effect on the ceramic powders because of steric hindrance[9,10] and electrostatic repulsive[11]. This anion polyelectrolyte adsorbs on the electronegative ceramic particles surface to increase the surface negative charge. And the adsorption capacity of ceramic powders surface for $RCOO^-$ is enhanced as the dispersant concentration increase. Thus, the absolute value of interfacial potential increases with increasing adsorption capacity of polyelectrolyte, which caused in the increase of the electronic double layer thickness and the absolute value of zeta potential. Moreover, this type of dispersing agent with long polymer chain which can make space steric effect on ceramic suspensions and hinder collision agglomeration and gravity sedimentation between particles. However, the polyelectrolyte that adsorbs on the particles surface is no longer increasing when the adsorption is saturated. With the increase of the sodium poly-carboxylic acid dispersant content, the excessive polyelectrolyte enters into the aqueous solution. Based on Gouy-Chapman diffuse double layer theory, high concentration electrolyte has an important effect on compressing double electrical layer. Consequently, the absolute value of zeta potential and the distance between ceramic particles is decreased. The long polymer chains intertwine together and generate bridging effect of ceramic particles. Thereafter, it causes the coagulation of the slurry.

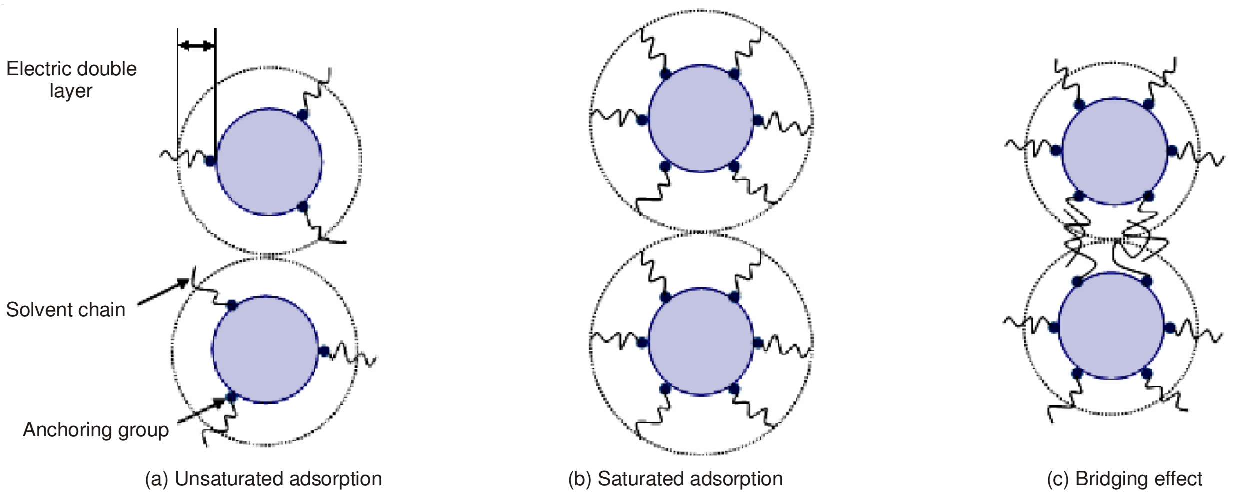

Fig. 2. Schematic illustration of the dispersant absorption on ceramic particle surface

Conclusion

In alkaline conditions, the ceramic slurry is provided with good dispersibility and the absolute value of zeta potential reaches the highest level at -35 mV with pH = 9. The dispersion of ceramic particles and the responsible for the fluidity increase caused by sodium poly-carboxylic acid dispersant, is related to both the electrostatic repulsion and the stereo hindrance. Only 0.06 % of dispersing agent is required at pH = 9, the absolute value of zeta potential reaches the maximum value of -42.5 mV, which is beneficial to disperse slurry.

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