

Fabrication of Bubble-free Compacts from Aqueous Suspensions by Electrophoretic Deposition

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Electrophoretic deposition (EPD) characteristics of positively-charged particles onto a cathode were investigated using aqueous alumina and zirconia suspensions. The deposition was performed using several kinds of metal substrates at different current densities. For most substrate materials, a large number of macro pores were introduced in the deposit and their size increased as the current density increased. However, no macro pores were formed in the deposit on a palladium substrate, regardless of the current density. The green density and sintering properties of the EPD deposits on a palladium substrate from aqueous suspensions were the same as from slip casting. Bubble-free alumina/zirconia laminate composites were also fabricated by EPD from aqueous suspensions.

Key words: Electrophoretic deposition, aqueous suspension, palladium substrate

1. INTRODUCTION

Electrophoretic deposition (EPD) is a colloidal processing technique for ceramics[1]. It has been employed to fabricate thin films, multilayered composites, functionally graded materials, *etc.*[2]. Non-aqueous suspensions are usually preferred for the EPD procedure to avoid the electrolysis of the solvent and obtain a bubble-free deposit[1,2]. However, an aqueous system has the advantages of low-cost processing, lower electrical potential requirement and lower environmental cost.

Water is decomposed into hydrogen and oxygen when dc current is passed between a pair of electrodes immersed in an aqueous suspension. The voltage (V) applied across the electrodes can be divided into three components. There are the decomposition voltage (E_D), the overvoltage at electrodes (E_O) and the voltage drop due to the ohmic loss in the interelectrode gap that is the product of the cell current (I) and the electrical resistance (R).

$$V = E_D + E_O + IR$$

The reversible decomposition voltage of water is 1.23 V at 25 °C and atmospheric pressure[3]. Under the practical operation conditions of EPD, no gas evolution is observed until at higher voltages owing to the overvoltage and ohmic losses. The overvoltage involves two contributions. Activation overvoltage results from the slowness of the electrode reaction. It varies with the electrode material and its surface condition. Concentration overvoltage arises as a result of drop of the concentration of carrier species, or surface-charged particles and ions, close to the electrodes. Ohmic losses are originated from the electrical resistances of suspension and the deposit layer on a substrate.

Some trials have been conducted for the fabrication of a bubble-free deposit from an aqueous suspension. The simplest method is to

reduce the applied voltage lower than the decomposition voltage of water, but the deposition rate is too low and it is not practical. Ryan *et al.* [4, 5] used porous molds expecting the generated gas would pass through the mold and it would reduce the trapped gas in the deposit. Clasen[6] suppressed the bubble formation in a compact by depositing on a microporous membrane which was placed in front of an electrode. Other studies involve the absorption of generated oxygen gas with the electrode using negatively-charged particles and an easily oxidizable anode like Zn[7-10]. In this case, metal cations of the substrate easily come out and contaminate the deposit. In this study, the EPD characteristics of positively-charged particles onto various cathodic substrates were investigated using an aqueous alumina suspension. Fabrication of zirconia/alumina laminate composites was also attempted by EPD from zirconia and alumina aqueous suspensions.

2. EXPERIMENTAL PROCEDURE

Alumina (Sumitomo Chem. Co., Ltd. AKP-50, average particle size of 0.20 μm) and zirconia

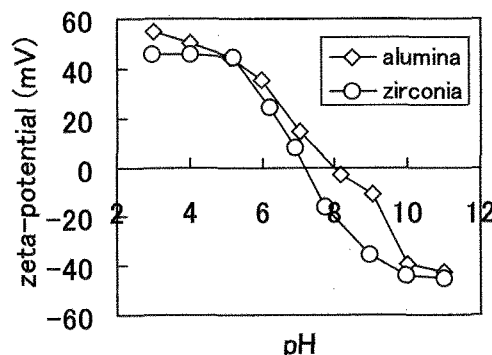


Fig. 1 Zeta potential of alumina and zirconia as a function of pH.

(Tosoh TZ-3Y, 60 nm) powders were dispersed at pH 4 in distilled water by ultrasound and aqueous suspensions of 5 vol% of solid were formulated. Analytical grade HNO_3 solution was used for pH adjustment. Figure 1 shows the zeta potential as a function of pH for alumina and zirconia aqueous suspensions. The zeta potentials of alumina and zirconia at pH 4 are +51 mV and +45 mV, respectively, which values are sufficiently large to keep the suspensions stable.

EPD of alumina particles was carried out at a constant current condition of 0.25–1.50 mA/cm^2 . The suspension was slowly stirred using a magnetic stirrer during the EPD. Four kinds of metal sheets, nickel, platinum, palladium and stainless steel, were used as a cathodic substrate. A stainless steel sheet was used as an anode. The electrode distance was 2 cm. Voltage variation between the electrodes was monitored during the constant current deposition. Deposits were dried at room temperature and separated from the substrate. The deposit surfaces formed on various substrates were observed by an optical microscope and a scanning electron microscope (SEM). To investigate the presence/absence of bubbles in the deposit, internal microstructure was observed by SEM for the polished surfaces after the sintering at 1350 °C for 2h. Bulk density of as-deposited bodies was measured by Archimedes' method using kerosene.

Laminate composites were fabricated by sequential deposition alternatively changing the zirconia and alumina suspensions. Samples were dried after the deposition and separated from the electrode. The laminates were sintered at 1400 °C for 2h. Microstructure observation was conducted by SEM.

3. RESULTS AND DISCUSSION

3-1. Effect of substrate materials on the formation of bubble-free deposits

The voltage variation as a function of time during a constant current deposition at 0.75 mA/cm^2 is shown in Fig. 2. The voltage jumped

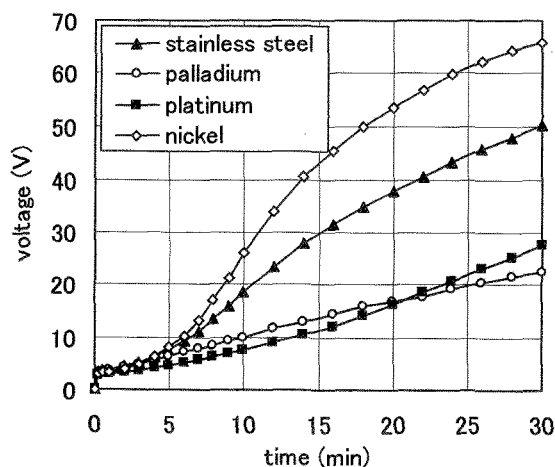


Fig. 2. Voltage variation as a function of time during constant-current deposition at 0.75 mA/cm^2 .

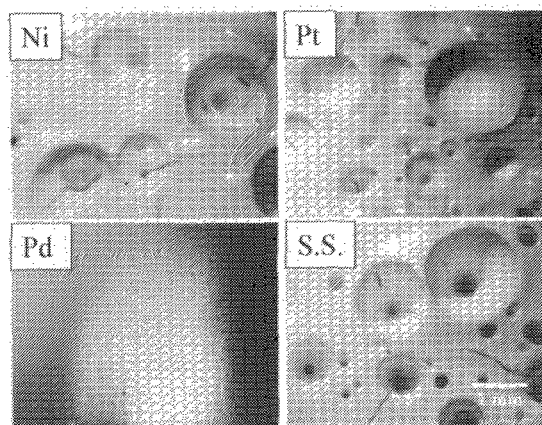


Fig. 3. Micrographs of the alumina deposit surfaces formed onto various substrates at a constant current density of 0.75 mA/cm^2 .

up in the first ten seconds followed by gradual increase with deposition time. The measured voltages were different with substrate materials probably because of the difference of deposition rates. The voltages were considerably higher than the theoretical decomposition voltage of water during EPD for all the substrates. Figure 3 shows the optical micrographs of the deposit surfaces after the deposition for 30 minutes at 0.75 mA/cm^2 . A lot of macro pores are observed on the surfaces of the deposits formed on the nickel, platinum and stainless steel substrates. However, no macro pores are observed for the deposit on the palladium substrate. Titanium substrate also gave a similar porous deposit though it is not shown here. This result is probably due to the excellent hydrogen absorbability of palladium. The effect of the variation of current densities on the bubble formation was compared using the stainless steel and palladium substrates. The voltage variation during a constant-current deposition at 0.25–1.50 mA/cm^2 is shown in Fig. 4. During the EPD the

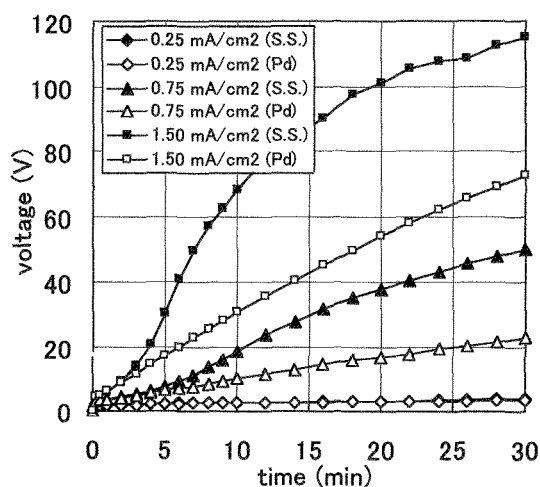


Fig. 4. Voltage variation as a function of time during constant-current deposition onto the stainless steel (S.S.) and palladium (Pd) substrates at 0.25–1.50 mA/cm^2 .

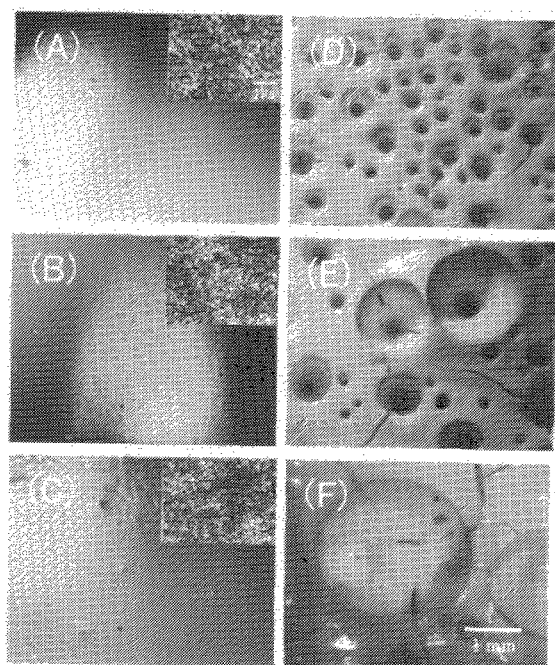


Fig. 5. Micrographs of the alumina deposit surfaces formed on a stainless steel (S.S.) and a palladium (Pd) substrate at various current densities: (A) Pd-0.25 mA/cm², (B) Pd-0.75 mA/cm², (C) Pd-1.50 mA/cm², (D) S.S.-0.25 mA/cm², (E) S.S.-0.75 mA/cm², (F) S.S.-1.50 mA/cm².

voltages were much higher than the theoretical decomposition voltage of water for all the experiments. Figure 5 shows the optical and scanning electron micrographs of the deposit surfaces after the deposition for 30 minutes at various current densities. Stainless steel substrate gives porous deposits and the size of the pore increases with current density. However, no macro and micro pores are observed for the deposits on the palladium substrate regardless of current density. Green densities of the as-deposited bodies are shown in Table I. Green densities of the deposits on the stainless steel substrate are low and the value decreases with current density. However, green densities of the

Table I. Green densities of the EPDed compacts on the stainless steel (S.S.) and palladium (Pd) substrates at different current densities. The compact formed on the stainless steel at 1.50 mA/cm² was too brittle to measure the green density.

	current (mA/cm ²)	relative density (%)
S.S.	0.25	50.5
S.S.	0.75	46.6
Pd	0.25	60.5
Pd	0.75	60.6
Pd	1.50	60.5

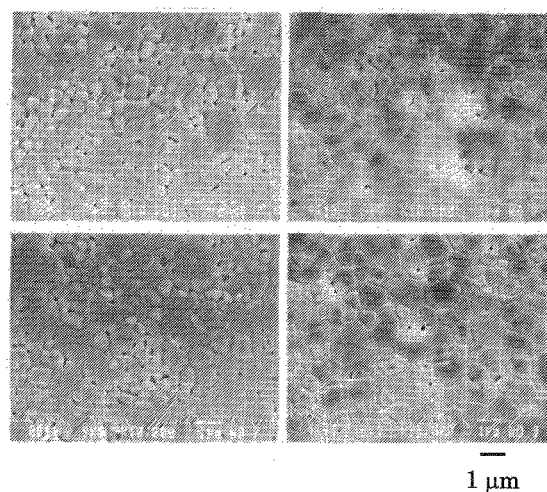


Fig. 6. Sintered microstructures alumina from EPD onto a Pd substrate and by slip casting with a plaster mold: (A) Pd-0.25 mA/cm², (B) Pd-0.75 mA/cm², (C) Pd-1.50 mA/cm², (D) slip casting.

deposits on the palladium substrates are high and the value is constant regardless of current density. Figure 6 shows the sintered microstructures of the deposits on the Pd substrate (A-C) and by slip casting with a plaster mold (D). Slip casting was carried out using another suspension prepared at the same condition. It is probable that some small pores in the EPDed bodies are not originated from hydrogen bubbles but owing to the lowness of sintering temperature because those pores are also observed in the slip-casted body. Making use of palladium substrate is simple and effective method to eliminate large pores originated from the hydrogen bubbles.

3-2. Synthesis of laminate composites

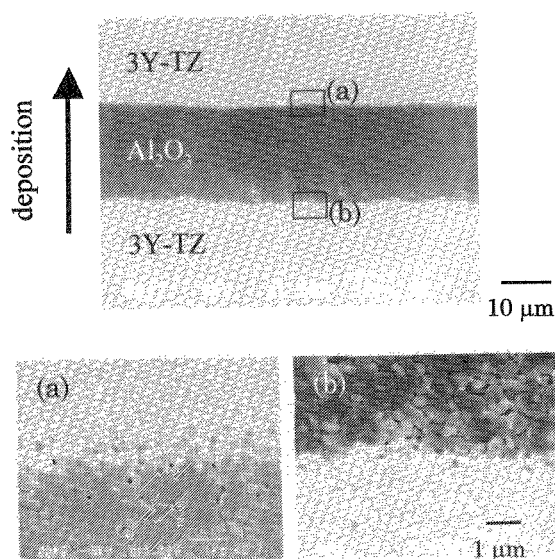


Fig. 7. SEM micrographs of 3Y-TZ/Al₂O₃ laminated composite from aqueous alumina and zirconia suspensions.

Fabrication of zirconia/alumina laminate composites from zirconia and alumina aqueous suspensions was performed using a palladium substrate. Varying the deposition time under a constant current mode controlled the thickness of each layer. Microstructure of the laminate composite is shown in Fig. 7. Interfaces of each layer are well bonded and no bubbles are observed in the deposit. It is demonstrated that EPD is an effective technique to synthesize laminar ceramic composites even from aqueous suspensions.

4. CONCLUSIONS

Generally, EPD from aqueous suspensions produces deposits containing bubbles. However EPD onto palladium substrates produces bubble-free deposits since palladium electrodes absorb hydrogen caused by electrolysis of water. The green density and sintering properties of the EPD deposits on a palladium substrate from aqueous suspensions are the same as from slip casting. This simple and useful method will replace the use of non-aqueous suspensions with aqueous ones for EPD processing.

Acknowledgement

The authors wish to thank Prof. P. S. Nicholson at

McMaster University and Dr. P. Sarkar at Alberta Research Council for their valuable comments.

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(Received December 17,1999 ; Accepted February 15,2000)