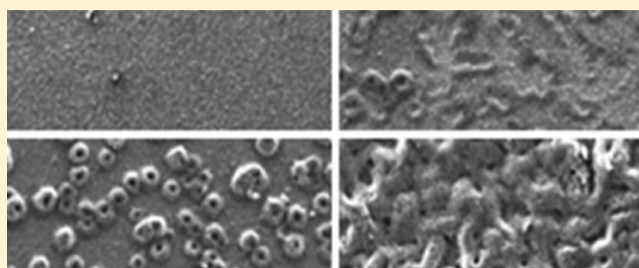


Deposition Patterns of Porcelain Coatings Obtained by Electrophoretic Deposition in Acetone. Part 1. Voltage and Time Effect

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ABSTRACT: Homogeneous surface morphologies are of interest to form different functional coatings. In order to verify if these morphologies could be observed and controlled in an electrophoretic cell, voltage and time effect have been studied on the deposition patterns of porcelain particle on a stainless steel substrate. The suspensions were prepared at 1 wt % of porcelain submicronic particles using acetone as dispersing media. The EPD experiments were carried out at 400, 600, and 800 V at deposition times of 1, 15, 30, 45, and 60 s. The morphology of the particle deposit patterns were characterized by scanning electron microscopy. At 1 s, submicronic particles without any pattern formation were observed on the stainless steel substrate. At subsequent deposition times, the patterns evolved from worm like forms to ring like forms and finally to labyrinth-type agglomerates of particles depending on voltage and deposition times. At deposition times longer than 60 s, the particle deposit patterns were difficult to observe. The coatings obtained at deposition times below this value were subjected to thermal treatments at 900 °C for 2 h. The patterns were maintained after the sintering process, exhibiting dense, homogeneous, and crack-free surface coatings.



INTRODUCTION

The electrophoretic deposition (EPD) consists of three fundamental steps: (1) the formation of a stable, charged suspension, (2) electrophoretic transport of the particles to the deposition electrode, and (3) deposition. The first two steps have received considerable attention, to the point that such processes are well understood. The deposition step, however, is less understood in part due to the complexity of such a process. Therefore, fundamental studies approaching several deposition conditions should be performed in order to advance in elucidating the different deposition phenomena.¹

Previous studies carried out in thin layers of charge-stabilized colloidal spheres subjected to low voltages between parallel plate electrodes showed highly organized patterns that emerged when electrohydrodynamic forces competed with gravity. Depending on the conditions, these spheres formed levitating clusters with morphologies ranging from tumbling clouds to toroidal vortex rings to writhing labyrinths.^{2–4} The formation of spatial-temporal patterns in systems far from equilibrium has been described as a phenomenon created by fluid convection caused by dielectric fluids movement under the action of an electric field.⁵ The driven force of electro-convection was attributed to the interaction of the electric field with an unbalanced charged particle which could be transported within the fluid movement.⁶ An example of electrodynamics convection in thin films of crystals, in pneumatic liquid exposed to direct and alternative fields, has been shown by Williams.⁷ Electro-convection phenomena associated with the

application of electric fields was also observed by Han and Grier.^{2–4} They showed the tendency of colloidal particles to form chains in oscillatory electrical fields (AC). In that case, the effect of bipolar interactions induced by electrical fields on the formation of particle patterns was documented.^{2–4} Under constant electric field application (DC), charged particles conducted over electrode surfaces by DC have induced labyrinth-like patterns in aqueous medium.⁸ Generally, these complex and interdependent processes are attributed to result from the effect of forces actuating on particles.⁹

This work was carried out in order to study the high voltage and time effect on the particle patterns formation during the EPD process in electrophoretic cells having relatively large interelectrode gap. Industrial grade acetone was used as suspension medium of porcelain particles. Voltages of 400, 600, and 800 V were applied during the experiments, with deposition times of 1, 15, 30, and 60 s. The separation of the electrodes within the cell was 1 cm. The aim of the investigation was to show that different homogeneous and crack-free surface coating topographies could be produced from an EPD process that may be scaled-up for functional applications such as the Lotus effect. Therefore, the correct

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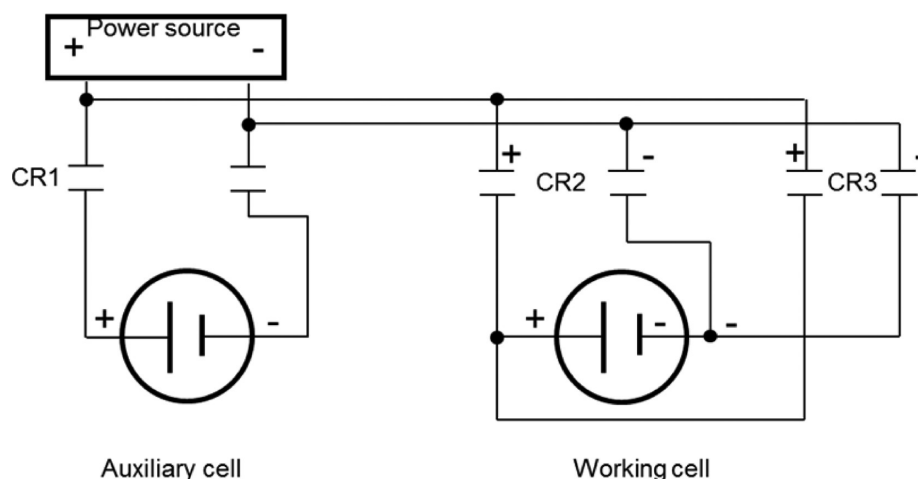


Figure 1. Electric circuit used to control the electrophoretic deposition of porcelain particles. The relays that control the passage of current are labeled as CR1, CR2, and CR3.

control of the experimental parameters should lead to functional coating depositions for high performance systems.

EXPERIMENTAL SECTION

The ceramic material employed in this work was dental porcelain (Dentsply CERAMCO) with the following chemical composition (wt %): Al_2O_3 : 8.69; K_2O : 4.75; NaO : 4.42; CaO : 0.43; MgO : 0.53; SnO : <0.50; F_2O_3 : 0.06; SiO_2 : 81.12. The average particle size of the porcelain was 1 μm . The electrokinetic potential (Z potential) of the porcelain in industrial grade acetone with 0.125 $\mu\text{S}/\text{cm}$ conductivity was -10 mV at 25 $^\circ\text{C}$. The EPD experiments were performed with suspensions containing 1 wt % of dental porcelain powder.

The EPD was carried out in an electrophoretic cell having an interelectrode gap of 1 cm, using a working electrode of 1.25 cm diameter. Typical high voltage sources have a response time of several seconds. For this reason, when using these devices, it is not feasible to study the effect of applying high DC voltages in short periods of time, i.e., less than 5 s.

The experimental setup used in this work consisted of one voltage source (BIO-RAD 3000) and two cells. One of them served as an auxiliary cell, while the second was the working cell. The system operated as follows: the selected applied voltage was imposed to the auxiliary cell, and once the desired voltage was reached and stabilized, a relay opened the electric circuit allowing the passage of current. In these operating conditions, the working cell received instantaneously the applied voltage. Thus the electric system allowed the long response time of the high voltage source to be avoided. The referred circuit is shown in Figure 1.

The EPD was carried out under constant voltage conditions. To evaluate the systems behavior, plots of deposition kinetics and current density as a function of time were obtained. The amount of mass deposited on the substrate was evaluated by weighting the substrate before and after the deposition process. The applied voltages were 400, 600, and 800 V, while the deposition times used during the experiments were 1, 15, 30, 45, and 60 s. Lower voltages were not used because of the high resistivity of the acetone solution. The morphology of the particle deposit patterns was characterized by scanning electron microscopy using a Jeol JSM 6300 microscope.

RESULTS AND DISCUSSION

With the setup shown in Figure 1 not just the behavior of electrical parameters can be monitored. This setup allows high voltages to be applied even in very short periods of time, i.e., 1 s. Such control of the applied voltage permits the changes in macroscopic particle patterns on the working electrode to be studied. It is possible to follow the evolution of the morphological characteristics of the electrode surface as a function of time. Similar patterns as those found in this work have been reported previously for thin horizontal cells with a very small electrode separation (100 μm) under relatively low applied voltages.^{2–4} The high voltages used in this work considerably increase the limit current of the system, forming unstable gradient layers at the cell. Unbalanced charge layers will form and after reaching a critical thickness will break into vortices. Then, there will be the continuous formation and growth of vortices due to the convective transport, a mechanism that leads to the formation of particle patterns.¹ The patterns obtained in this work depend on applied voltage and time of deposition. Figure 2 characterizes the effect of these two variables over the particle patterns formed. Four different patterns were observed: dispersed nanoparticles (NP), wormlike colloidal vortices (WCV), colloidal vortex rings (CVR), and labyrinthine patterns (LAB).

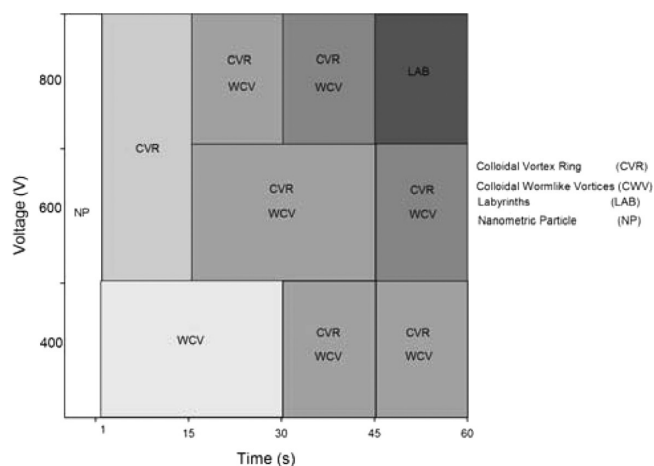
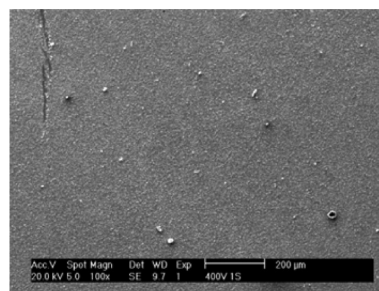


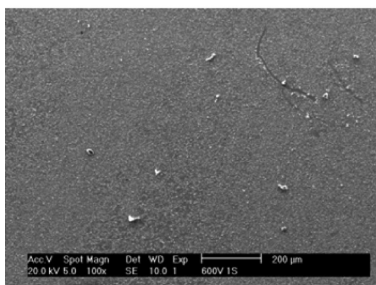
Figure 2. Patterns formation induced by controlled voltage and time during EPD of porcelain particles in acetone.

and dense labyrinths (LAB). For example, at 15 s and a voltage between 400 and 800 V, CVRs are formed, whereas at 800 V and 60 s, LABs are developed on the surface. The diagram in Figure 2 shows that, if films of dispersed nanoparticles are required, times shorter than 1 s should be considered. From these observations, it is inferred that the smallest particles reached the highest electrophoretic velocity, and therefore, these were the first ones in being deposited, as stated in a previous work.¹⁰

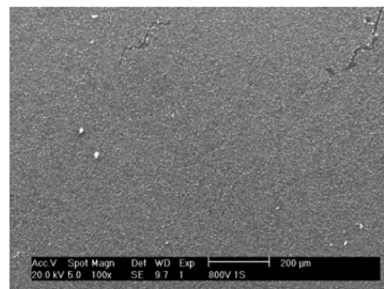
The effect of voltage and time on the morphology of the electrode's surface is shown in the following micrographs obtained by SEM. As can be observed in Figure 3, at short



(a)



(b)



(c)

Figure 3. Porcelain coatings obtained at a deposition time of 1 s. 100× magnifications: (a) 400, (b) 600, and (c) 800 V.

deposition times (1 s), a uniform coating of submicronic particles can be observed at 400 (3a), 600 (3b), and 800 V (3c). There is no any particle pattern formation yet. This behavior indicates that, at such a short time, the electrohydrodynamic convection phenomenon is not yet induced in the system. Based on this evidence, it can be inferred that a given time is needed before significant evolution on the morphology's characteristics can be evident due to changes in the conductivity gradients close to the electrodes. At 1 s, the

unbalanced charged layer is not fully developed; that is, there is no vortex formation. After some time, the vortex will form and grow.

The micrograph shown in Figure 4 is a magnification of the image presented in Figure 3c. Overall, the characteristics of this

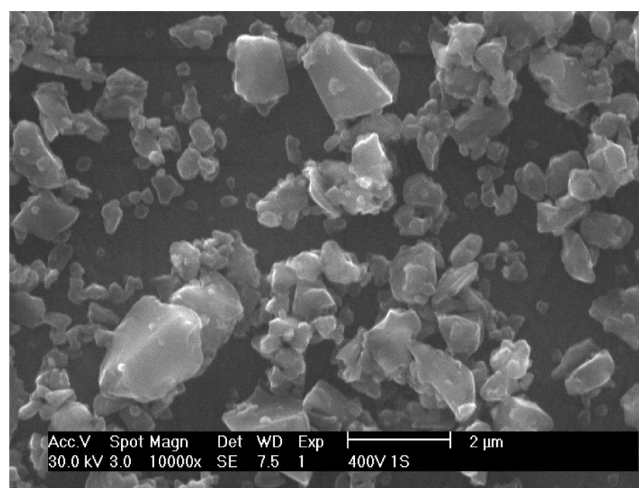


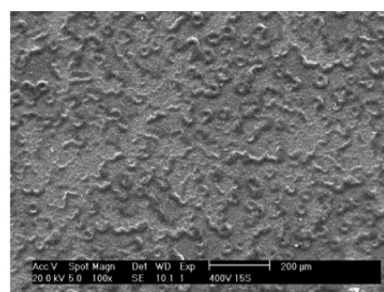
Figure 4. Porcelain coatings obtained at a deposition time of 1 s and 800 V. 10 000× magnifications.

coating indicate the presence of a homogeneous surface formed by submicronic particles.

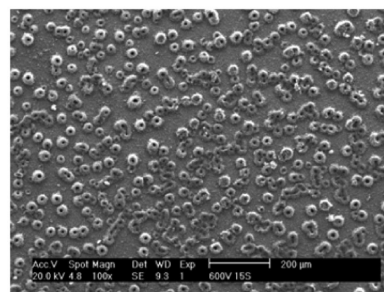
The first patterns to develop from the surface coating according to the diagram of Figure 2 are WCVs, followed by CVRs, as confirmed by the SEM micrographs of Figure 5a–c. Then a combination of both appears as deposition time and voltage are increased. This patterns evolution is shown in the micrographs of Figure 5, taken at a time of 15 s. At this time, the electrohydrodynamic convection process becomes more complex due to the conductivity gradients and the nanoparticle patterns follow this turbulence. Therefore, at 400 V, WCVs are formed (Figure 5a), followed by the development of CVRs at 600 V (Figure 5b). As voltage is increased to 800 V, a pattern showing the combination of WCVs and CVRs can be observed (Figure 5c).

A variety of patterns were observed at higher voltage and longer time of deposition. It is evident that, as the system is taken far from equilibrium, the vortices will combine and grow as described by Van Tassel.¹ Therefore, Figure 6 shows the patterns configuration at 60 s. It can be observed that the combination of WCVs and CVRs continues (Figure 6a) and eventually the LAB patterns build up at the surface (Figure 6b,c). Clearly, when voltage and time reach higher values, the surface morphology is modified. At 60 s and 800 V a more dense coating composed only of LAB patterns is obtained (Figure 6c). The same phenomena occurred at 400 and 600 V at longer times. Summarizing, the variety of patterns evolve as the coating thickness increases as a result of the accumulation of particles. As the thickness of the coatings increases, the electro-convection phenomena are less influential on particle pattern formation and more dense coatings are obtained, forming a smoothest surface topography.

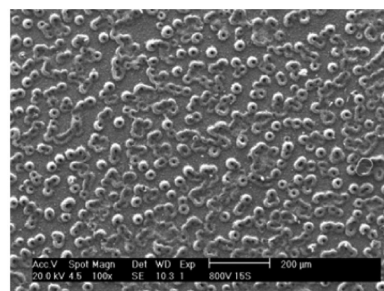
Figure 7 shows detailed views of the CVRs formed at the three different voltages and a time of deposition of 30 s. At 400 V, the CVRs start to develop and some ring centers can be distinguished (Figure 7a). The rings are completely built up at 600 and 800 V (Figure 7, panels b and c, respectively) with



(a)



(b)

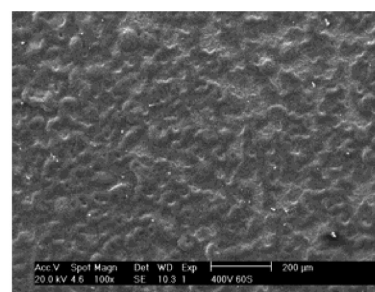


(c)

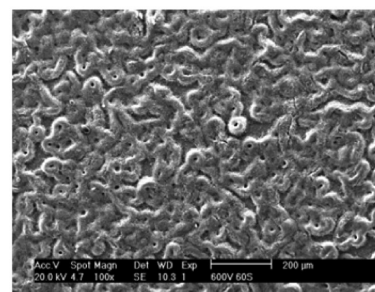
Figure 5. Patterns of deposited porcelain obtained by EPD at 15 s. (a) WCVs formed at 400 V, (b) CVRs formed at 600 V, and (c) a combination of WCVs and CVRs at 800 V.

clearly defined boundaries, i.e., under these voltage and time conditions, the electro-convective transport is higher and increases the transport of porcelain particles to the electrodes surface. The appearance of similar rings after applying between 2 and 4 V in an electrophoretic cell with 200 μm interelectrode gap was reported by Han and Grier.^{2,3} However, the CVRs in Figure 7 show different morphology than those reported previously, where the rings showed central crystalline cores.^{2,3} Under the experimental conditions, the rings seem to build up on the porcelain film formed earlier (see Figure 3) into a donut-like shape. Moreover, another difference with respect to the rings obtained by Han and Grier is that no diffuse coronas surrounding the rings emerge in the CVRs of Figure 7.

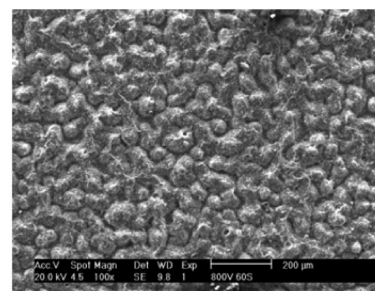
This means that, under the high voltages used in this work, the electro-convective phenomenon leads to the formation of dense and homogeneous coatings. The field-driven flux of ions and charged particles induce flows in the surrounding electrolyte that give rise to electrohydrodynamic instabilities and therefore the formation of a variety of morphologies, as is described in the diagram shown in Figure 2. For example, the micrograph in Figure 8 shows the LAB patterns formed at 800



(a)



(b)



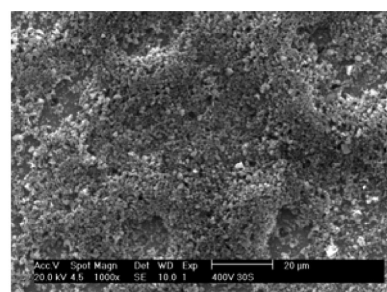
(c)

Figure 6. Patterns of deposited porcelain obtained by EPD at 60 s. (a) WCRs and CVRs at 400 V, (b) WCRs, CVRs, and LABs at 600 V, and (c) LABs at 800 V.

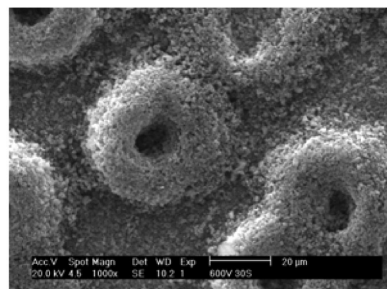
V and 60 s. From this figure, it is possible to infer that as the thickness of the coating increases, the electro-convective phenomena are less influential on particle pattern formation and more dense coatings are obtained.

In order to show the evolution of the mass transport of particles to the substrate, kinetic plots of porcelain deposition in acetone suspension are shown in Figure 9. It can be observed that the amount of deposited mass increases as a function of time (1, 15, 30, 45, or 60 s) under all of the three applied voltages. Moreover, it is clear that a larger mass of porcelain is deposited at higher voltages. For example, at 60 s the deposition of mass is 2.7, 2.1, and 0.75 mg/cm^2 at 800, 600, and 400 V, respectively.

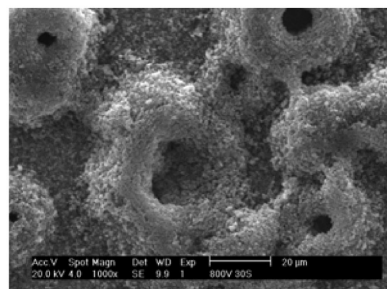
Figure 10 shows the current density–deposition time relationship observed for the three applied voltages. The current density decreases as the time varies from 1 up to 60 s. This may be due to a resistive barrier created during the growing of the coatings on the electrodes surface which opposes the current flux in the electrophoretic system.¹¹ Consequently, the decrease in current density can be explained in terms of the thicker coatings formed, at longer deposition



(a)



(b)



(c)

Figure 7. CVRs of porcelain deposited at 30 s: (a) 400, (b) 600, and (c) 800 V.

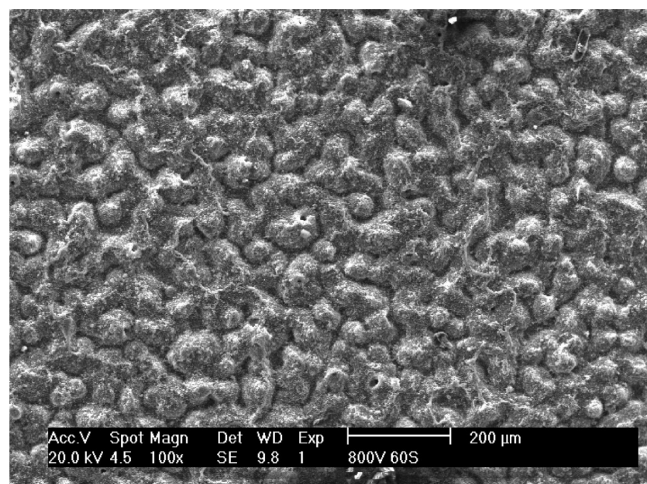


Figure 8. LAB patterns of porcelain deposited at 800 V and 60 s.

times under constant applied voltages, i.e., higher resistance to current flux. For example, at 800 V, the current density decreases from 1.1 mA/cm² at 1 s to 0.9 mA/cm² at 60 s. These

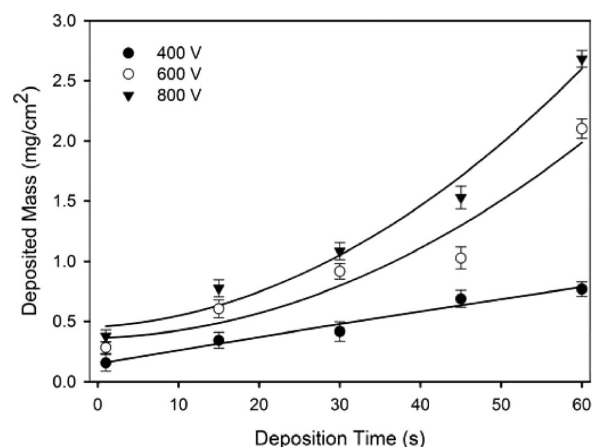


Figure 9. Kinetics of porcelain electrophoretic deposition in acetone suspension at 1 wt % solid loading.

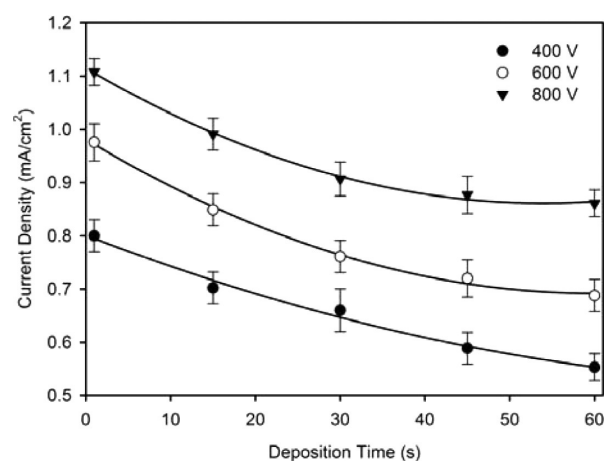


Figure 10. Current density-deposition time relationships at the three different applied voltages.

results are in good agreement with the larger amounts of deposited mass at longer deposition times (Figure 9).

The effect of heat treatment on the porcelain particles patterns formed by the EPD process is shown in Figure 11. This pattern corresponds to a coating developed under deposition conditions of 800 V and 5 s and then sintered at

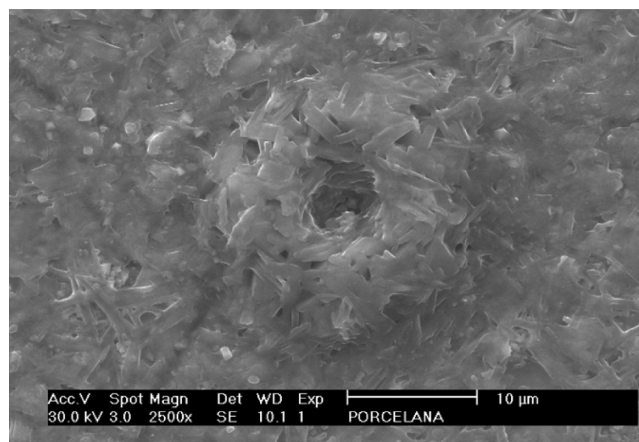


Figure 11. Patterns of porcelain deposited at 800 V and 5 s and then sintered at 900 °C for 2 h.

900 °C for 2 h. These deposition conditions lead to the formation of donut-like shapes. The patterns were maintained after the sintering process, exhibiting dense, homogeneous, and crack-free surface coatings, and after heat treatment the surface is smoother and less porous, with the formation of laminar layers.

■ CONCLUSIONS

The electro-convective phenomena induced in the electrophoretic cell under the experimental conditions were shown to be dependent on voltage and deposition time.

At 1 s, a uniform and dispersed deposition of nanometric particles was observed at any of the three applied voltages used in this work. This result demonstrated that, by applying voltage pulses for a short period of time, homogeneous and crack-free coatings of nanometric particles may be formed.

At subsequent deposition times, the patterns evolved from worm like forms associated with small amounts of particles moved by the concentration gradients, to ring like forms, and then to surface morphologies containing both patterns. Finally, at higher voltages and relatively longer deposition times (60 s), i.e., under electrohydrodynamic convection control, the morphology showed dense labyrinth-like agglomerates.

The patterns were maintained after submitting the samples to a sintering process, exhibiting dense, homogeneous, and crack-free surface coatings. At deposition times longer than 60 s, the particle deposit patterns were difficult to observe. As the thickness of the coatings increased, the electro-convection phenomena were less influential on particle pattern formation, and more dense coatings were obtained with smoothest surface topography.

The results indicated that well-controlled EPD processes can be considered as an alternative to produce different surface morphologies for functional coatings applications such as the Lotus effect.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Van Tassel, J. J. *Electrophoretic deposition: fundamentals, mechanisms and examples with an in depth examination of the ion depletion effect*; PhD. Thesis, The Pennsylvania State University, University Park, PA, 2004.
- (2) Han, Y.; Grier, D. G. *J. Chem. Phys.* **2005**, *122*, 164701.
- (3) Han, Y.; Grier, D. G. *J. Chem. Phys.* **2006**, *125*, 144706.
- (4) Han, Y.; Grier, D. G. *J. Chem. Phys.* **2012**, accepted.
- (5) Orlik, M.; Rosenmund, J.; Doblhofer, K.; Ertl, G. *J. Phys. Chem. B* **1998**, *102*, 1397–1403.
- (6) Trau, M.; Saville, D. A.; Aksay, I. A. *Langmuir* **1997**, *13*, 6375–6381.
- (7) Williams, R. J. *Chem. Phys.* **1963**, *39*, 384–388.
- (8) Trau, M.; Saville, D. A.; Aksay, I. A. *Science* **1996**, *272*, 706–709.
- (9) Han, Y.; Grier, D. G. *Nature* **2003**, *424*, 267.
- (10) Mondragón-Cortez, P.; Vargas-Gutiérrez, G. *Mater. Lett.* **2004**, *58*, 1336–1339.

- (11) Sarkar, P.; Nicholson, P. S. *J. Am. Ceram. Soc.* **1996**, *79*, 1987–2002.