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Rheological and Electrophoretic Deposition Behavior of ZnO Nano-powder in Aqueous Suspensions

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It is of interest in preparing uniform deposits of nano-ceramic materials in aqueous suspension. In this study, the rheological behavior and electrophoretic deposition (EPD) of ZnO nano-powders were investigated. A polyelectrolyte, polyethylenimine(PEI), is used to disperse ZnO nano-powders in an aqueous suspension, and the rheological properties of ZnO suspension were studied by measuring viscosity versus pH and dispersant amount. The EPD was carried out using well-dispersed suspension by depositing the positively-charged particles on palladium cathode and the deposit behavior was explored. Bubble-free deposits of nano-ZnO with uniform microstructure were successfully obtained.

Key words: Nano-ZnO, electrophoretic deposition, rheological properties, aqueous suspension

1 INTRODUCTION

Increasing interests have been focused on the processing strategies of inorganic ceramic materials [1-3]. Electrophoretic deposition (EPD) is a straightforward method for the assembly of charge-carried particles on electrode from stable colloidal suspensions by a DC electric field [4]. Compared with other conventional considering procedures, the thickness and morphologies of obtained materials via EPD can be controlled precisely by varying electrochemical parameters; moreover, uniform and complex-shaped deposits with high green densities on the electrode is obtained readily with a high deposit speed, it is prominent in the case of the suspensions of nano-powders. Non-aqueous suspensions have been often chosen to obtain bubble-free materials [5]. EPD in aqueous media should have the advantage of non-aqueous media due to the low environmental and financial cost [6]. However, it is a challenge using aqueous suspension to suppress the electrolysis of water, which causes the formation of bubbles. Our previous studies have shown that the bubble-free deposits are successfully obtained by depositing onto palladium cathodes because palladium readily absorbs hydrogen caused by electrolysis of water [7].

ZnO is well-known as a semiconductor material with a band gap of 3.2 eV, which has potential application to sensors, solar cells, photo-electronic devices, etc. However, very few works have focused on the colloidal behaviors of ZnO powders [8]. We are interested in the rheological and the EPD properties of nano-sized ZnO powder since the stability of the suspension affects the deposition characteristics. It is well known that ZnO is a amphoteric oxide, ZnO is hydrated to form Zn(II) cation at acidic pHs lower than 6.3, and it forms hydroxide layers in water at basic pHs, $Zn(OH)_2$ is in equilibrium with the species of Zn^{2+}, $Zn(OH)^+$, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$. In this study, pH range of 7 – 11 is chosen to prepare suspension, where the ZnO particle is usually negatively charged. In order to get bubble free deposits by using palladium cathode, ZnO particle should be positively charged. A cationic electrolyte was used to give the ZnO particles positive charge potential and good dispersion in aqueous media. Dense, bubble-free ceramic deposits with uniform microstructure were fabricated using nano-sized ZnO by aqueous EPD processing.

2. EXPERIMENTAL PROCEDURE

ZnO nano-powder with an average particle size of 40nm was used. A polyelectrolyte, polyethylenimine (PEI: $-(CH_2-CH_2-NH-)_n$) with an average molecular weight of 10000 was used to modify the ZnO nano-powder and 5vol% ZnO aqueous suspensions were prepared. Zeta potential (ζ) versus pH of the suspensions was measured on a zeta-potential analyzer (LEZA-600, Otsuka Electronics Co., Ltd.) in a 10^{-2} mol dm^{-3} NaCl solution. The rheological properties of the ZnO suspensions were studied on an R-type rotational viscometer (RC-500, Toki Sangyo Co. Ltd.). The EPD was performed using a dc power source operating at a constant current of 3 mA cm^{-2}. A stainless steel sheet was used as an anode and a palladium sheet with a deposition area of 8 cm^2 was used as a cathode. They were faced with each other at a distance of 2cm. The relation between the deposit weight and time was investigated at different suspension pHs. After drying, the deposits were separated from the substrate and sintered at different temperatures. The green densities of the ZnO compacts were measured by Archimedes' method. The microstructure of obtained green compacts was observed by a scanning electron microscope (JSM-5400, JEOL Inc., Japan).

3. RESULTS AND DISCUSSION

3.1 Zeta potential of ZnO powder

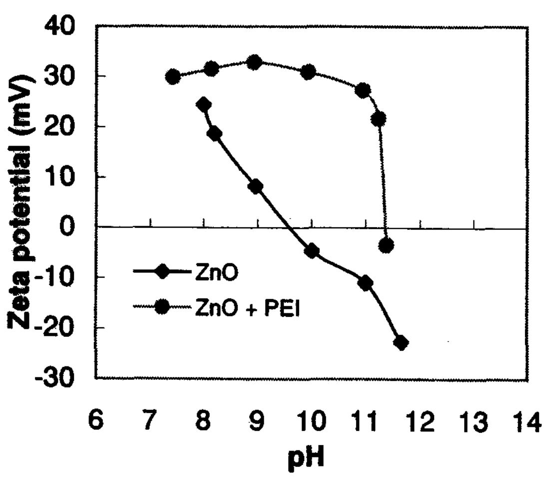


Fig. 1 ζ-potential of ZnO with and without PEI addition

Since ZnO is easily dissolved in acid, ζ potential of the ZnO nano-powder was measured in basic pHs, which is shown in Fig. 1. The isoelectric point (IEP) of the powder is *ca.* pH = 9.6. ZnO has relatively high positive charge at about pH 8, and it decreases until IEP and then turn into negative charge with further pH increasing. PEI addition gives the ZnO surface high positive charge in the pH region of 7-11, the surface charge changes to negative rapidly above pH 11 and the IEP moves to pH 11.3 (Fig. 1), indicating that the PEI is an effective dispersant to modify the ZnO nano-powder. PEI has imido groups, —NH, which are ready to adsorb protons in the solution and it charges positively according to the following reaction [9]:

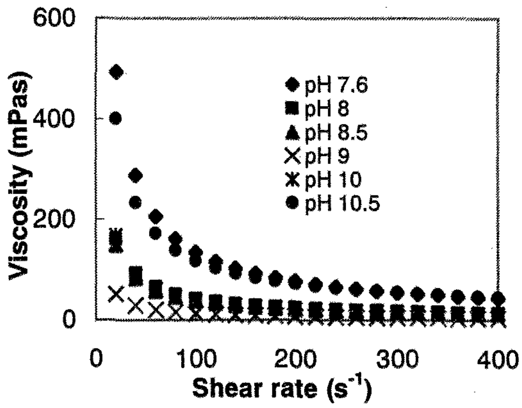
$$-(CH_2-CH_2-NH-)_n + H_3O^+ \longrightarrow -(CH_2-CH_2-NH_2^+-)_n + H_2O \quad (1)$$

Fig. 1 shows that surface modified ZnO particles with PEI could be deposited on the cathode in the pH 8 to 11 when a dc electric current is supplied.

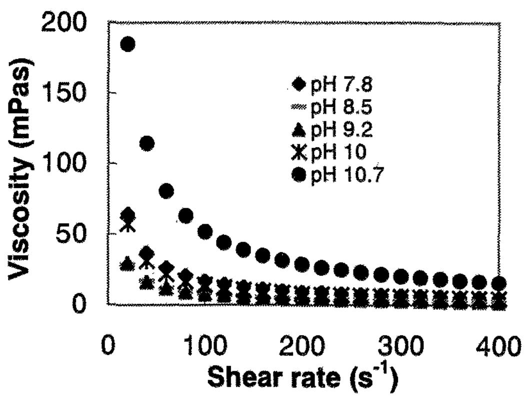
3.2 Rheology of ZnO suspensions

Rheological behavior of the ZnO suspensions was characterized by measuring their viscosity and shear stress. In the absence of PEI or small amount of PEI less than 0.5 wt%, the suspensions were too viscous to measure the viscosity with our equipment at any pHs. Fig. 2 shows the viscosity of 5vol% suspensions versus shear rate with the variation of pH and the amount of PEI (1 wt%, 1.5 wt% and 2 wt%). In the ranges of pH < 8.5 and pH > 10, regardless of the amount of PEI, the viscosities of the suspensions are shear thinning with the increase of shear rate, which are characteristics of pseudoplastic fluids, indicating the flocculation of the suspensions. In the range of 8.5 < pH < 10, the viscosities of the suspensions almost remain constant under different shear rates, which are characteristics of Newtonian fluids, indicating the well dispersion of the suspensions.

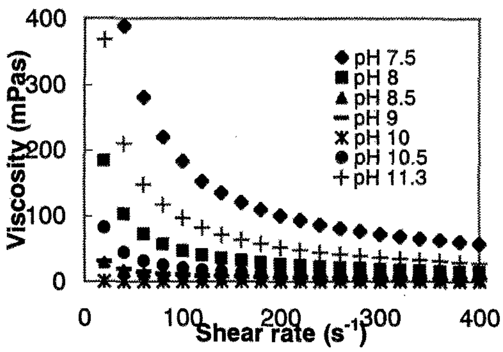
Fig. 2 also indicates that the viscosities of the suspensions with 1.5 wt% and 2 wt% PEI contents are lower than that with 1 wt% PEI. It is considered that stable suspensions with the lowest viscosity in the range pH 8.5 - 10 should be suitable for EPD. Hence, EPD properties were investigated for the suspensions in this pH region with 1.5 wt% and 2 wt% PEI additions.



(a)



(b)



(c)

Fig. 2 Viscosity of 5 vol% ZnO suspensions *vs*. pH with (a) 1 wt% (b) 1.5 wt% (c) 2 wt% PEI addition

3.3 Electrophoretic deposition behavior of ZnO particles

Fig. 3 shows the deposit weight of the 5vol% ZnO suspensions *vs*. time during EPD prepared at different pH with 1.5 wt% PEI contents. The deposit weight nearly increases linearly with deposition time in the measured pH

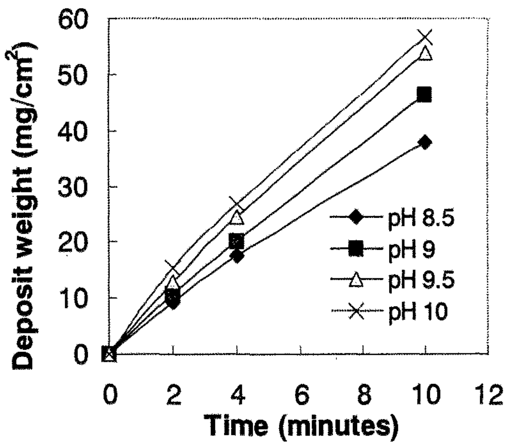


Fig. 3 Deposit weight of 5vol% ZnO *vs*. time at different pH with 1.5 wt% PEI addition

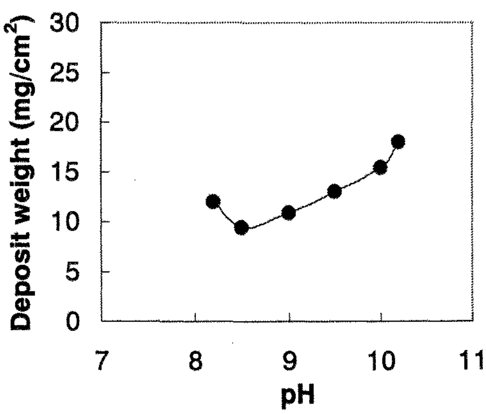


Fig. 4 Deposit weight of ZnO suspensions *vs*. pH with 1.5 wt% PEI content deposited for 2 min

region. Fig. 4 shows the deposit weight after the deposition for 2 min. *vs*. pH, which is related to the viscosity of the suspension. In this experiment, no deposition occurred at pH < 7.8 and pH >10.5 probably because it is very difficult for the particles to move for the oppositely charged electrode in a too much viscous suspension. The deposition rate in the pH range of 10-10.5 is higher than that in pH 8.5-9.5 depending on the amount of PEI addition. This is because some flocculation of the suspension can enhance the deposition rate to some extent [10]. However, this kind of deposit easily slips off because of the low deposit density, and dense, thick films are not obtained in this pH region. In the case of pH 8.5-10, though the deposition rate is a little lower, steady and thick deposits were prepared.

Therefore, the deposits obtained in this pH region were sintered to observe microstructure.

3.4 Density and microstructure of green bodies

Green densities of the deposits prepared in the pH range of 8.5 - 10 with different PEI content are between 43 % and 45 %, which are good enough for nano-sized powders. All the surfaces of the green bodies looked to be uniform and they had no bubbles caused by water electrolysis. Figs. 5 shows the typical SEM photographs of the surfaces. SEM images show that bubble-free deposits with uniform surfaces are readily prepared using the EPD processing.

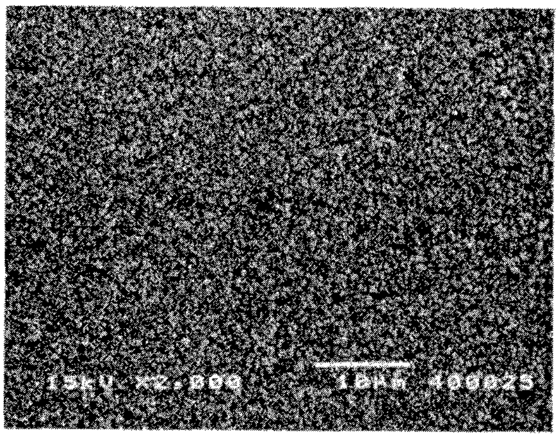


Fig. 5 Microstructure of green bodies with 1.5 wt% PEI addition at pH 9

4. CONCLUSIONS

PEI is an effective surfactant to disperse the nano-ZnO suspensions and modify the particles positively charged. Well-dispersed ZnO suspensions were obtained in the pH range of 8.5-10 with 1-2 wt% PEI addition, which are suitable for EPD processing. Uniform and bubble-free nano-ZnO deposits have been obtained in this experiment. Aqueous EPD processing was demonstrated to be an easy approach to produce dense, uniform, bubble free nano-ceramic deposits on palladium cathode, which has significant potential for the economic mass production of a wide variety of components.

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