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The zeta-potential measurement for concentrated aqueous suspension by improved electrophoretic mass transport apparatus – application to Al_2O_3, ZrO_3 and SiC suspensions

M. HASHIBA, H. OKAMOTO, Y. NURISHI, K. HIRAMATSU*
*Department of Chemistry, Faculty of Engineering, and *College of Technology, Gifu University, 1-1, Yanagido, Gifu 501-11, Japan*

The zeta-potentials for Al_2O_3, ZrO_2 and SiC particles in concentrated suspensions were determined by an improved mass transport apparatus in order to obtain reliable and reproducible data on particle dispersion in the slip casting process. The values of isoelectric point for each particle were as follows: pH $\simeq$ 8 for Al_2O_3, $\simeq$5 for monoclinic ZrO_2, $\simeq$6.5 for tetragonal ZrO_2, $\simeq$4 for α-SiC and $\simeq$5.5 for β-SiC. It was suggested that the values of zeta-potentials for those particles were affected by the chemical and physical state of the particle surfaces, i.e. crystal structure, comtamination and hydration, etc. The apparatus used in this experiment will be also available for use with suspensions containing surfactants in practical slip casting.

1. Introduction

The evaluation of surface characteristics of ceramic particles is very important in controlling the forming process such as dry pressing, slip casting, extrusion and injection moulding. For example, in slip casting the surface properties of particles in the medium affect the stabilization of a suspension which is attributed to balance between the van der Waals attractive forces and Coulomb repulsive forces caused by adsorbed ions on the particle surfaces [1]. The zeta-potential, which is an electrical potential at the slip plane between particles and medium, is an important guide to those interfacial properties. The determination of zeta-potentials has usually been conducted by the microscopic observation of moving particles or the moving boundary method [2]. However, these methods cannot easily be applied to concentrated suspensions. A simple mass transport apparatus, which is appropriate to investigating concentrated suspensions, has been presented and improved by a few investigators [3–7]. This method is based on the Hittorf method to determine transference numbers of electrolytes. The quantity of a suspended particle migrating to or from a collection cell is measured gravimetrically, after applying a desirable potential gradient to a suspension for a certain time, because the ratio of mass to charge of a particle is very large compared with that of an ion. The purpose of this paper is to determine the zeta potentials for concentrated suspensions containing high-temperature engineering materials such as Al_2O_3, ZrO_2 and SiC powders as part of the series of investigations on the dispersion of particles in the slip casting process.

2. Experimental details

Each powder used in this study was from a commercial source. Physical data for the powders are shown in Table I. Fig. 1 shows micrographs of powders observed in a transmission electron microscope (Hitachi H 800). The size of all particles was submicrometre or below. A suspension of each powder, 20% by weight, was first prepared and then an ultrasonic processor was used to deflocculate them. The pH of the suspension was adjusted by adding HCl or NH_4OH. Fig. 2 shows the experimental apparatus which was in some ways similar to that proposed by Visca *et al.* [6]. A few researchers [2–7] have previously pointed out some problems in mass transport measurement as follows: (1) choice of electrode, (2) contamination of the suspension by electrode materials, (3) Joule heating, and (4) particle settling, etc. Development of particle settling in a quiescent suspension gave rise to the difference of gravity of suspensions between collection cell and reservoir, thus the intermixing of suspensions occurred through an orifice and the cell increased in weight [5]. The characteristics of the apparatus used in this experiment were as follows. (1) An Ag/AgCl electrode was used as both anode and cathode, which was stable over long times during electrophoretic measurements. (2) Each electrode was connected through a salt bridge to the suspension in order to prevent the contamination by electrode materials. It also avoided the suspensions forming a dense barrier layer on the electrode. (3) A large orifice diameter (5 mm) was available to operate with lower applied current and to produce large weight changes in before and after runs. (4) When the surface of the suspension in the reservoir

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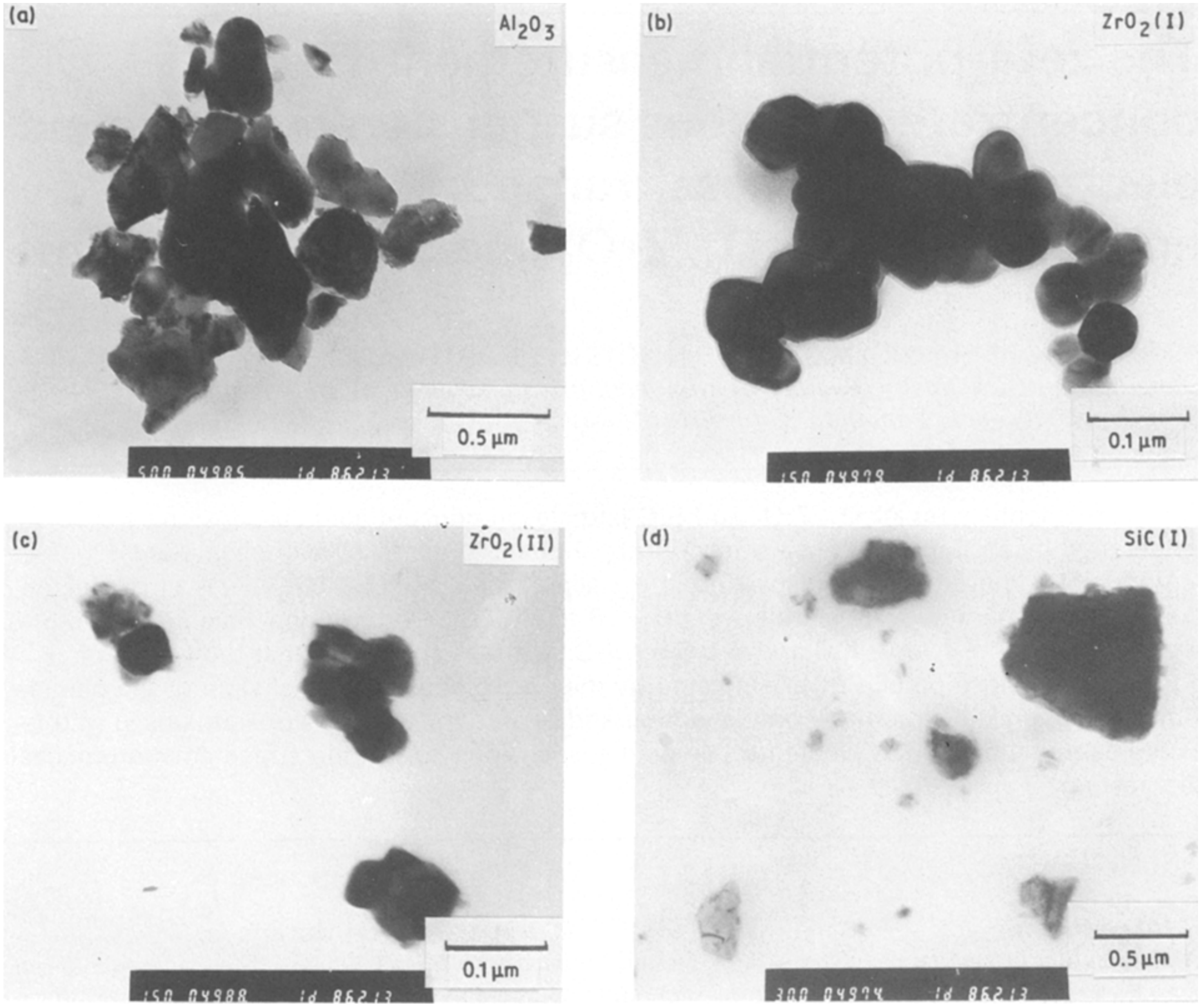

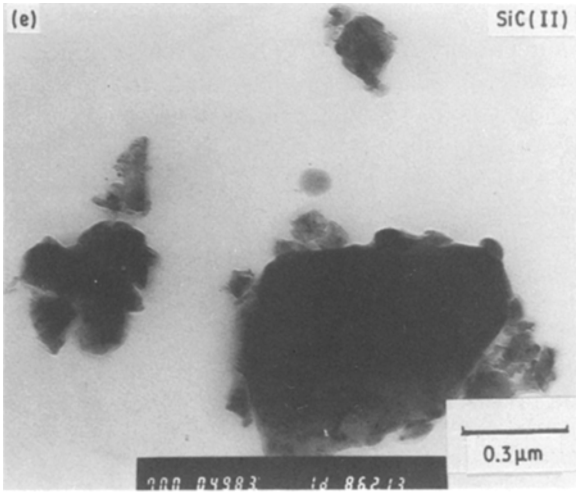

Figure 1 Transmission electron micrographs of Al_2O_3, ZrO_2 and SiC particles.

agreed with the upper level in the collection chamber, as shown in Fig. 2, settling problems could be minimized by allowing the same settling rate of particles in the collection chamber and reservoir. First the collection chamber of the cell was filled with the suspension. The cell was weighed carefully and then immersed in the same suspension as used in the reservoir. After electrical connections had been made, a suitable current was passed through the suspension. The current was stopped after a certain time, the cell removed from the reservoir and thoroughly rinsed with distilled water and then carefully wiped. The cell was weighed to determine the number of particles migrated. Electrophoretic mobility, v_e, of solid particles was calculated by the Long and Ross equation [3]

$$m = MEAtv_e(1/1 - f)(\varrho_s/\varrho_s - \varrho_m) \qquad (1)$$

where m is the amount of solids which moved into the chamber, M the concentration of solids in suspension, E the potential gradient applied to the suspension, A the cross-sectional area of the orifice, t the time, v_e the electrophoretic mobility, f the volume fraction of the solids, ϱ_s the specific gravity of the solids, ϱ_m the specific gravity of the medium, $(1/1 - f)$ the factor to correct for the counterflow velocity of the liquid forced out of the apparatus by the inflowing suspended material, and $\varrho_s/\varrho_s - \varrho_m$ the factor to convert change in mass of suspension to change in mass of solids (based on net weight gain = weight of solids moved in − weight of liquid moved out).

TABLE I Physical data of the powders used in this experiment

Powder	Grade	Crystal structure	Average grain size (µm)
Al_2O_3	Alcoa A16-SG	α	0.2
ZrO_2 (I)	Toyo Soda TZ-0	monoclinic	0.05
ZrO_2 (II)	Toyo Soda TZ-3Y (3 mol% Y_2O_3)	tetragonal	0.06
SiC (I)	Syowa Denko	α	0.5
SiC (II)	Syowa Denko	β	0.3

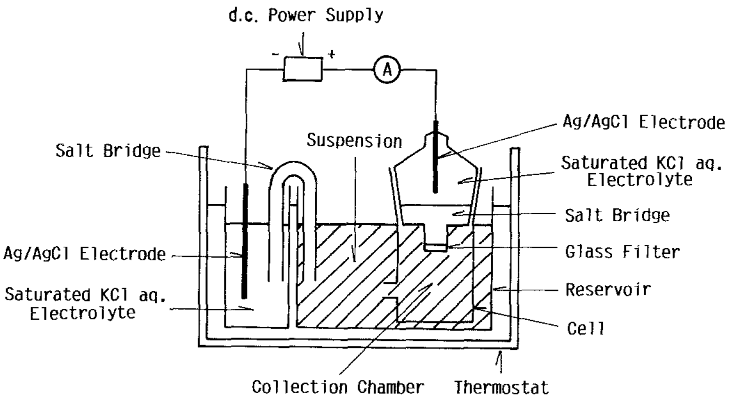

Figure 2 Electrophoretic mass transport apparatus.

3. Results and discussion

The potential gradient was computed from the current, the conductance of the suspension and the cross-sectional area of orifice of the cell. In order to confirm the reliability of mobility values obtained by this apparatus on concentrated suspensions, the correct operation of the apparatus must be checked by confirmation of the theoretical requirements, i.e. the linear relationship between weight gain or loss of the cell and the current passed through suspensions, and the linearity between mass transport rate and electric field strength. Figs 3 and 4 show that these relations are well satisfied.

Zeta potentials were calculated from the mobility, v_e, using the Smoluchowski equation [1]

$$\zeta = 4\pi\eta v_e/\varepsilon \qquad (2)$$

where ζ is the zeta potential, η the viscosity of the medium, and ε the dielectric constant.

Fig. 5 shows the zeta potential–pH curves for the suspensions of each powder. As shown in Fig. 5a, the curve for an alumina shows an isoelectric point (i.e.p.) at a pH of $\simeq 8$. The values of the i.e.p. for ZrO_2 (m) and (t) are at pH $\simeq$ 5 and 6.5, respectively (Fig. 5b). The i.e.p. values of these oxides agree with those compiled by Parks [8]. The surface charge of a particle may be formed by the following mechanism

$$MOH_2^+ \xleftarrow{H^+} M\text{-}OH \xrightarrow{OH^-} MO^- + H_2O$$

i.e. the hydroxides usually form at the oxide surfaces in an aqueous medium; the potential at the surfaces is controlled by the dissociation of hydroxyls or the adsorption of protons. Hunter [1] has pointed out that adding more acid at first causes an increase in zeta potential, but at higher acid concentrations the acid itself begins to contribute to the ionic strength; it will, therefore, affect an extension of the double layer, i.e. the electrical double layer is compressed, and zeta potential is diminished in magnitude.

As shown in Fig. 5, the decrease in zeta potential at low pH and the increase of that at high pH must be attributed to the compression of the double layer because of the increase of the concentration of the so-called counter ions at values of pH. Pask [9] has reported the effect of a small amount of active silica on the zeta potential of alumina particles; on ageing in a suspension at any pH or leaching by HF solution, the i.e.p. shifted from the original value. As seen from these results, the difference in the zeta potential between ZrO_2 (m) and (t) shows that it is necessary to take into consideration the stabilizing agent (Y_2O_3) and the crystal structures of ZrO_2 and also the contamination at the surfaces of those particles, i.e. the chemical and physical states at the particle surfaces considerably affect the zeta potentials and the i.e.p. values of those particles. Fig. 6 shows the curves for α-SiC and β-SiC. The i.e.p. for each suspension is at pH $\simeq$ 4 for α-SiC and pH $\simeq$ 5.5 for β-SiC. The i.e.p. for β-SiC was higher in value in comparison with that (pH $\simeq$ 3.5) reported by Persson *et al.* [10]. The surface of these particles are usually covered by thin films of silica [11]. When this thin film grows, the i.e.p. will reach a value near that of silica (pH = 2 to 3.7) [1]. Because the covalent bond of silicon carbide was strong in comparison with that of the oxide [12], its particle in

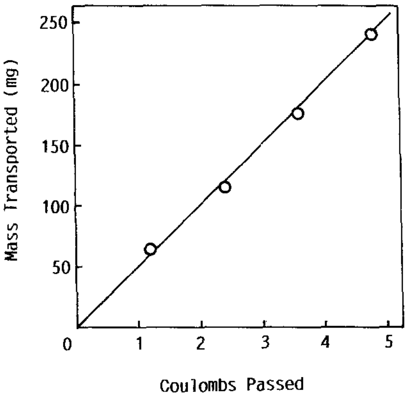

Figure 3 Linear relationship between weight change of the cell and the current passed through suspensions with 20 wt% Al_2O_3 at pH = 4.7.

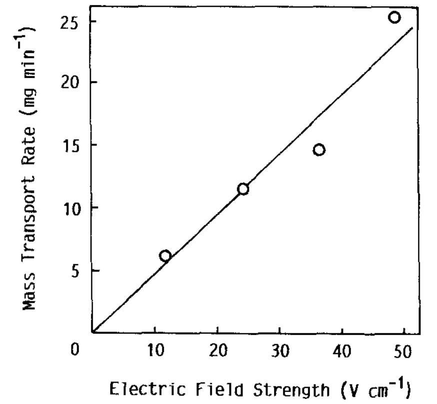

Figure 4 Linearity between mass transport rate and electric field strength for 20 wt% Al_2O_3 suspensions at pH = 4.7.

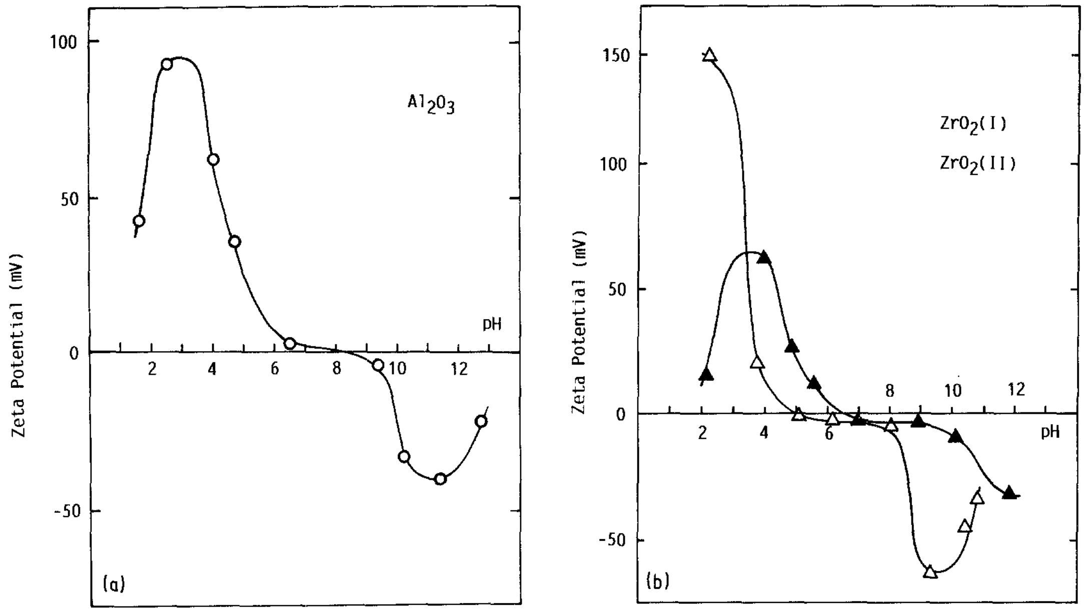

Figure 5 Plots of zeta potential against pH for (a) Al_2O_3 and (b) ZrO_2 suspensions.

the medium would represent a low wettability because of the hydrophobic property of the SiC particle; the particle surfaces must retain a low hydration state. As seen in Fig. 6, the causes of the absolute value of the zeta potential of SiC particle representing a low value in comparison with that of the oxide, have to be attributed to the low degree of hydration at the particle surfaces. In controlling the slip casting process, it is necessary to examine the properties of particle surfaces by electron spectroscopy for chemical analysis or Auger electron spectroscopy and to elucidate the relations between the zeta potential, the surface properties of particles, and rheological properties of suspensions. In conclusion, it was found that the simple electrophoretic apparatus improved by our laboratory was applicable to the concentrated suspensions containing Al_2O_3, ZrO_2 and SiC particles. This apparatus will be also available for use with suspensions containing surfactants in practical slip casting.

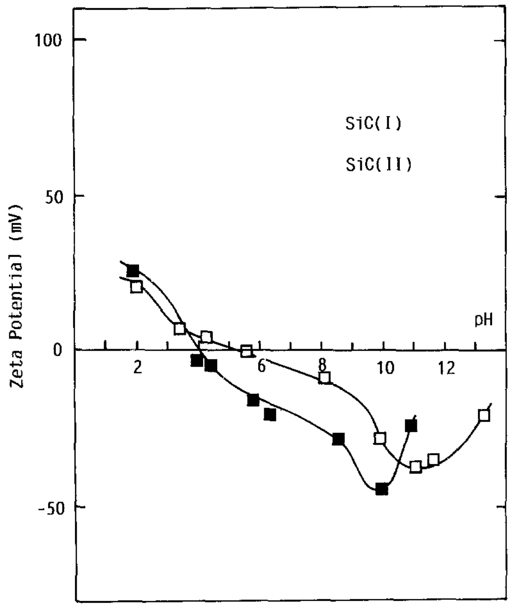

Figure 6 Plots of zeta potential against pH for SiC suspensions.

References

1. R. J. HUNTER, "Zeta Potential in Colloid Science" (Academic, London, 1981).
2. R. P. LONG and S. ROSS, *J. Colloid Sci.* **20** (1965) 438.
3. S. ROSS and R. P. LONG, *Ind. Eng. Chem.* **61** (1969) 58.
4. R. P. TISON, *J. Colloid Interface Sci.* **52** (1975) 611.
5. S. D. JAMES, *ibid.* **63** (1978) 577.
6. M. VISCA, S. ARDIZZONE and L. FORMARO, *ibid.* **66** (1978) 95.
7. P. SENNET and J. P. OLIVIER, *Ind. Eng. Chem.* **57** (1965) 33.
8. G. A. PARKS, *Chem. Rev.* **65** (1965) 177.
9. J. A. PASK, *Bull. Amer. Ceram. Soc.* **58** (1979) 1163.
10. M. PERSSON, L. HERMANSSON and R. CARLSSON, "Ceramic Powders", edited by P. Vincenzini (Elsevier, Amsterdam, 1983) p. 735.
11. T. SASAKI, Y. FUKATSU and T. ISEKI, *Yogyo-Kyokai-Shi* **95** (1987) 646.
12. L. PAULING, "The Nature of the Chemical Bond," 3rd Edn (Cornell University Press, New York, 1960).

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