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Hydrothermal and electrophoretic deposition of lead zirconate titanate (PZT) films

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Abstract

Hydrothermal synthesis in conjunction with colloidal processing has been used to make PZT films in an aqueous solution. Fine PZT powders with a particle size of 200 nm and a narrow particle size distribution were synthesised hydrothermally at 300°C. After washing, a dispersant (di-ammonium citrate) was added to the slurry to make a stable suspension. Electrophoretic deposition (EPD) was then employed to deposit PZT films directly from the hydrothermal PZT suspensions. The effects of the synthesis conditions on the particle size and size distribution of the PZT powders are briefly discussed. Various stabilisation mechanisms for the hydrothermal slurries have been investigated. The effects of the slurry properties and deposition parameters on the microstructure of deposited films are discussed. It is shown that PZT films with a thickness < 5 μm can be deposited via EPD on Pt wires. However, the limitation of electric field, which must be below the decomposition voltage of water, resulted in an inferior packing density during deposition. The films had to be sintered at relatively higher sintering temperatures (> 1000°C) in comparison with powder compacts. In addition, interaction with the substrate was observed when PZT films were deposited and sintered on Pt-coated alumina substrates.

Keywords: Films; Hydrothermal; PZT; Suspensions

1. Introduction

Lead zirconate titanate (PZT) is a ferroelectric ceramic material used extensively in piezoelectric applications such as sensors and actuators. One of the main problems in fabricating reliable and high performance PZT ceramics by conventional solid-state reaction routes is the volatility of PbO at high temperatures (> 900°C). The loss of PbO in both the calcination and sintering stages will lead to fluctuation in the PZT composition which, in turn, strongly affects the sintering behaviour and the electromechanical properties. Low temperature processing of PZT ceramics, therefore, is desirable. Hydrothermal processing offers a way for low temperature synthesis of nano-sized ceramic powders in aqueous solution. Low temperature sintering is possible with nano-sized powders because of their high surface areas. However, nano-sized powders are very susceptible to agglomeration and hard agglomerates are likely to be formed during the drying of nano-powders from solution. One possible way to overcome this is to carry out the shape forming process directly from the hydrothermal slurries. We have shown that PZT ceramics fabricated using colloidal processing (direct coagulation casting) of hydrothermally synthesised slurries can be sintered at temperatures as low as 850°C.[1] Electrophoretic deposition (EPD) is a colloidal processing method which has been used for fabricating ceramic thick films and coatings.[2] In this paper, the hydrothermal and colloidal processing of PZT films is reported.

2. Experimental

PZT powders were synthesised hydrothermally at temperatures up to 300°C for 2–6 h from lead acetate trihydrate, zirconium acetate solution and tetra-iso-propyltitanate. KOH was used as a mineraliser. The detailed procedure is described in reference.[3] After synthesis, the PZT suspension was washed and centrifuged repeatedly

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until the supernatant became pH 7. A dispersant, diammonium citrate (DAC, $NH_4OOCCH_2C(OH)(COOH)CH_2COONH_4$), was then added. The particle size distribution was measured using a laser diffraction particle size analyser (Coulter LS 130). The surface charge of the PZT particles in suspension was studied through the measurement of electrophoretic mobility (Coulter Delsa 440) on 1 vol.% powder suspensions in the presence of 0.01 M KNO_3 aqueous solution which acts as a buffer to suppress the effect of counter ions on the electrophoretic mobility. EPD was then used to make PZT films. Two parallel electrodes were placed at a separation distance of 2 mm in the suspension. A stainless steel plate and a substrate (Pt wire or Pt coated alumina) were attached to the negative and positive electrodes, respectively. A DC voltage of 4 V was applied between the elecrtrodes in the static suspension. The deposition time was varied from 5 to 30 min. The PZT films were sintered in a Pb-rich atmosphere at 1100°C for 5 min. The microstructure of the films was characterised using a scanning electron microscopy (JEOL JSM 5410) and an X-ray diffractometer (Hiltonbrooks DG2-2).

3. Results and discussion

3.1. Hydrothermal synthesis of submicron PZT powders

Previous work has shown that mineraliser concentration, temperature and time were the three most important parameters in determining the particle size and its distribution as well as the phase formation.[4] Fig. 1 shows that the particle size decreases and the size distribution narrows with the increasing synthesis temperature at a critical KOH concentration (0.4 M) and a given time (2 h). Submicron-sized PZT particles of ~200 nm with narrow size distribution could be synthesised at 300°C. Further decrease of the particle size was difficult with the current synthesis conditions since the hydrothermal process was found to be nucleation-predominant. Particle size growth/agglomeration took place rapidly as soon as the perovskite PZT was formed. Therefore, the PZT suspension synthesised at 300C was used in the EPD of PZT films.

3.2. Dispersion of hydrothermal PZT suspensions

The electrophoretic mobility of the hydrothermal PZT powder particles as a function of pH is shown in Fig. 2. The iso-electric point (IEP) of the hydrothermal PZT powder is pH 6.5, i.e. the particle surfaces are negatively charged when the suspension pH >6.5, and positively charged when the suspension pH <6.5. However, these conditions are undesirable for EPD processing, since at low pH, Pb^{2+} ions are selectively leached from the surface of the PZT particles,[5] while at high pH, bases such as aqueous ammonium solution have to be added to the suspension, resulting in the increase of the electrical conductivity of the suspension. During EPD processing, a low electrical conductivity is necessary to control the secondary electrode effects such as gas evolution and heating. The evolution of gas damages the deposits, while heating causes flocculation.[6] Thus, electrosteric stabilisation using a dispersant (DAC), rather than electrostatic stabilisation using pH control is preferred. The particle surfaces are negatively charged over a wide pH range when treated with 0.25 wt.% DAC of the PZT powder (see Fig. 2).

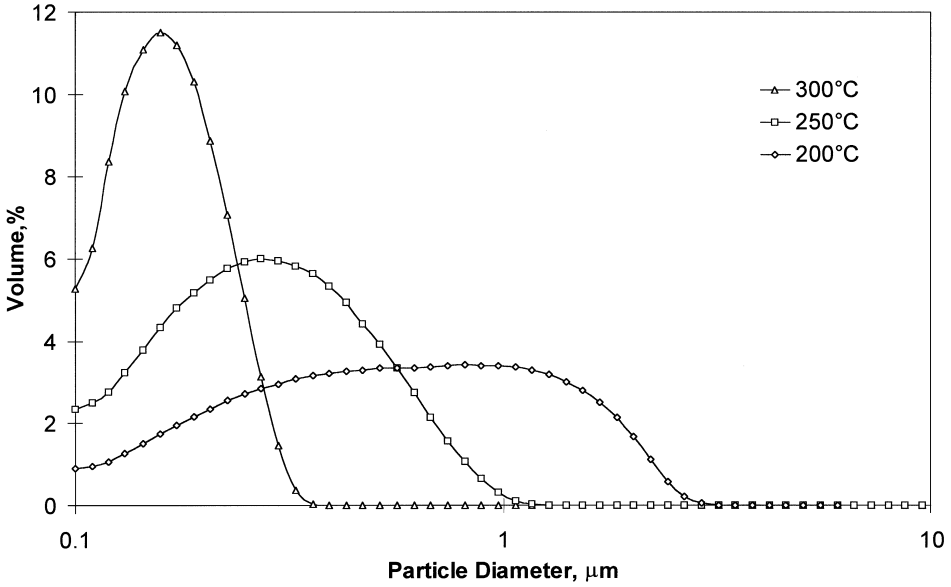

Fig. 1. Effect of hydrothermal synthesis temperature on the particle size distribution, showing that the particle size decreases and the size distribution narrows with increasing hydrothermal synthesis temperature.

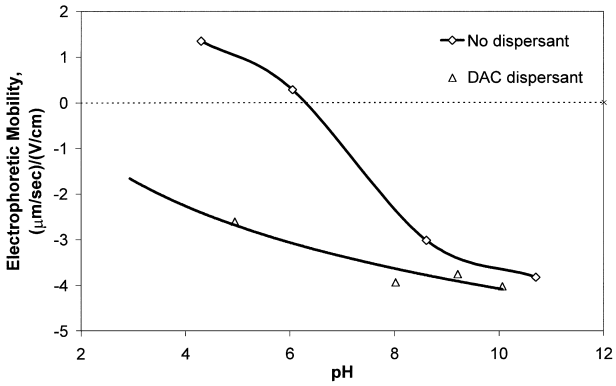

Fig. 2. Electrophoretic mobility versus pH curves for a hydrothermal PZT suspension with and without dispersant.

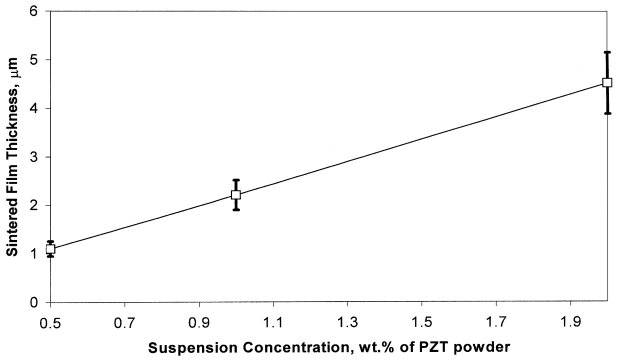

Fig. 3. Effect of the suspension concentration on the sintered thickness for PZT films deposited using EPD.

3.3. Electrophoretic deposition of PZT films

Fig. 3 shows the effect of the suspension concentration on the sintered PZT film thickness. The corresponding SEM micrographs are shown in Fig. 4(a)–(c). The film thickness increases linearly with increasing suspension concentration, but the microstructure shows that microcracking occurs when the film thickness is about 5 μm probably due to the large shrinkage of the hydrothermal PZT powder during sintering. A relatively uniform film is obtained when the suspension concentration is 1 wt.% of the PZT powder.

Electrolysis of water can produce a foam of oxygen and/or hydrogen gases which is adsorbed on the substrate (e.g. Pt wire), resulting in pore formation in the deposited films. The operation voltage should be, therefore, held

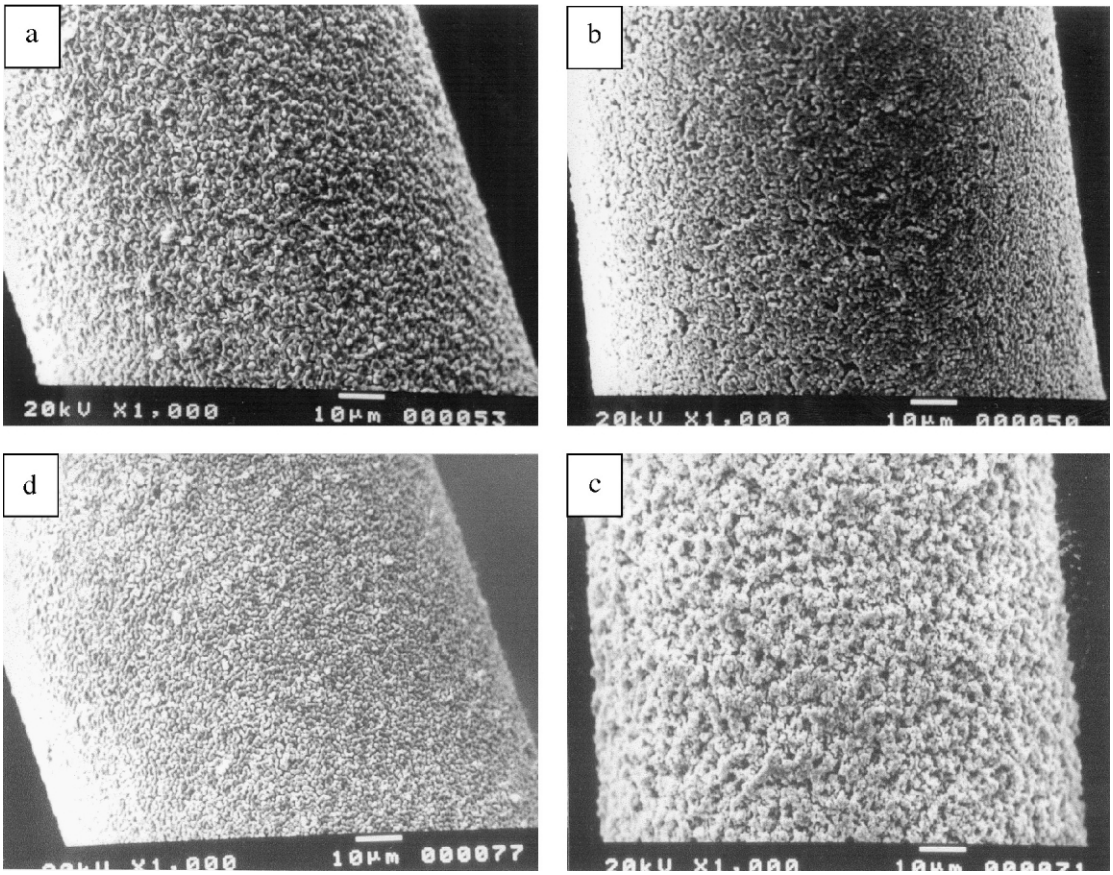

Fig. 4. Sintered PZT films deposited for 10 min on Pt wire from the hydrothermal PZT suspensions with concentration (wt.% of PZT powder) of: (a) 0.5; (b) 2.0; (c) 1.0. In comparison, a PZT film from a 1.0 wt.% suspension but deposited for 30 min shows agglomeration (d).

below the decomposition voltage of water, which is about 2 V. Experimental observation showed that the formation of bubbles on the electrode could be prevented if the voltage was below 4 V. The possibility of increasing the electrical field by reducing the distance between the electrodes seems limited because any distance below 2 mm makes it practically impossible to deposit thicker films. Because of the above limitation, the green density of the films deposited under such a limited electrical field in an aqueous suspension is inferior to their corresponding green compacts. The sintering temperature is consequently higher for the films than that for green compacts produced from the same powder.[1]

The effect of a longer deposition time of 30 min on the film morphology is shown in Fig. 4(d). Agglomeration was formed during the prolonged deposition time. It has been reported that the current density during the EPD processing decreases rapidly with time.[6] This may be attributed to a gradual increase in the thickness of deposit and, therefore, in the resistance to current flow. The rapid decrease in the current density results in the decrease of the effective field between the electrodes, which is a cause of the decrease in deposition rate. After 10 min time, the current density has decreased by 80%. The colloidal particles coagulate during their transfer to the electrodes under such a weak electrical field as shown in Fig. 4(d), especially in the later stages of deposition.

The deposition rate of the PZT particles on Pt-coated alumina substrates was slower than on the Pt wire, probably because of the discontinuity of the Pt coating, resulting in a reduced current density, and thus a discontinuous EPD film. Evidence for interaction of the sintered PZT films with the alumina substrates was also obtained. Hexagonal shaped crystals observed by SEM on the surface of the sintered films were identified by XRD as $PbAl_{12}O_{19}$.[7]

4. Conclusions

Hydrothermal synthesis in junction with colloidal processing has been used to make PZT films from aqueous solutions. PZT films of thickness < 5 μm could be made via EPD from submicron-sized (~200 nm) hydrothermal PZT particles. However, the limitation of electric field, which must be below the decomposition voltage of water, resulted in an inferior packing density during deposition compared to green compacts. Consequently the films had to be sintered at higher temperatures ($> 1000°C$) in comparison with powder compacts. Prolonged deposition times also led to agglomeration. In addition, PZT films deposited on Pt coated alumina substrates have shown a strong interaction between the PZT films and alumina substrates.

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