

Application of constant current pulse to suppress bubble incorporation and control deposit morphology during aqueous electrophoretic deposition (EPD)[☆]

L. Besra, T. Uchikoshi^{*}, T.S. Suzuki, Y. Sakka

Nano Ceramics Center, Fine Particle Processing Group (WPI Center Initiative for Materials Nanoarchitectronics), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Received 21 April 2008; received in revised form 5 July 2008; accepted 9 July 2008

Available online 18 April 2009

Abstract

Electrophoretic deposition (EPD) from aqueous suspension generally forms deposits containing enormous pores because of evolution of hydrogen gas at cathode and oxygen at anode due to electrolysis of water on application of DC electric field. We have demonstrated through this investigation on aqueous EPD of alumina suspension as an example that application of pulsed DC instead of the conventionally used continuous DC is a convenient and effective way to control and suppress the amount of bubble incorporation in the deposit. Bubble-free deposits of reasonable yield were obtained at suitable pulse widths and/or duty cycle. The deposit yield and bubble incorporation decreased progressively with decrease in the pulse width and duty cycle of the applied pulse current. A characteristic deposition window was found in the current vs. pulse width plot within which smooth and bubble-free deposits are obtained. The window is wider at low-applied currents compared to that at higher currents implying that it is easier to control the pulsed EPD at lower applied currents. No deposition occurred below the window whereas deposits with incorporated bubbles formed above the window. Possible mechanisms involved in pulsed EPD have been advocated on the basis of amount of hydrogen evolved/pulse due to the electrolysis of water. The discrete amount of H₂ evolved/pulse was higher for larger pulse widths leading to incorporation of more bubbles and vice versa. This was verified by monitoring the gain in weight of palladium (Pd) electrode used as cathode for electrolysis experiment since it is known to absorb hydrogen.

© 2009 Published by Elsevier Ltd.

Keywords: Suspensions; Al₂O₃; Electrophoretic deposition; Pulse current

1. Introduction

Electrophoretic deposition (EPD) is a simple and useful colloidal process wherein deposition of charged particles occur on the oppositely charged electrode surface, from a stable suspension of the particles dispersed in a suspending liquid, under the influence of an applied DC electric field. The method has recently gained considerable interest in a wide range of novel applications in traditional and advanced ceramic materials, coatings to fabricate thin/thick films, multilayered composites, functionally graded materials, hybrid materials, self-supported

components, as well as micropatterned colloidal assemblies and nanotechnology.^{1–21} The major advantages and attractiveness of EPD is its simple apparatus, high rate of deposition, little restriction in the shape of substrate, suitability for mass production, reliability of the process, and no requirement for binder burnout as the green coating contains few or no organics. Compared to other advanced ceramic processing techniques, the EPD process is very versatile since it can be modified easily for specific application. In particular, despite being a wet process, EPD offers easy control of the thickness and morphology of a deposited film through simple adjustment of the operating conditions.

The primary step of an EPD process is preparation of a suspension, which is stable and develops surface charge on the particles dispersed in it. Most of the work on EPD reported in the literature has been done using non-polar organic solvents as the suspending medium.^{7,21} This is obviously because of several problems caused during EPD when water is used as the

[☆] This study was supported in part by the Grant-in-Aid for Scientific Research of the JSPS and by World Premier International Research Center Initiative (WPI) on Materials Nanoarchitectronics, MEXT, Japan.

^{*} Corresponding author.

E-mail address: uchikoshi.tetsuo@nims.go.jp (T. Uchikoshi).

suspending medium.¹⁵ The main problems are related to electrochemical reactions in the electrodes when a current is passed through, which seriously decreases the efficiency of the process and the uniformity of the deposit. Firstly, water electrolysis promotes the formation of H₂ and O₂ that can be retained as pores in the ceramic deposit. The gas bubbles generated at the electrode surface might also disturb the electrophoresis of the particles and suppress their deposition. Secondly, during EPD, the corrosion potential of most common metal is largely surpassed. This facilitates oxidation of the electrode and migration of metallic impurities in the opposite direction to that of the migrating particles. In most cases these impurities are retained in the deposit as heterogeneities and/or residual porosity, thus degrading its expected properties.²⁰ Another electrokinetic phenomena occurring during aqueous EPD is water electro osmosis, which consists of the movement of the liquid phase because of the external electric field. This may be helpful in demoulding of self-supported deposits as it accelerates drying of surface in contact with electrode, but leads to crack formation in thick deposits as a consequence of the drying gradient. The preference for organic liquids as suspending medium for EPD is due to their higher density, good chemical stability and low conductivity because of the absence of ions. However, most organic liquids are of low dielectric constant, which may sometimes limit the development of charge on the particles as a result of lower dissociating power. This may necessitate application of very high-electric field strengths to achieve reasonable yield at acceptable deposition times. Furthermore, severe safety precautions have to be met, if organic, often flammable solvents are used, especially in case of high voltages and/current densities.^{18,19} Finally, disposal of hazardous organic solvent waste and treatment of the suspension for its recovery as well as the absorption of volatile cracking products during heat treatment can prevent the introduction an EPD facility into an existing production line.¹⁹ But the use of aqueous system has important advantages since it requires much lower applied voltages and the environmental problems associated with organics are avoided.⁷ The use of water also enables higher temperature control during the process and faster kinetics, in addition to important health benefits, benign environment and low cost.^{9–11} These advantages have promoted a significant interest to develop water-based EPD to process technical ceramics.^{12–14}

Several approaches have been investigated and reported in the literature. The simplest method is to conduct EPD experiments at voltages lower than the decomposition voltage of water (1.23 V at 25 °C), but the deposition rate is negligible and not practical. Ryan et al.^{16,17} investigated the use of porous mould to separate and suppress bubble contamination in the deposit but found it to be ineffective. Other approaches include placing an ion permeable microporous membrane in front of the electrode,^{18,19} or to separate two compartment EPD cell containing a catholyte in the cathode compartment and an anolyte in the anode compartment.²⁰ The drawback of the above method is that the green density of the deposit obtained is low and is associated with high shrinkage (up to 30%) during drying and sintering. Moreover, deposition by the method is limited only on ion-exchange membrane. Other studies have involved

anodic deposition of the negatively charged particles on easily oxidisable anode like Zn, but the release of metal cations from the anodic material into the suspension leads to contamination of the deposit.^{21,23} Winkle²⁴ suggested addition of a suitable compound to the solution during electrodeposition of polymer film. The hydrogen produced at the cathode during the electrodeposition reacts with this non-gaseous compound rather than becoming hydrogen gas and forming bubbles. Wang et al.²⁵ designed a two-chamber electrochemical apparatus consisting of a physical barrier that prevents any trapped gas or gas generated during processing from residing in areas that can cause defects on the substrate. The apparatus contains two adjacent chambers and two separate electrolyte-containing fluids separated by a membrane, which prevents the gas from being transferred into the opposing chamber. The method is however complicated and expensive. Sakurada et al.²⁶ obtained bubble-free deposits of zirconia on anodic substrates of palladium or stainless steel by adding hydroquinone (HQ) to the alkaline aqueous suspension during EPD. The oxygen produced by electrolysis of water during EPD was believed to be consumed by the chemical oxidation of HQ to quinone (Q) at high pH in alkaline solution enabling bubble-free deposit on the anode substrate. Our recent studies have shown that the deposition on palladium cathodic substrate can produce bubble-free deposits with high density since palladium readily absorbs the hydrogen gas.^{11,27–29} In our previous communication, we presented a method based on application of constant voltage pulse for obtaining dense and bubble-free deposit by electrophoretic deposition from aqueous suspension.³⁰ Continuing with our investigation on pulsed EPD, here we present the application of constant current pulse to control the amount of bubble incorporation as well as to obtain bubble-free deposit during aqueous EPD.

2. Experimental

α -Alumina (Al₂O₃) powder (Sumitomo AKP-50) used in this study had an average particle size of 0.20 μ m. It was first dispersed in ultrapure distilled water by ultrasonication at 160 kW for 10 min, to break up the agglomerates. The pH of the suspension was adjusted by nitric acid and sodium hydroxide. The zeta potential of the suspension as measured by a laser electrophoresis zeta-potential analyser (LEZA-600, Otsuka Electronics Co., Osaka, Japan) indicated the isoelectric point (iep) of the alumina powder to be at pH 7.9. The alumina powder surface is positively charged at pH below 7.9 and is negatively charged at pH above 7.9. The EPD experiments were carried out in a manner similar to that in our previous communication.³⁰ Stainless steel (316L) plates of 2 cm \times 5 cm \times 0.4 mm dimension were used as deposition as well as counter-electrode. The electrodes were immersed into the suspension in a glass beaker and deposition was carried out on an area of 2 cm \times 2 cm with the inter-electrode distance maintained at 20 mm for all the experiments. Unless otherwise mentioned, the EPD experiments were conducted with 5 vol% suspension.

Pulsed EPD was conducted at constant current mode by application of a series of direct current pulse of equal amplitude separated by periods of zero current, using a source meter (Model

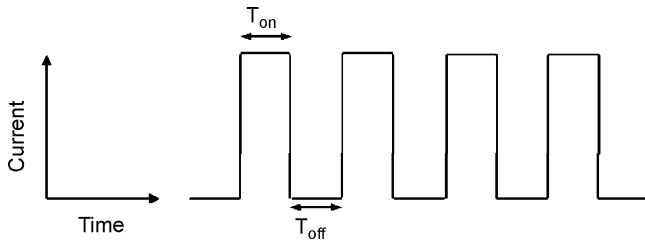


Fig. 1. Schematic of constant current pulse of 50% duty cycle.

2611, Keithley Instruments, Inc., USA). Simple square-wave pulses of desired duty cycles were used. The duty cycle (dc) of the pulse [i.e. $dc = T_{on}/(T_{on} + T_{off})$] were varied by keeping the pulse ON time (T_{on}) constant and varying the pulse OFF time (T_{off}). Fig. 1 shows a typical current pulse wave of 50% duty cycle. Unless and otherwise mentioned, deposition was carried out for a total pulse ON time (T_{on}) of 3 min. It must be noted that the actual time of experiment was much more than 3 min, and increased with decrease in pulse width. The influence of pulse width and duty cycle on deposit yield and quality was studied. The obtained deposits were dried overnight in air at room temperature and weighed together with the substrates to determine the deposit weight. The deposit quality was examined macroscopically by optical photographs recorded using a stereomicroscope.

3. Results and discussion

3.1. EPD by continuous DC

Preliminary experiments on application of constant current EPD conducted in either continuous mode or pulsed mode at varying pH revealed that the homogeneity of deposit obtained at pH above iep on anode substrate were very poor compared to cathodic deposition conducted at pH below iep. Although, such observations have not been reported in the literature, we made similar observations during constant voltage EPD as well.³⁰ It formed non-uniform deposits in patches on anode. A probable reason for formation of inhomogeneous deposits with more bubbles for anodic deposition compared to the cathodic ones may be based on differential solubility of hydrogen and oxygen in water. The solubility of hydrogen in water at 25 °C and 1 bar pressure is about 1617.6 mg/L whereas that of oxygen is only about 43.3 mg/L. Therefore, the hydrogen gases evolved are likely to get dissolved and/or diffused away easily from the cathode surface compared to dissolution and diffusion of oxygen from the anode. This could result in high residence time of oxygen gases near the anode compared to the residence time of hydrogen near the cathode. Higher residence time of oxygen gas near the anode will adversely influence and limit mass transport of particles to the electrode surface leading to more inhomogeneous morphology of deposits during anodic EPD. At pH values very near the iep, thick deposits seem to form on the electrode surface in the suspension but their adhesiveness to the surface was very weak for which they fall off when taking out from the suspension. Similar observations were made during our previ-

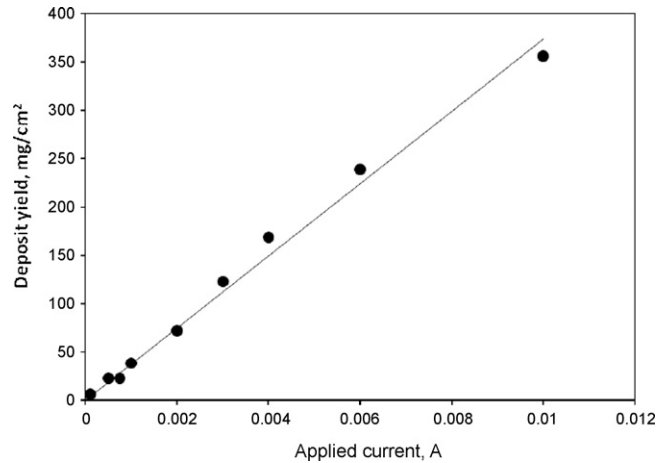


Fig. 2. Deposit yield as a function of applied current during continuous DC EPD [suspension: 5 vol%, pH 4.5, deposition time: 3 min, inter-electrode distance: 20 mm].

ous studies on constant voltage pulsed EPD as well.²⁹ The poor adhesion is attributed to spontaneous bulk flocculation of particles by van der Waals attraction because of small magnitude of zeta-potential and absence of a strong electrostatic repulsion force near the iep. The gravity effect of the aggregate thus formed is perhaps higher than the electrophoretic effect. The green density of the deposit obtained at pH away from the iep were found to be higher than those obtained near the iep. For example, the density of deposit obtained from 5 vol% suspension at applied current of 0.004 A decreased from about 60% at pH 4.5–50% at pH 7.5. This is expected because the particles are well dispersed away from iep because of electrostatic repulsion on account of high zeta-potential. Hence they form deposits of well-packed compacts by electrophoresis compared to that near iep. Therefore, all the subsequent studies on pulsed EPD were conducted at pH below iep. Incorporation of bubbles in the deposit was also found to be higher at pH value away from iep. Fig. 2 presents the deposit yield as a function of applied current during constant current EPD in continuous mode for 5 vol% alumina suspension at pH 4.5, and deposition time of 3 min. As expected, it shows a linear increase in deposit yield with increasing current in accordance with Hamaker's law.^{3,31} Fig. 3 shows the surface morphology of the deposits obtained at different constant currents applied in continuous mode. It clearly indicates that the amount of bubble incorporation gets decreased with decrease in the applied current from 0.004 A to 0.0005 A. This is because of decrease in electrolysis of water with decreasing currents. We obtained bubble-free deposits at 0.0005 A but with a very low yield of about 22.3 mg/cm². The corresponding variation in voltage during the EPD process as a function of time is shown in Fig. 4. For applied currents below 0.001 A, the voltage initially rises and attains a steady state and constant value within 10 s. At applied current of 0.001 A and above, the voltages continue to rise gradually after the initial attainment of steady value. The increase is steeper for higher applied current. There appears a direct relationship between the rise in voltage and bubble incorporation in the deposit. Lower the rise in voltage, lower is the bubble incorporation and vice versa.

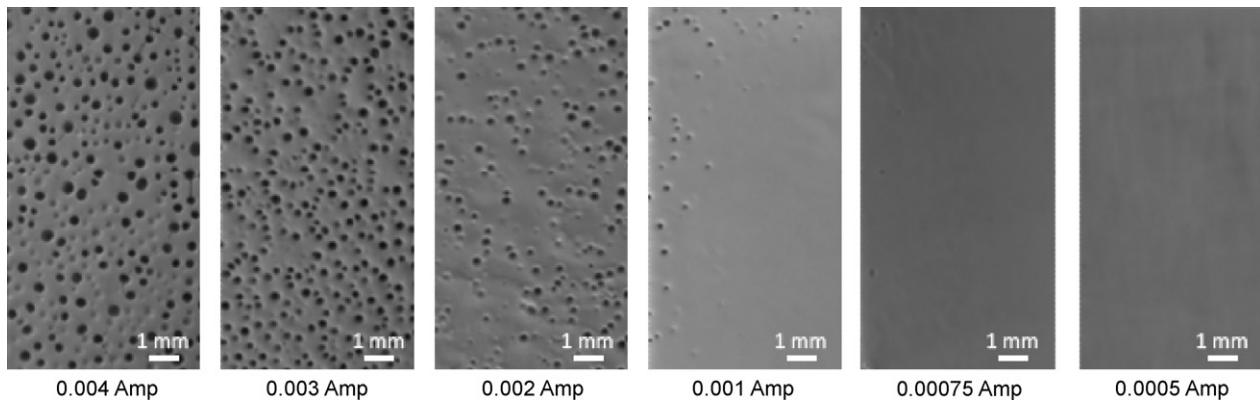


Fig. 3. Surface morphology of deposits obtained by continuous DC EPD in constant current mode [suspension: 5 vol%, pH 4.5, deposition time: 3 min, inter-electrode distance: 20 mm].

3.2. EPD by pulse current

3.2.1. Effect of pulse width

Pulsed EPD was conducted at constant amplitude of applied currents but at varying pulse widths for each applied currents. Fig. 5 presents the deposit yield as a function of pulse widths for each applied current. It must be noted that a current pulse of 180 s, is equivalent to continuous DC EPD for 3 min. It is evident from the figure that maximum yield is obtained at continuous DC for each applied current. Application of pulse current invariably decreases the deposit yield. The yield is higher for high-applied currents for each of the pulse widths investigated. For each applied current, the yield initially increases rapidly with increase in pulse widths in the lower region of pulse widths. The increase becomes gradual and tends to attain a plateau with further increase in pulse width.

Fig. 6 presents the surface morphology of deposits obtained at different pulse widths for 0.004 A and 0.006 A applied current. It clearly shows maximum bubble incorporation in the case of continuous DC for both applied currents. The bubble incorporation decreases on application of pulse current. In general, more bubbles are found on deposits formed with high pulse width than

those formed at low pulse widths. Bubble-free deposits were obtained at current pulses smaller than or equal to 0.005 s, for applied current of 0.004 A, and at a pulse width of 0.001 s, for the applied current of 0.006 A. The bubble-free deposit yield of 109 mg/cm^2 at 0.005 s, pulse of 0.004 A and the yield of 56.2 mg/cm^2 at 0.001 s, pulse of 0.006 A applied currents are significantly higher than the deposit yield of only 22.3 mg/cm^2 obtained by continuous DC EPD at 0.0005 A (Figs. 2 and 3).

A series of experiments were conducted at different pulse widths at close ranges for each of the applied currents to determine the range within which macroscopically bubble-free deposits are obtained. Fig. 7 presents a comprehensive plot of such range of pulse widths for each applied current for 5 vol% alumina deposited on steel substrates at pH 4.5. Similar to our earlier observation on constant voltage pulse EPD,³⁰ there exists a window in the plot of pulse width vs. applied current with a lower limit of pulse width below which deposition does not occur. There also exists an upper threshold limit of pulse width above which deposits invariably contained bubbles. Homogeneous and bubble-free deposits are obtained within this window of pulse width. As an example, the lower limit of pulse width for 0.004 A applied current is 0.001 s, and the upper limit is

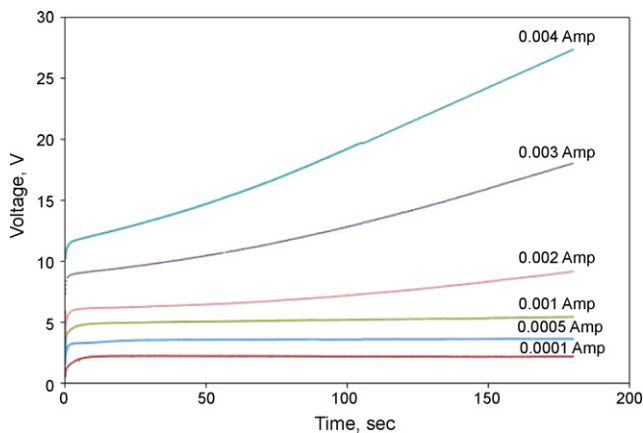


Fig. 4. Variation in voltage with time during constant current continuous DC EPD of alumina suspension at different applied currents [suspension: 5 vol%, pH 4.5, substrate: stainless steel (316L), deposition time: 3 min, inter-electrode distance: 20 mm].

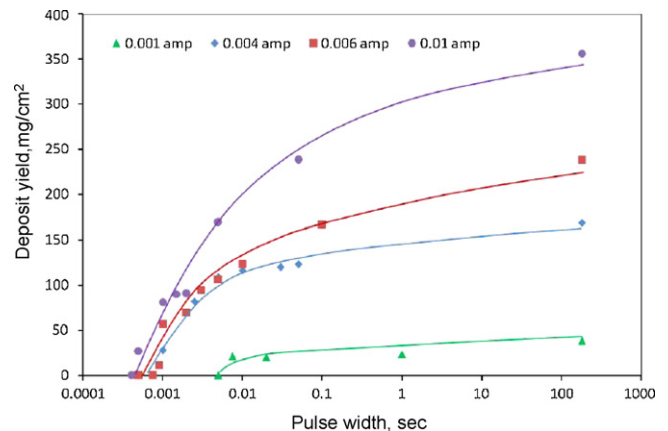


Fig. 5. Deposit yield as a function of pulse width during pulsed DC EPD at constant current mode [suspension: 5 vol%, pH 4.5, substrate: stainless steel (316L), pulse ON time: 3 min, pulse duty cycle: 50%, inter-electrode distance: 20 mm, pulse width of 180 s, is equivalent to continuous DC EPD of 3 min].

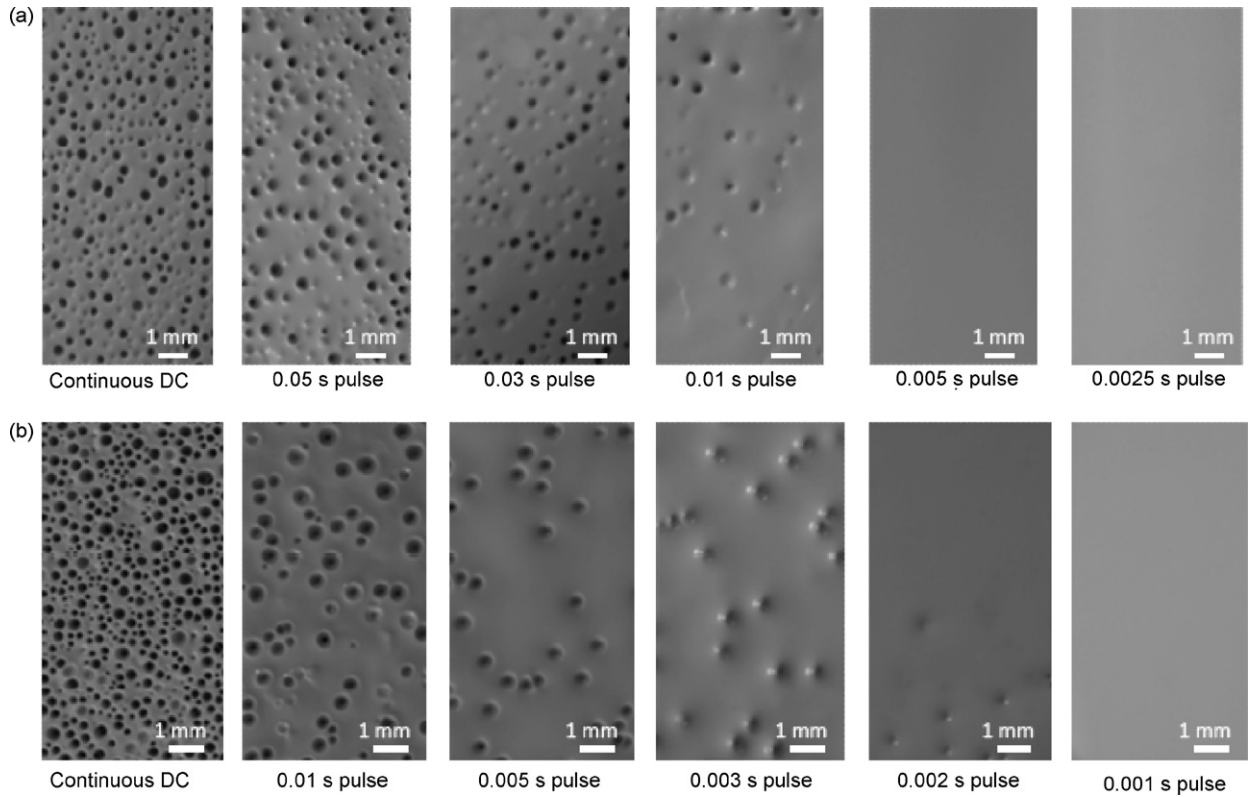


Fig. 6. Surface morphology of deposits obtained by pulsed DC EPD in constant current mode (a) applied current: 0.004 A, (b) applied current: 0.006 A [suspension: 5 vol%, pH 4.5, substrate: stainless steel (316 L), pulse ON time: 3 min, pulse duty cycle: 50%, inter-electrode distance: 20 mm].

0.005 s. Such window of pulse width was found to be broader at low-applied currents and very narrow at higher applied currents. Hence it is very critical to set the pulse width carefully specially at higher currents. It may be easier to control bubble suppression at low currents because of broader window of pulse width. But since the deposit yield is lower at very low currents, optimization is necessary depending on the desired yield.

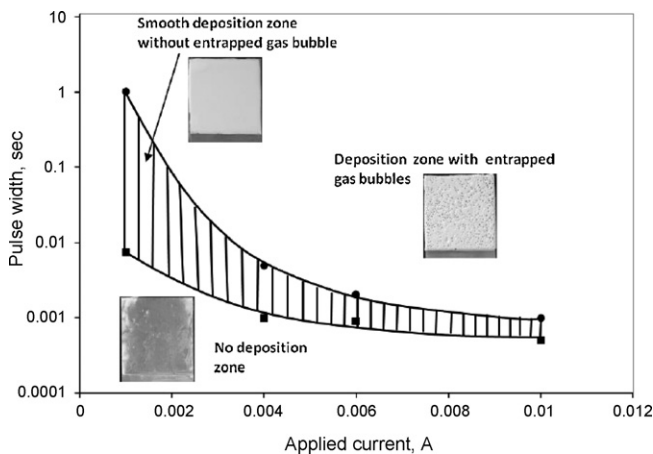


Fig. 7. Pulse-width vs. applied voltage diagram showing the window (hatched region) in which bubble-free deposits are obtained during pulsed DC EPD at constant current mode [suspension: 5 vol%, pH 4.5, substrate: stainless steel (316 L), pulse ON time: 3 min, pulse duty cycle: 50%, inter-electrode distance: 20 mm].

Fig. 8 shows the variation in voltage with time for varying pulse widths at constant applied current of 0.004 A. It shows voltage profile similar to that observed for continuous DC EPD shown in Fig. 4. For very low pulse widths up to 0.005 s, the voltage attains a steady state after about 10 s, and then remains constant. For pulse widths above 0.005 s, the voltage tends to increase continuously after the steady state value. Coincidentally, bubble-free deposits are obtained at pulse widths up to 0.005 s. The deposits contained bubbles at higher pulse widths. This suggests that the voltage value is also a useful indicator

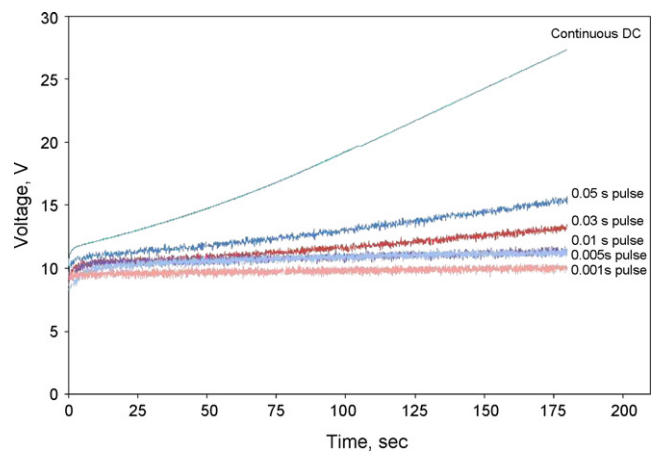


Fig. 8. Variation in voltage with time during pulsed constant current EPD [applied current: 0.004 A; pulse ON time: 3 min; pulse duty cycle: 50%, suspension: 5 vol%, pH 4.5, inter-electrode distance: 20 mm].

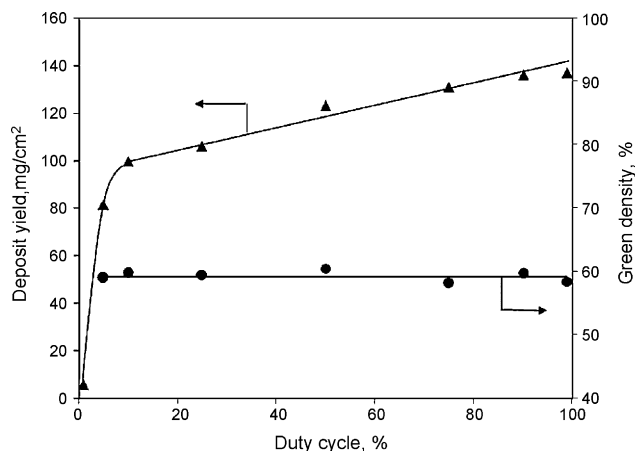


Fig. 9. Effect of duty cycle on yield and green density of deposits obtained by constant current pulsed EPD of 5 vol% alumina suspension [pH 4.5; applied current 0.004 A, $a_{\text{on}} = 0.05$ s].

of identifying bubble formation during constant current pulsed EPD. Higher the rise in voltage, more was the bubble incorporation and vice versa.

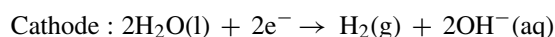
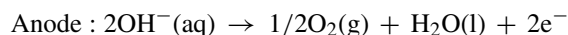
3.2.2. Effect of duty cycle

T_{on} of the pulse represents the portion of the pulse cycle for which the voltage is ON, and T_{off} is the portion of the cycle for which the voltage is OFF. By changing the T_{on} and T_{off} we could change the frequency of pulse application at constant current. Experiments were conducted to study the influence of varying duty cycle from 1% to 99% on deposit yield, surface morphology and green density. Fig. 9 shows the yield and green density of deposits obtained at 0.004 A applied current as a function of duty cycle with a constant T_{on} of 0.05 s, and varying T_{off} . No deposition occurred at very low duty cycle lower than 1%. The deposit yield increased very rapidly through duty cycle between 1% and 10%. There is a linear increase in deposit yield with increasing duty cycle between 10% and 99%. The deposit formed at 1% duty cycle was very thin and formed only on a small patch for which density could not be measured. The green density of all the other deposits obtained at duty cycles higher than 1% remained almost constant at 59%. This is again in agreement with our previous study on constant voltage EPD in which the density remained constant due to the formation of only open pores and absence of any closed pores.³⁰ The corresponding surface morphology is shown in Fig. 10. It clearly indicates that the surface morphology do not change markedly with decrease in duty cycle from 99% to 50%. But further decrease in duty cycle below 50% results in minimization of bubble incorporation. Bubble-free deposit with a yield of 81.5 mg/cm² is obtained at 5% duty cycle.

3.3. Mechanism

The application of pulse current (PC) is not new and have been used extensively for electrodeposition of metals from their inorganic salt solutions.^{32–38} But to the best of our knowledge, it has not been utilised for electrophoretic deposition of ceramic

powder in aqueous suspension possibly because the basic underlying mechanism is not clearly understood. This is evident from the fact that in the literatures available on pulse plating, no attempt has been made to describe the involved mechanism. The primary questions that remain unanswered for pulsed EPD are: (i) what makes the particles migrate towards the deposition electrode during OFF time (T_{off}) of the pulse when the applied current is zero, and (ii) why bubble incorporation minimises on application of pulse current. It is perceived that when continuous DC is applied, the mass transport of particles due to the electrophoretic effect and their deposition at the electrode is a continuous process. During pulsed EPD, the mass transport of the particles from bulk suspension towards the electrode surface is likely to continue even during the current interruption due to their inertia of mobility caused by the effect of preceding current ON duration (T_{on}). The continuity in mass transport during T_{off} was verified using Microelectrophoresis Apparatus Mark-II (M/s. Rankbrothers Ltd., UK) with provision for a video display. The particles continued to move across the grids in the video monitor towards the electrode of opposite polarity for a few more seconds after switching off the DC supply before it finally stopped moving. One of the reason contributing to minimization of bubble incorporation during constant voltage pulse EPD³⁰ was attributed to the decrease in current with decreasing pulse size. It is indeed verified from continuous current EPD results shown in Fig. 3 of this investigation that a decrease in applied current results in minimization of bubbles but with a very low yield. However, it is intriguing to observe minimization of bubble in the case of constant current pulsed EPD. There can be several possibilities: (i) the hydrogen or oxygen emitted at the electrode interface might be partly diffused away from the substrate during the duration of current interruption (T_{off}) and suppressed from being incorporated in the deposit during pulse EPD,^{39,40} (ii) the discrete amount of gas generated by electrolysis of water during each ON time (T_{on}) of a pulse is expected to be significantly less compared to a single continuous DC. Theoretically, a summation of the gas generated by all the pulse may be same as the total gas evolved by electrolysis of water on application of continuous current. We believe that the gas evolution and dissipation in the case of pulse current electrolysis is a dynamic process in which the gas generation sites on the electrode surface for a pulse keep changing with pulse and may be different from the preceding and succeeding ones. Such evolution of gas at different sites for each pulse ON time will lead to presence of uncoalesced micro and nanosized bubbles uniformly distributed throughout. Incorporation of such small bubbles will not produce any macro-bubbles in the deposit. Since it is known from electrochemistry that ampere \times time = coulombs; 96,485 coulombs = 1 Faraday; and 1 Faraday = one mole of electron, we made an estimate of the theoretically possible amount of hydrogen generation during each pulse ON time (T_{on}) for all the pulse widths from the following decomposition reaction in which two moles of electrons produced one mole of H₂ gas:



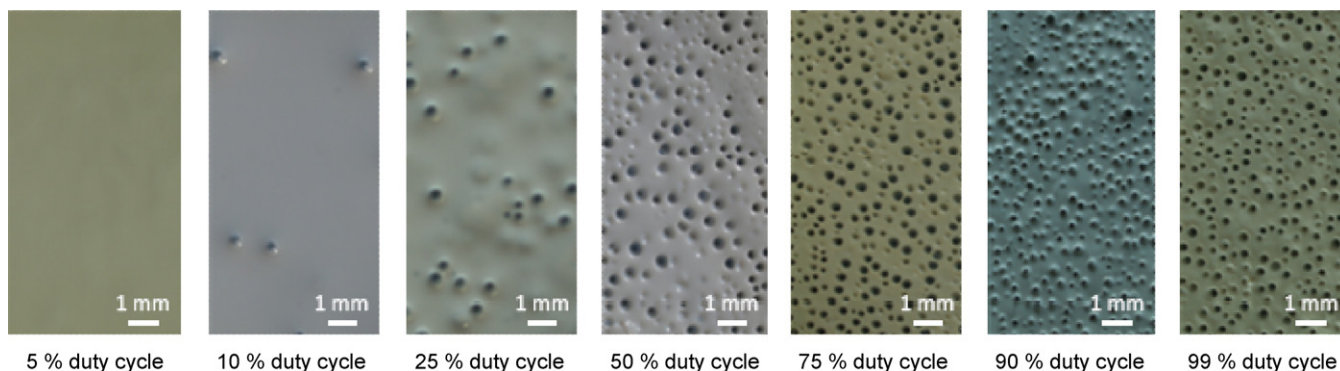


Fig. 10. Influence of duty cycle on surface morphology of deposits obtained by constant current pulsed EPD of 5 vol% alumina suspension [pH 4.5; applied current 0.004 A, $T_{\text{on}} = 0.05$ s].

The overall cell reaction is:

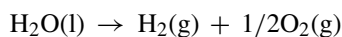


Fig. 11 presents a comprehensive summary of the estimated amount of H_2 at different pulse width as a function of the applied current. It clearly indicates that the H_2 evolved/pulse is significantly less compared to continuous DC. Also, the larger pulse widths produce higher amount of H_2 gas than the smaller ones. As an example, the amount of H_2 evolved during continuous DC electrolysis on application of 0.004 A for 3 min, is 3.7311×10^{-3} mg. The corresponding amount of H_2 evolved during each of the pulse ON time of 0.1 s, for the same applied current of 0.004 A is 2.0728×10^{-6} mg.

We have made a direct experimental verification of H_2 evolution during electrolysis of distilled water by continuous and pulsed current by monitoring the gain in weight of a palladium (Pd) cathode suspended into the electrolysis bath from an analytical balance (Mettler Toledo, Model AG 204; measurement accuracy: 0.1 mg), which is generally used for estimating density of bulk materials by Archimedes' method. Since palladium (Pd) is known to absorb hydrogen,^{12,27,28} the gain in weight

of the Pd electrode can be directly attributed to the amount of hydrogen absorbed by it. Fig. 12 shows the weight gain as a function of time. It indicates linear increase in weight of the electrode with increasing time. As expected, maximum weight gain is noticed in the case of continuous current and it decreases progressively with decrease in pulse size. It is also noticed that the weight gain at the end of the total pulse ON time of 3 min, for different pulses are not equal to that due to continuous current. It decreases with decrease in pulse size. Therefore, it is possible that not all the hydrogen evolved are absorbed by the palladium electrode. Some of the hydrogen may have been dissipated away. Hence, for the same applied current, the amount of gas evolution by electrolysis and their presence near the electrode can be controlled simply by varying the pulse size. With this argument, the bubble generation and incorporation in the deposit for the case of continuous DC EPD is expected to be the maximum and have been indeed experimentally found to be true. With decreasing size of pulse width the amount of bubble incorporation has been found to decrease because of decrease in electrolysis and uniform distribution of the H_2 gas without coalescence at lower pulse sizes.

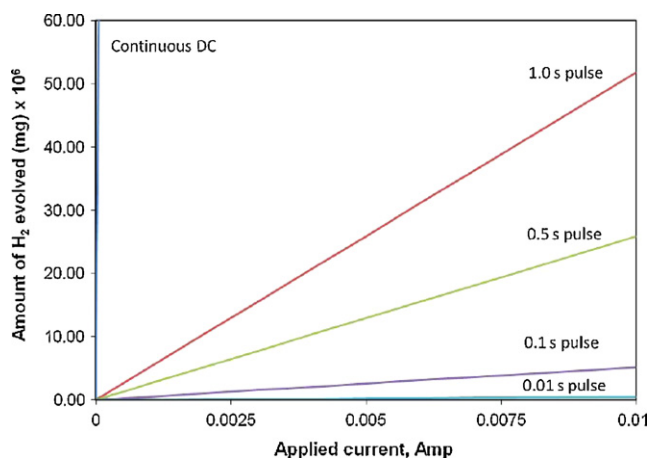


Fig. 11. Possible amount of hydrogen evolved during the ON time (T_{on}) of each pulse cycle as a function of applied current estimated from electrolysis of pure water [pH 7.04].

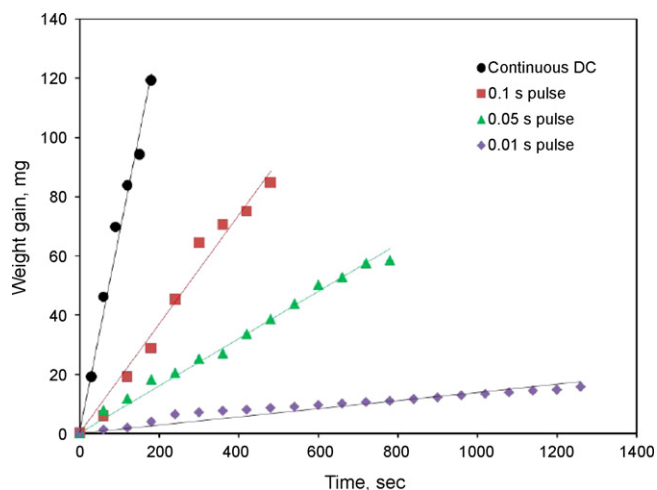


Fig. 12. Weight gain of Pd electrode with time of electrolysis at different pulse sizes of 50% duty cycle [pH: 7.04; applied current: 0.001 A; total pulse ON time: 3 min].

4. Conclusions

Based on the above investigation the following conclusions can be made:

- Application of a pulse current of suitable width enables controlling the amount of bubble incorporation and obtaining smooth, bubble-free deposit by electrophoretic deposition from aqueous suspension.
- The yield of deposits obtained at the end of the experiment by constant current pulse EPD is generally less than that obtained by EPD using continuous current. The deposited weight decreases progressively with decrease in pulse width.
- The deposit yield is higher for higher applied current in the whole range of pulse widths.
- There exists the narrow window in the plot of applied current vs. pulse width within which bubble-free deposits are obtained by continuous current pulsed EPD. For any applied current, there is no deposition at pulse widths smaller than the lower limit of the window. At pulse widths above the upper limit of the window, the deposits invariably contained bubbles in them.
- The width of the deposition window for obtaining bubble-free deposit is wider and lies at higher value of pulse for lower applied currents compared to that for higher applied currents. It indicates that it is more convenient and practicable to control the pulse EPD for obtaining bubble-free deposit at lower applied currents but at the expense of deposit yield.
- Yield and bubble incorporation in the deposit could also be controlled by controlling the pulse duty cycle. Lower the duty cycle, less was the bubble incorporation and vice versa.
- Green density of deposits obtained at all the duty cycles for an applied current is same.
- The suppression of bubbles during pulsed current EPD is possibly due to low H₂ evolution by pulsed current electrolysis and their uniform dissipation and minimization of their coalescence in forming bigger bubbles.

Acknowledgment

One of the authors LB is thankful to National Institute for Materials Science (NIMS) for the postdoctoral fellowship.

References

1. Put, S., Vleugels, J., Anne, G. and Van der Biest, O., Functionally graded ceramic and ceramic-metal composites shaped by electrophoretic deposition. *Colloids Surf. A: Physicochem. Eng. Aspects*, 2003, **222**, 223–232.
2. Sarkar, P., Datta, S. and Nicholson, P. S., Functionally graded ceramic/ceramic and metal/ceramic composites by electrophoretic deposition. *Composites Part B*, 1997, **28B**, 49–54.
3. Besra, L. and Liu, M., A review on fundamentals and applications of electrophoretic deposition (EPD). *Prog. Mater. Sci.*, 2007, **52**, 1–61.
4. Corni, I., Ryan, M. P. and Boccaccini, A. R., Electrophoretic deposition: from traditional ceramics to nanotechnology. *J. Eur. Ceram. Soc.*, 2008, **28**, 1353–1367.
5. Rogach, A. L., Kotov, N. A., Koktysh, D. S., Ostrander, J. W. and Ragoisha, G. A., Electrophoretic deposition of latex based 3D colloidal photonic crystals: a technique for rapid production of high quality opals. *Chem. Mater.*, 2000, **12**, 2721–2726.
6. Zhang, Q., Xu, T., Butterfield, D., Misner, M. J., Ryu Du, Y. and Emrick, T., Controlled placement of CdSe nanoparticles in block copolymer templates by electrophoretic deposition. *NanoLetters*, 2005, **5**(2), 357–361.
7. Negishi, H., Yamaji, K., Imura, T., Kitamoto, D., Ikegami, T. and Yanagishita, H., Electrophoretic deposition mechanism of YSZ/n-propanol suspension. *J. Electrochem. Soc.*, 2005, **152**(2), J16–22.
8. Ferrari, B. and Moreno, R., Electrophoretic deposition of aqueous alumina slip. *J. Eur. Ceram. Soc.*, 1997, **17**, 549–556.
9. Bailey, R. C., Stevenson, K. J. and Hupp, J. T., Assembly of micropatterned colloidal cold thin films via microtransfer molding and electrophoretic deposition. *Adv. Mater.*, 2000, **12**(24), 1930–1934.
10. Holgado, M., Garcia-Santamaria, F., Blanco, A., Ibisate, M., Cintas, A., Miguez, H., Serna, C. J., Molpeceres, C., Requena, J., Mifsud, A., Meseguer, F. and Lopez, C., Electrophoretic deposition to control artificial opal growth. *Langmuir*, 1999, **15**(14), 4701–4704.
11. Tang, F. Q., Uchikoshi, T., Ozawa, K. and Sakka, Y., Electrophoretic deposition of aqueous nano- γ -Al₂O₃ suspensions. *Mater. Res. Bull.*, 2002, **37**(4), 653–660.
12. Garcia, P., Ferrari, B., Moreno, R., Sanchez-Herencia, A. J. and Colomer, M. T., YSZ/Ni-YSZ semi-cells shaped by electrophoretic deposition. *J. Eur. Ceram. Soc.*, 2007, **27**(13–15), 4241–4244.
13. Zhao, J., Wang, X. and Li, L., Electrophoretic deposition of BaTiO₃ films from aqueous suspensions. *Mater. Chem. Phys.*, 2006, **99**(2–3), 350–353.
14. Uchikoshi, T. and Sakka, Y., Electrophoretic deposition characteristics of alumina particles in aqueous media. *J. Ceram. Soc. Jpn.*, 2004, **112**(5), S63–S66.
15. Moreno, R. and Ferrari, B., Effect of the slurry properties on the homogeneity of alumina deposits obtained by aqueous electrophoretic deposition. *Mater. Res. Bull.*, 2000, **35**, 887–897.
16. Ryan, W. and Massoud, E., Electrophoretic deposition could speed up ceramic casting. *Interceramics*, 1979, **2**, 117–119.
17. Ryan, W., Massoud, E. and Perera, C. T. S. B., Fabrication by electrophoresis. *Trans. Brit. Ceram. Soc.*, 1981, **80**, 46–47.
18. Clasen, R., Ceramic transactions, vol 54, *Science Technology and Applications of Colloidal Suspensions*. Ed. by Adair, J.H., Casey, J.A., Randall, C.A., and Venigalla, S., *Am. Ceram. Soc.*, Westerville, OH, 1995, pp. 169–184.
19. Tabellion, J. and Clasen, R., Electrophoretic deposition from aqueous suspension for near-shape manufacturing of advanced ceramics and glasses-applications. *J. Mater. Sci.*, 2004, **39**, 803–811.
20. Kanamura, K. and Hamagami, J., Innovation of novel functional material processing technique by using electrophoretic deposition process. *Solid State Ionics*, 2004, **172**, 303–308.
21. Ferrari, B., Farinas, J. C. and Moreno, R., Determination and control of metallic impurities in alumina deposits obtained by aqueous electrophoretic deposition. *J. Am. Ceram. Soc.*, 2001, **84**(4), 733–739.
22. Tang, F. Q., Sakka, Y. and Uchikoshi, T., Electrophoretic deposition of aqueous nano-sized zinc oxide suspensions on a zinc electrode. *Mater. Res. Bull.*, 2003, **38**(2), 207–212.
23. Winkle, M.R., Elimination of Film Defects due to Hydrogen Evolution During Cathodic Electrodeposition. US Patent 5,066,374, November 1991.
24. Wang, Y., Liu, F.Q., Duboust, A., Neo, S.S., Yuh Chen, L., and Hu, Y., Hydrogen Bubble Reduction on the Cathode Using Double Cell Design. US Patent 7,229,535 B2, June 2007.
25. Sakurada, D., Suzuki, K., Miura, T. and Hashiba, M., Bubble-free electrophoretic deposition of aqueous zirconia suspensions with hydroquinone. *J. Mater. Sci.*, 2004, **39**, 1845–1847.
26. Uchikoshi, T., Ozawa, K., Hatton, B. D. and Sakka, Y., Dense, bubble-free, ceramic deposits from aqueous suspensions by electrophoretic deposition. *J. Mater. Res.*, 2001, **6**(2), 321–324.
27. Uchikoshi, T., Hisashige, T. and Sakka, Y., Stabilisation of Ytria aqueous suspension with polyethyleneimine and electrophoretic deposition. *J. Ceram. Soc. Jpn.*, 2002, **110**, 840–843.
28. Tang, F. Q., Uchikoshi, T. and Sakka, Y., Electrophoretic deposition behavior of aqueous nanosized zinc oxide suspensions. *J. Am. Ceram. Soc.*, 2002, **85**(9), 2161–2165.
29. Besra, L., Uchikoshi, T., Suzuki, T.S., and Sakka, Y., Bubble-free aqueous electrophoretic deposition (EPD) by pulse-potential application. *J. Am. Ceram. Soc.*, in press.

31. Hamaker, H. C., Formation of deposition by electrophoresis. *Trans. Faraday Soc.*, 1940, **36**, 279–283.
32. Sing, M.W., and Sing, F. Y., Pulse Electroplating Process. US Patent 4,789,437, December 1988.
33. Ghosh, S. K., Grover, A. K., Dey, G. K., Totlani, M. K. and Nanocrystalline, Ni-Cu alloy plating by pulse electrolysis. *Surf. Coat. Technol.*, 2000, **126**, 48–63.
34. Mahalingam, T., Chitra, J. S. P., Ravi, G., Chu, J. P. and Sebastian, P. J., Characterisation of pulse plated Cu₂O thin films. *Surf. Coat. Technol.*, 2003, **168**, 111–114.
35. Lallemand, F., Ricq, L., Deschaseaux, E., De Vettor, L. and Bercot, P., Electrodeposition of cobalt-iron alloys in pulsed current from electrolytes containing organic additives. *Surf. Coat. Technol.*, 2005, **197**, 10–17.
36. Chan, K. C., Qu, N. S. and Zhu, D., Quantitative texture analysis in pulse reverse current electroforming of nickel. *Surf. Coat. Technol.*, 1998, **99**, 69–73.
37. Pavlatou, E. A., Raptakis, M. and Spyrellis, N., Synergistic effect of 2-butyn-1,4-diol and pulse plating on the structure and properties of nickel nanocrystalline deposits. *Surf. Coat. Technol.*, 2007, **201**, 4571–4577.
38. Obradovic, M. D., Bosnjakov, G. Z., Stevanovic, R. M., Maksimovic, M. D. and Despic, A. R., Pulse and direct current plating of Ni-W alloys from ammonium-citrate electrolyte. *Surf. Coat. Technol.*, 2006, **200**, 4201–4207.
39. Sakura, Y., Tsuchiya, I., and Mano, K., Metal Plating Method. US Patent 6,641,710 B2, November 2003.
40. Arlt, K., Eckert, K., Stockbrink, M., Schulte, R., Berlin, H., and Nienhaus, G., Pulse-modulated DC Electrochemical Coating Process and Apparatus. US Patent 6,197,179 B1, March 2001.