JOURNAL OF MATERIALS SCIENCE **39** (2004) 819–823

Synthesis and microstructural manipulation of ceramics by electrophoretic deposition

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Critical issues of electrophoretic deposition (EPD) and its potential for fabricating high-performance ceramics are reviewed. Deposition kinetics under constant-current and constant-voltage conditions are discussed. The process of submonolayer formation of mono-sized silica particles as a function of deposition time during EPD has been discussed and is shown to have a remarkable similarity with the atomic thin-film growth (10000 times smaller scale) process of Molecular Beam Epitaxial (MBE) process. Ceramic coatings by EPD are described and strategies to avoid cracking are outlined. Discussion on avoiding cracking using the Reaction Bonded Aluminium Oxide (RBAO) process is also described. The versatility of the EPD process towards fabrication of a wide spectrum of composite microstructures is discussed together with references. Potential use of EPD in the fabrication of Micro-Solid Oxide Fuel Cell (μSOFC) has also been discussed.

1. The process of electrophoresis deposition (EPD)

Electrophoresis Deposition (EPD) is a colloidal forming technique where charged, colloidal particles from a stable suspension are deposited onto an oppositely charged substrate by the application of a dc electric field. In recent years, the ceramic community has come to understand that good forming techniques are the key to achieving reliable product properties and performance. Good forming techniques should have three major capabilities: ability (1) to produce a dense and homogeneous green body, (2) to produce complicated shapes effectively and easily, and (3) to allow flexibility in microstructural manipulation i.e., able to fabricate a wide spectrum of composite microstructures ranging from dispersed, laminated, fiber-composites to functionally graded materials etc. Illustrations in this paper will demonstrate that EPD has all of these capabilities and can produce various types of high-perfection microstructures, if practiced right. This paper will also address some critical issues and myths of the EPD process, and why EPD is a potential processing technique for fabrication of high-performance and high-perfection ceramics and coatings.

In a homogeneous green body, the spatial distribution of all of its constituent phases, including voids, should be uniform and narrow. Lange *et al.* [1] have shown that voids with high particle coordination number are difficult to remove during sintering and will exist in the sintered product as flaws. These flaws or defects in the final products will degrade their properties, rendering them unreliable and weak. Thus, it is prudent to choose an effective forming or consolidation technique that can produce a dense and homogeneous green body where particles are tightly and uniformly packed and distributed homogeneously. This will, in turn, reduce the size and distribution of voids, thus minimizing defects in the sintered products. Fig. 1 is a schematic illustration of a poor and ideal consolidation process. In contrast to poor consolidation, an ideal consolidation will result in no cracking and warpage of the product during drying and sintering. Thus, the sintered product will be free from flaws or defects, lowering sintering temperatures and/or shorter soaking times, and resulting in more reproducible final densities ensuring better dimensional control of finished products.

EPD is a colloidal ceramic forming technique where one can control "the state of dispersion of particles in suspension" or "suspension structure" (via careful

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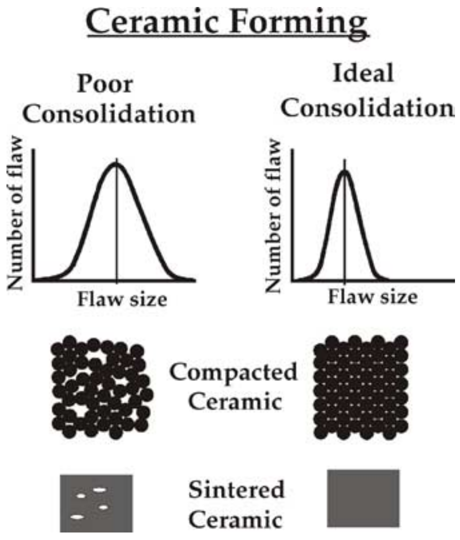

Figure 1 Schematic illustration of a poor and ideal consolidation of ceramics.

manipulation of interparticle forces) and its evolution during consolidation (via proper choice of processing parameters) in order to produce near ideal dense and homogeneous green bodies and microstructures. Sarkar *et al.* [2] have provided an example of such a microstructure made from mono-size silica spheres (dia. $\approx 0.5\ \mu$m) by the EPD process. The microstructure [2] shows the close packing of the silica spheres and a very narrow distribution of voids that can be easily removed during sintering. Sarkar *et al.* [2] have clearly demonstrated the capability of EPD forming technique to deliver a dense and homogeneous green body. The EPD process can also deposit powder uniformly on electrodes having complicated shapes and, as a result, can produce geometrically complicated shapes. However, in the case of bulk ceramics, after shape forming, the substrate (depositing electrode) needs to be separated from the deposit. Commercial viability of EPD depends on the effective separation of the substrate from the deposit. In the case of simple geometry, separation can be done by careful and controlled drying of the deposit. For complicated shapes, a combustible substrate that can be removed during the sintering process could be used. In the case of coatings, the sample often develops cracking during drying and sintering, and the success of EPD to this area depends on overcoming this problem. In general, commercial success of EPD is limited by a better understanding of how to control the EPD process precisely and consequently higher trained operators as compared to other common forming methods such as slip casting or injection molding.

Section 1 of this paper addresses the kinetics and dynamics of submonolayer formation during EPD, Section 2 provides examples of various ceramic coatings and addresses how to avoid cracking during drying and sintering, followed by Section 3 that demonstrates the versatility of the EPD process to produce a wide spectrum of complex microstructures.

1.1. Kinetics of electrophoretic deposition

To make EPD commercially more viable, one needs to understand the kinetics of the EPD process in order to (a) control and manipulate deposition rate and (b) achieve flexibility in microstructural manipulation. In 1940, during a study of the phenomena of the EPD, Hamaker [3] observed that the deposited weight or yield of the EPD varies linearly with the amount of the charge passed. Hamaker proposed that the amount deposited or yield is proportional to the concentration of the suspension, time of deposition, surface area of the deposit, and the electric field.

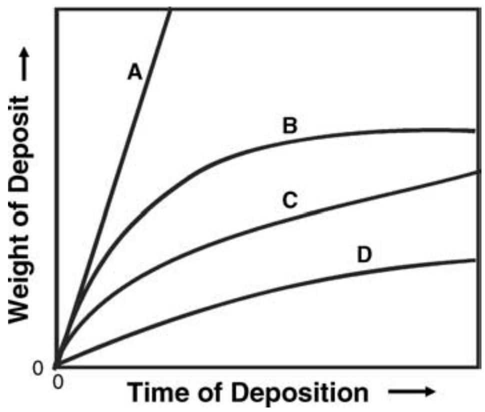

Figure 2 Schematic of Kinetics of EPD process.

It is important to mention that EPD is a non-Faradic process [4]. It follows laws different from those governing electroplating. Electrophoretic deposition can be conducted under either constant voltage or constant current conditions. Deposition can be performed under either of these conditions keeping the suspension concentration either constant or changing (concentration of suspension decreasing) with deposition time. Fig. 2 demonstrates the schematic plots of weight of deposit as a function of time of deposition for these four deposition conditions: curve A (constant-current and constant-suspension concentration), curve B (constant-current but decreasing suspension concentration), curve C (constant-voltage and constant-suspension concentration) and curve D (constant-voltage but decreasing suspension concentration). Except in Curve A where the rate of deposition is constant with time, the rate of deposition decreases asymptotically with deposition time in either curve B, or C, or D. The final yield (after sufficient deposition time allowed) and rate of deposition are the highest in Curve A, followed by curves B, C, and D respectively. The effect of decreasing suspension concentration on the reduction of the final yield and rate of deposition is obvious during either constant-current (curves A and B) or constant-voltage (curves C and D) EPD. Comparison of curves A (constant-current) and C (constant-voltage) clearly reveals that even if the suspension concentration is kept constant during deposition in both of them, (a) the rate of deposition was constant in curve A while it decreased asymptotically with time in curve C and (b) final yield was considerably higher in curve A than that in curve C. Thus, the deviation of curve A from curve C is not due to a decreasing suspension concentration but is due to a decrease of particle velocity as function of deposition time. Why is the particle velocity decreasing during constant-voltage (Curve C) deposition? Typically, the EPD deposit has higher electrical resistance than the suspension from which deposition takes place. Consequently, as the deposit grows with deposition time, the available electrical driving force or voltage per unit length of suspension decreases with time. This results in decreasing velocity of the particles, and thus the EPD yield and rate of deposition with time. EPD of the alumina-ethanol system that is stabilized by hydrochloric acid serves a good demonstration of this phenomenon. Sarkar *et al.* [5] reported that under constant-voltage/constant-suspension concentration conditions (curve C), it is nearly impossible to fabricate millimeters thick samples from the hydrochloric acid-stabilized-alumina-ethanol suspension because of high resistivity of deposit. In contrary, when the alumina-ethanol system is stabilized by acetic acid, the resistivity of the deposit is only marginally higher than the suspension and thick deposits can be produced without any problem under constant-voltage/constant-suspension concentration conditions. During EPD, passage of current causes electrode reactions, producing electrolytes. Probably, the extent of electrolytes produced and any polarization in the deposit resulted in the difference in deposit resistivity in alumina-ethanol system that was stabilized either with strong acid: HCl or weak acid: acetic acid. This needs further investigation. Thus, under constant-voltage/constant-suspension concentration condition (curve C), deposit resistivity plays a significant role on determining the EPD yield and rate of deposition. If the deposit resistivity equals that of the suspension during deposition, Curve A and C will be identical; i.e., there will be no difference between constant-current/and constant-voltage/constant suspension concentration deposition conditions. Curve D deviates from Curve A due to (a) the decrease of suspension concentration and (b) increase of deposit resistance with deposition. Thus, Fig. 2 clearly demonstrates that constant-current depositions are efficient and can provide better and easier control over the EPD deposition process.

1.2. Submonolayer formation during electrophoretic deposition: similarity with atomic-scale molecular beam epitaxial (MBE) growth process

Sarkar *et al.* [2] have followed the process of submonolayer formation as a function of deposition time during colloidal film growth of silica particles on a silicon wafer substrate by EPD. They compared the process of nucleation (or deposition of single particle), growth (or formation of a cluster of particles) and aggregation (or merging together of several particle clusters) of silica monolayers by the EPD technique with that for atomic thin-film growth (10000 times smaller scale) process via molecular-beam epitaxy (MBE). They have shown a striking similarity between the two growth processes. Like the atomic thin-film growth process (MBE), the entire nucleation, growth and aggregation process during EPD of silica particles can be broadly classified into two regions. Diffusion-limited aggregation (DLA) is the mechanism at low surface coverage when silica particles are deposited outside of clusters, diffuse randomly and stick to a cluster on touching them and the fractal dimension of the two-dimensional clusters is ∼1.65 [2]. As deposition proceeds, the clusters grow in size, deposition of particles inside the clusters become more and more important, and the cluster become increasingly more compact, producing a dense and closed-packed monolayer. This is termed as consolidation region where the fractal dimension of clusters rapidly changes from ∼1.65 towards 2 as the surface coverage increases [2].

To produce a dense, homogeneous and close-packed green body, EPD must be performed from a dilute, stable colloidal suspension where interparticle forces keep the particles well dispersed. During EPD from a dilute and stable suspension, particles are expected to move and deposit individually. In unstable suspensions, loose flocs or an ensemble of particles are expected to move and deposit together. Unlike in stable suspension, the growth and consolidation of these loose flocs or ensemble of particles during deposit formation may be different and needs further research. Furthermore, the electrical resistivity of these flocs (larger volume fraction of them is occupied with continuous phase) may be substantially different from that of a compact deposit (achieved in stable suspension) and the kinetics of deposition may be significantly different. Other areas of potential research are the dynamics of deposit formation from stable and unstable suspensions with polydisperse particles. It will be interesting to investigate whether the particles are segregated in suspension (different electrophoretic mobility) or they move as an ensemble of particles and how does it affect the homogeneity and density of the green deposits. Also, more imaginative research is needed to identify similarities and dissimilarities of the process of EPD with that of other external-field induced consolidation techniques such as sedimentation, slip-, pressure-, and centrifugal casting.

2. Ceramic coating by EPD: how to make it survive during drying and sintering

Depositing ceramic or other powder on a metal (or a conductive surface) by EPD is relatively simple, but the most important factor is how to avoid cracking in the ceramic coating during drying and sintering. During drying and sintering, the coating densifies and shrinks, but the substrate typically does not change dimension. As a result, tensile stresses are developed in the coating and are relieved by the formation and propagation of cracks that originate from flaws or defects in the coating.

There are several approaches that can be adopted to avoid cracking during drying. When a wet coating or green body undergoes drying, the origin of stresses in it is due to capillary forces. During drying, cracking can be avoided by minimizing capillary stresses either by using a low surface tension solvent like ethanol or avoiding fine pore structure in the coating. By adopting freeze/supercritical drying, capillary stresses can be removed altogether since in this process the solvent phase is sublimed. Furthermore, controlled slow drying via adjustment of vapor pressure of solvent in the drying medium will help control the capillary stresses and as a result, formation of drying cracks may be avoided.

During sintering, ceramic coatings typically suffer 10 to 15% linear shrinkage and the critical issue is how to avoid cracking. Traditionally, cracking during sintering is avoided by using a liquid phase during sintering; a good example is sintering of glass enamel on a metal substrate. The enamel composition is adjusted in such a way that its thermal expansion is closely matched with the substrate. As a result, it does not form crack during cooling from the sintering temperature. Sarkar *et al.* [6, 7] have used liquid phase sintering to avoid cracking in a superconductor coating on a silver substrate. The approach of liquid phase sintering is also equally effective in avoiding cracking in fiber composites. To avoid cracking during sintering, one can also use a substrate that also shrinks during sintering. Recently this approach has been used, particularly in SOFC fabrication where typically an YSZ electrolyte is added to a partially sintered or an unsintered anode substrate. During sintering, both the substrate and coating shrink, thereby avoiding cracks. Furthermore, the compositions of the substrate and coating are chosen such a way that their thermal expansion coefficients match to each other, minimizing any thermal stress and resultant cracking during cooling from the sintering temperature.

Another unique approach to avoid cracking during sintering is by using a reaction-bonding technique. Sarkar *et al.* [8] have found the development of tunnel and radial cracks during sintering of a polycrystalline alumina coating on a sapphire filament substrate. This is an interesting example where the substrate and the coating are from the same material. The substrate is a single crystal alumina filament that suffers no change in dimension during sintering, whereas the coating is a polycrystalline alumina made from alumina powder and has considerable shrinkage during sintering. To overcome these cracking, the RBAO (Reaction Bonded Aluminum Oxide) process [8] is used. In this process, the starting materials for the coating are alumina and aluminum powder. The sapphire filament is initially coated with a thin carbon or gold layer to make it electrically conductive. On this filament substrate, alumina and aluminum powder are co-deposited from an ethanol based Al_2O_3-Al suspension of predetermined composition by EPD. During sintering, Al oxidizes to alumina and, as a result, expands and counter balances the sintering densification shrinkage of Al_2O_3, thereby avoiding cracking [8].

3. Flexibility of EPD towards microstructural manipulation

Sarkar *et al.* [9–13] have demonstrated the versatility of EPD process towards synthesizing a wide spectrum of microstructures having different morphology and composition. They used EPD efficiently and with imagination to fabricate ZrO_2/Al_2O_3 continuous functionally graded material (FGM) [11] and planar and non-planar laminates of ZrO_2/Al_2O_3 having as many as 80 interlayers [10, 11]. They also demonstrated that the interface of layers in the planar and non-planar laminates are smooth and of high-perfection. They created the wavy layers in non-planar laminates by depositing on line electrodes on a printed circuit [11]. EPD has also been efficiently used to fabricate ceramic-fiber composites [11–13]. Using EPD, Sarkar *et al.* [13] fabricated composites where a graphite cloth was impregnated with zirconia powder and a Nicalon fiber mat was impregnated with ZrO_2/Al_2O_3 mixture and consolidated by hot pressing [11]. Recently, Illston *et al.* [14] and Boccaccini *et al.* [15] have fabricated ceramic-fiber composites where SiC (Nicalon) fiber mats were impregnated with SiO_2 and Al_2O_3 sol from their aqueous suspensions by a combination of EPD and dip coating process.

EPD can also be very well-suited for fabrication of small complex shapes. One area where the authors are actively involved and foresee considerable potential of

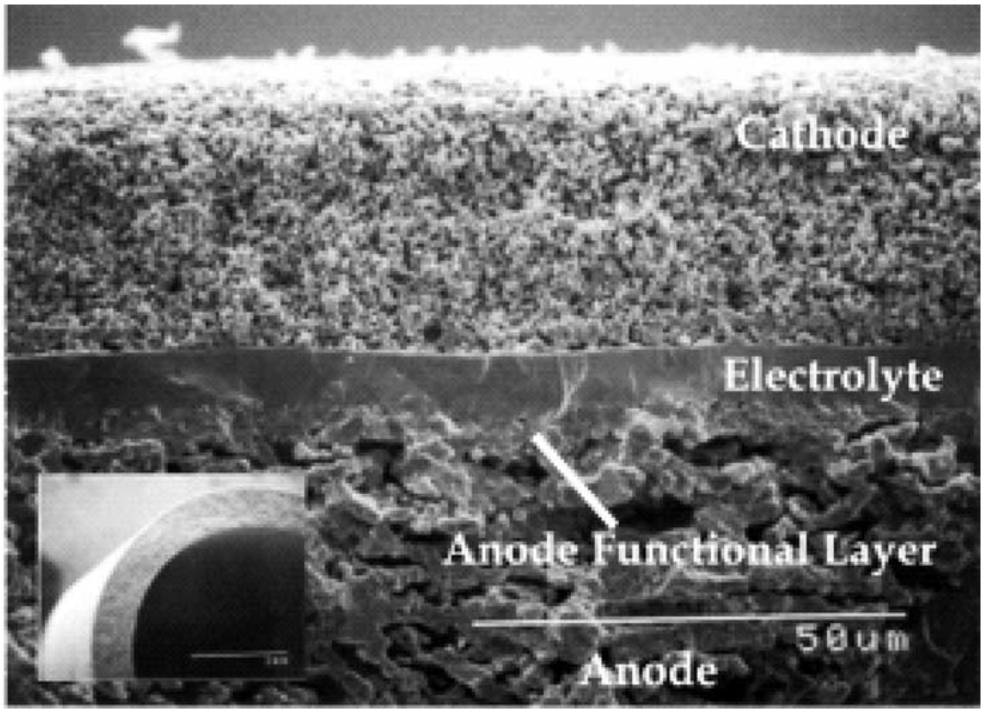

Figure 3 SEM micrograph of cross-sectional fracture surface of a single cell.

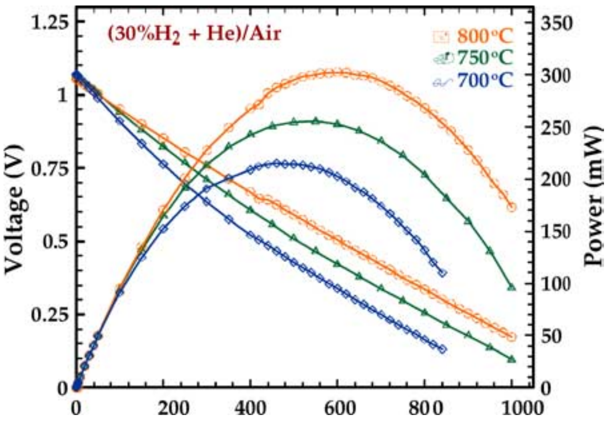

Figure 4 Voltage and power of cell as a function of current at 700, 750 and 800°C.

EPD is the fabrication of Micro-Solid Oxide Fuel Cell (μSOFC). Small diameter SOFC has two main potential advantages, substantial increase in the electrolyte surface area per unit volume of a stack and also quick start up. Since fuel cell power is directly proportional to the electrolyte surface area, a μSOFC stack has high potential to substantially increase the power per unit volume. Sarkar *et al.* [16] have demonstrated that power output of a cell synthesized by EPD is comparable to any standard tubular SOFC. A SEM micrograph of cross-sectional fracture surface of a single cell produced by EPD is shown in Fig. 3. The electrolyte layer of the cell is $<10\ \mu$m and anode functional layer is $\sim 5\ \mu$m. Fig. 4 shows the Current-Voltage (IV) and Current-Power (IP) plots of the single cell at three different temperatures. A mixture of 30% hydrogen and 70% helium was used as a fuel gas. The fuel gas contained 3% moisture as it was bubbled through water at 25°C. The fuel gas flow rate was 30 SCCPM. This cell has produced theoretical open circuit voltage indicating that the membrane does *not* have pinholes. Fig. 4 demonstrates that at all three temperatures, activation polarization are absent. Concentration polarization was not observed in the measurement range. Approximately a 2 cm length of the cell was coated with cathode; this is the active length of the cell during measurement. At 800°C, peak power output is over 300 mW with a corresponding voltage and current at ~0.5 V and ~600 mA respectively. At 750°C, peak power is ~255 mW and at 700°C, peak power is ~215 mW. Thus, Sarkar *et al.* [16] have clearly demonstrated that EPD can simplify the forming process and reduce the production cost considerably, which is one of the major barriers for commercialization of fuel cells.

4. Summary

Discussions in this paper clearly establish that EPD is a powerful and versatile forming or consolidation technique. If practiced right and with imagination, like an ideal consolidation process, it can (a) produce homogeneous and dense green bodies, (b) produce complicated shapes effectively and easily, and (c) allow flexibility in microstructural manipulation i.e., a wide montage of microstructures ranging from dispersed, laminated, fiber-composites to functionally graded materials can be fabricated by EPD.

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Received 3 March
and accepted 30 June 2003