Uniform Design for the Optimization of Al_2O_3 Nanofilms Produced by Electrophoretic Deposition

Gu Song[a], Guoqiang Xu[a], Yongkai Quan[a], Qingchun Yuan[b], Philip A. Davies[b]*

[a] National Key Laboratory of Science and Technology on Aero-Engine Aero-thermodynamics, School of

Energy and Power Engineering, Beihang University, Beijing 100191, China

[b] School of Engineering and Applied Science, Aston University, Birmingham, B4 7ET, UK

* Corresponding author p.a.davies@aston.ac.uk

Abstract

Surface modification by means of nanostructures is of interest to enhance boiling heat transfer in various applications including the organic Rankine cycle (ORC). With the goal of obtaining rough and dense aluminum oxide (Al_2O_3) nanofilms, the optimal combination of process parameters for electrophoretic deposition (EPD) based on the uniform design (UD) method is explored in this paper. The detailed procedures for the EPD process and UD method are presented. Four main influencing conditions controlling the EPD process were identified as: nanofluid concentration, deposition time, applied voltage and suspension pH. A series of tests were carried out based on the UD experimental design. A regression model and statistical analysis were applied to the results. Sensitivity analyses of the effect of the four main parameters on the roughness and deposited mass of Al_2O_3 films were also carried out. The results showed that Al_2O_3 nanofilms were deposited compactly and uniformly on the substrate. Within the range of the experiments, the preferred combination of process

parameters was determined to be: nanofluid concentration of 2 wt%, deposition time of 15 mins, applied voltage of 23 V and suspension pH of 3, yielding roughness and deposited mass of 520.9 nm and 161.6×10^{-4} g/cm^2, respectively. A verification experiment was carried out at these conditions and gave values of roughness and deposited mass within 8% error of the expected ones as determined from the UD approach. It is concluded that uniform design is useful for the optimization of electrophoretic deposition requiring only 7 tests compared to 49 using the orthogonal design method.

Keywords

Electrophoretic deposition; Nanofilms; Uniform design; Surface modification; Boiling heat transfer enhancement; Statistical analysis

1. Introduction

Surface modification is promising to enhance boiling heat transfer in several industries including solar thermal power plant, organic Rankine cycle (ORC), desalination and refrigeration. Modifications like microscale pin fins, microchannels and microporous coatings on the boiling surface have proven to be effective methods in improving the heat transfer coefficient (HTC) [1]. Recently, nanostructure coatings on the surface, to increase the roughness and the active nucleation site density, have gained more and more attention not only because of the increase of HTC but also because of the delay of critical heat flux (CHF) [2, 3].

Electrophoretic deposition (EPD) is a convenient technique to produce homogeneous

nanofilms from nano suspensions. Compared to other processes like molecular beam epitaxy, spray pyrolysis and pulsed laser deposition, EPD has advantages of 1) high speed, 2) easy control of process parameters, 3) possibility of coating substrates with complex shape, and 4) low cost and simplicity [4, 5]. In EPD, charged powder particles dispersed in a liquid are attracted by an electric field towards a conductive substrate of opposite charge where they deposit as a permanent coating. The thickness and morphology of a deposited film depends on many parameters like suspension concentration, deposition time, applied voltage and suspension pH. The challenge is to find out the optimal combination of process parameters for the rough and dense deposited nanofilms obtained by EPD.

As summarized in Table 1, several papers have been published on this topic providing a variety of results [1, 6-15]. For example, Tang et al. [6, 7] stated that the pH value, ionic conductivity and viscosity are key factors of the EPD process. Dense, uniform and bubble-free films of γ-Al$_2$O$_3$ and ZnO were obtained with the use of well dispersed suspensions. And the addition of surfactant and sintering under higher temperature were necessary. Tang et al. [8] investigated the mechanism of EPD behavior of an aqueous suspension with a dispersant of polyethylenimine (PEI) to modify the surface charge of the TiO$_2$ powders. The result reflected the synergetic effect of the viscosity and conductivity of the suspension as well as the surface electric charge of the particles in determining the deposition behavior of the particles. Santillán et al. [10] indicated that the rheology of nanosuspensions is very important for the achievement of good-quality coatings by EPD. Dense and uniform films were obtained using suspension with 1 wt% TiO$_2$ containing iodine exhibited shear-thickening flow behavior. Kishida et al. [11] prepared γ-Al$_2$O$_3$ coatings on

stainless steel by the EPD method and gave the optimal parameters as: concentration of 3.5 wt%, deposition time of 8 s and applied current of 100 mA. Tian et al. [12] investigated the influence of different parameters on the Al_2O_3 particle distribution uniformity using the orthogonal test. They found that the particle concentration and current density of EPD were the most important parameters, whereas voltage and deposition time were less important. The particle distribution became less uniform as particle concentration and current density increased. Miao et al. [13] used nanofluids and the EPD process to prepare a nanostructured ZnO thin film and studied the influences of parameters on the deposited mass, morphology and microstructure. The deposited mass increased almost linearly with an increase in suspension concentration and deposition time, which is contrary to the findings of Tian [12]. Chang and Wei [9] investigated suitable fabrication parameters for the EPD process of CuO nanofilm and mentioned that it is necessary to apply a sintering process to the nanofilm to increase its compactness and hardness. Firouzdor et al. [14, 15] used an EPD process to deposit Ti and TiO_2 coatings as the diffusion barrier for nuclear reactor cladding applications. They proved that sintering at temperature less than 1000℃ for around 15 h will improve the density of the coating. White et al. [1] investigated the influence of ZnO nanofilm deposited by EPD on boiling performance and a nearly 200% increase in HTC was measured with the deposition time of 10 mins. The ZnO nanofilm increased the active nucleation site density and created a porous layer with capillary wicking thus enhancing boiling.

This brief review shows that the results of the different researchers are not always in agreement and sometimes contradict each other. There is no clear relationship between input parameters and output results of deposited films. Hence, the uniform design (UD) method of

experimental design was introduced here to optimize the process parameters for the suitable quality and quantity of deposited nanofilms obtained by EPD.

The aim of experimental design is in general to (i) understand the effects of the factors in an experiment and their interactions, and (ii) to model the relationship between response Y and factors $(X_1 \ldots X_s)$ using a minimum number of experiments [16]. Uniform design was proposed by Fang and Wang in 1978 [17, 18]. It is based on the quasi-Monte Carlo method or number-theoretic method and has a wide range of applications [16, 19-20]. Compared with conventional statistical methods, such as the orthogonal and Taguchi designs, Uniform design further reduces the number of experiments needed.

In the present study, with the goal of obtaining rough and dense Al_2O_3 nanofilms, the optimal combination of process parameters for EPD based on the UD method has been investigated. The detailed procedures for the EPD process and UD method are presented. A series of tests have been carried out based on the UD method. Regression and statistical analysis are applied to treat the UD experimental data, and the optimised conditions are verified experimentally. Sensitivity analyses of the effect of the four main parameters on the roughness and deposited mass of Al_2O_3 films are also carried out. Finally the preferred combination of process parameters of Al_2O_3 nanoflims for EPD is given.

Table 1 Overview of EPD parameters used in previous research

Author [reference]	Year	Nano particle	Base fluid	Electrode	Optimal parameters
Tang [6]	2002	γ-Al_2O_3 33 nm	Deionized water	Cathode:Palladium sheet Anode:Stainless steel sheet	5 vol.%, 3mA/cm^2, 600 s, pH range of 5-6
Tang [7]	2002	ZnO 40 nm	Deionized water	Cathode:Palladium sheet Anode:Stainless	5 vol.%, 0.375mA/cm^2, pH range of 8.5-10 with the addition of PEI as

5

				steel sheet	surfactant, high temperature sintering
Tang [8]	2006	TiO_2 30 nm	Deionized water	Cathode:Palladium sheet Anode:Stainless steel sheet	5 vol.%, 0.375mA/cm^2, pH value corresponds to the addition amount of PEI
Chang and Wei [9]	2007	CuO 30 nm	Distilled water	Stainless steel	0.2 wt%, 230 V, 5 mins, 100 mA, pH=6
Santillán [10]	2008	TiO_2 21 nm	Acetylacetone with addition of iodine	Cathode:Stainless steel planar Anode:Stainless steel foil	1 wt%, 10-15 V, 120 s, pH=5
Kishida [11]	2009	γ-Al_2O_3	Ethanol water 1:1	Cathode:Stainless steel Anode:Aluminum cylinder	3.5 wt%, 8 s, 100 mA
Tian [12]	2009	Al_2O_3 20 nm	Ethanol with $MgCl_2$	Cathode: copper plate Anode: titanium plate	8 g/L, 0.5 A/dm^2
Miao [13]	2010	ZnO 4-8 nm	Isopropanol (IPA)	Cathode:platinum Anode: ITO conductive glass	0.0045-0.0065 M, 250 V, 8 mins, aging time: 2-3 days
White [1]	2011	ZnO 40 nm	Propylene glycol (PG)	Stainless steel disc	7 wt%, 20 V, 10 mins
Firouzdor [14, 15]	2013	Ti/ TiO_2	Acetylacetone with additive of triethanolamine	Cathode: T91 steel Anode: platinum	0.5 wt%, 20 V, ph=5, sintering at 850 ℃ for 15 h

2. Uniform design

The principle of UD is to replace the complete combination of all possible experimental parameters by a small number of experimental trials uniformly distributed within the parameter space [19]. The number theoretic method is used to determine the parameters for the trials. Thus the chosen trials are proven to approximate well the complete combination of experimental parameters [16]. The tables for arranging different experiment trials have been listed in Fang and Wang's book [21] and the new version of table used in this study was

generated using the statistical software of Data Processing System (DPS) [22].

Based on the practical problem and preliminary experiments, the four main influencing conditions (nanofluid concentration, deposition time, applied voltage and suspension pH) acted as the independent variables (X_1, X_2, X_3 and X_4), each of which have 7 levels, and the evaluation indicators of the EPD process were: roughness of deposition film (Y_1) and deposited mass (Y_2) as the dependent variables, respectively. The range of each factor was as follows: nanofluid concentration, X_1 (0.5~1.75 wt%); deposition time, X_2 (3~15 mins); applied voltage, X_3 (5~23 V) and suspension pH, X_4 (1~7). The $U_7(7^4)$ uniform design form was selected as shown in Table 2. If the orthogonal design method was selected under the same condition, at least 49 (7^2) trials will be needed. That means 42 trials have been saved with the use of uniform design.

Table 2 Four-factor seven-level $U_7(7^4)$ uniform design table

Exp.No.	Factor 1, X_1	Factor 2, X_2	Factor 3, X_3	Factor 4, X_4
1	4	3	1	1
2	3	7	6	2
3	7	1	4	3
4	5	4	7	5
5	1	5	3	4
6	2	2	5	7
7	6	6	2	6

A quadratic polynomial stepwise regression analysis was accomplished to explore the dependence of the four main influencing conditions on the roughness of deposition film (Y_1) and deposited mass (Y_2) separately. The commonly used quadratic model is expressed as follow.

$$y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{1 \le i \le j \le 4} \beta_{ij} x_i x_j + e \tag{1}$$

Where β_0, β_1,…, β_k are unknown constant coefficient and e is random error with

expected value $E(e)=0$ and analysis of variance $Var(e)=\sigma^2$. The results of the regression model and statistical analysis were carried out using DPS software.

3. Experimental methods

3.1. Material preparation and characterisation

Gamma phase aluminum oxide (γ- Al_2O_3) nanopowder, used as the coating material in this study, was purchased from Sigma-Aldrich (product number: 544833). The nanopowder has a specific surface area larger than 40 m^2/g and a mean particle size of approximately 50 nm. The preparation of Al_2O_3 nanofluid for the EPD process followed the two-step method [23]. The desired amount of Al_2O_3 nano powder was added into 160 ml deionized water at 40℃ with no dispersants. The pH of the dispersion was adjusted by adding 37% hydrochloric acid under the range of pH 1 to pH 7. After one hour of stirring, the suspension was ultrasonicated using a 80W ultrasonic cleaner (VWR International, LLC) at room temperature for 120 minutes to break agglomerates and enhance the dispersion. The water inside the ultrasonic cleaner was changed every 15 minutes to offset the temperature rise caused by the ultrasonic energy. Then the pH of the dispersion was tested and adjusted again to reach the desired value for the EPD process.

Round discs of 304-stainless steel were used as the substrate to be coated with the Al_2O_3 particles. The discs had a diameter of 40 mm and thickness of 3 mm (this size was chosen to suit a boiling heat transfer rig constructed for future research). One side of the disk was polished using a Metaserv universal polisher to eliminate the effect from the machining process and control its surface starting roughness.

The polished surface was soaked in the mixture of ethanol and acetone solution for one minute, and then cleaned by deionized water. At last, rub the surface dry slightly and weighted using an electronic analytical balance to be ready for the EPD.

The particle size of Al_2O_3 in dispersion was analysed by laser scattering using a Malvern high performance particle sizer, using stagnant standing diluted samples. The coating surface of the Al_2O_3 deposited films was examined by a scanning electron microscope (SEM) for its morphology. Atomic force microscope (AFM, Bruker dimension 3100) was used to measure the 3D shape and roughness of deposited films in nanoscales.

3.2. EPD procedure

A glass breaker was used as the EPD vessel and two stainless steel discs were used as electrodes with a separation of approximately 2 cm, as shown schematically in Fig. 1. The discs were connected through wires to a 0-50 V DC power supply. As the Al_2O_3 nanoparticles normally has a positive surface charge [11], the nanoparticles move towards the cathode and the cathode surface is coated. In order to evaluate the optimal EPD process parameters, a series of tests with different combinations of operational parameters (nanofluid concentration, deposition time, applied voltage and suspension pH) were carried out based the $U_7(7^4)$ uniform design form. After deposition, the coated disc was carefully removed from breaker and allowed to dry over 24 h in a covered container to slow down the vaporization of moisture and minimise cracking. After drying, the mass of deposited films was calculated from the weight difference of the samples before and after the EPD process divided by the area of disc.

4. Results

4.1 Characterisation of the Al_2O_3 suspension and the stainless steel disc

In this study, only the highest concentration (2 wt%) of nano suspension's particle size distribution was analysed by a Malvern particle sizer. The sample was taken after 120 minutes ultra-sonication at pH 3. The laser scattering on the Al_2O_3 suspensions showed size shifting due to deposition. However, particles in the range of 50 nm were detected, in agreement with the product specification. A representative size distribution is shown in Fig. 2. The nanofluid scattered uniformly gave a first peak at 46.4 nm and a second peak at 291.6 nm. The distribution of nanoparticles size smaller than 100 nm showed lower intensity but higher volume compared with the nanoparticles size larger than 100 nm. This result shows that just few single particles were present in the suspension; the majority existed as agglomerates of several particles together.

The photograph and SEM image of the smooth stainless steel disc before EPD process was shown in Fig 3(a). The polisher eliminated most of the effect from the machining process. From the AFM image of the smooth disc as shown in Fig 4(a), the max height of the surface is 65.5 nm and the roughness is 21.4 nm.

4.2 Uniform design experimental results

The experimental design according to table $U_7(7^4)$ of UD method and the results of the experiments were shown in Table 3. Three random areas of each sample were selected to measure the surface roughness of deposited films by AFM. The result shows that sample 4

had the highest roughness of 487.3 nm and sample 7 the biggest deposited mass of 266.2×10^{-4} g/cm^2.

Figure 3 presents the photographs and SEM images of the deposited sample 4 and sample 7 compared with the smooth stainless steel disc before EPD process. It can be seen that both sample 4 and sample 7 have a uniform layer of nanofilm after EPD process and sample 7 is a little denser than sample 4 because of its bigger mass. However, some pores are present on the two surfaces because electrolysis of water occurred and hydrogen gas was generated. Nanoparticles of deposited film combined with only weak Van der Waals force. The hydrogen evolution at the electrodes is inevitable under the electric field which causes bubbles to be trapped within the deposit. And cracks were also found on the surface of sample 4 as shown in Figure 3, one possible reason is that the highest deposition voltage led to an intense EPD process making the nanofilms insufficiently compact. Some special procedures can be adopted to suppress and eliminate the bubble incorporation, such as the use of absorbing or porous electrode materials [4], the application of pulsed DC [24, 25], or sintering the sample at high temperature [7, 26]. Such detailed studies may be the subject of future work. The three-dimensional AFM images of the disc samples were shown in Fig 4. The max height of the nanofilms of sample 4 and sample 7 is 1800 nm and 989.4 nm, respectively. Compared with the smooth stainless steel disc without EPD, the roughness of the surface with nanostructures greatly increased by more than ten times.

Table 3　The experimental design and the results according to $U_7(7^4)$ uniform design table

Exp.No.	wt%, X_1 (%)	Time, X_2 (mins)	Voltage, X_3 (V)	pH, X_4 (~)	Roughness, Y_1 (nm)	Deposited mass, Y_2 (10^{-4} g/cm^2)
1	1.25	7	5	1	78.5	4.7
2	1	15	14	2	282.1	45.3
3	2	3	20	3	444.3	157.1

4	1.5	9	23	5	487.3	106.3
5	0.5	11	11	4	351.3	27.6
6	0.75	5	17	7	119.9	4.3
7	1.75	13	8	6	215.1	266.2

5. Analysis and discussion

In this section, a regression model and statistical analysis for UD experimental data are applied. And a verification experiment is conducted under the optimal conditions. At last, sensitivity discussion of the effect of the four main parameters on the roughness and deposited mass of Al_2O_3 films are carried out.

5.1. Uniform design analysis

With the goal of obtaining the optimal combination of process parameters for EPD, a quadratic polynomial stepwise regression analysis was carried out to explore the dependence of the nanofluid concentration X_1, deposition time X_2, applied voltage X_3 and suspension pH X_4 on the roughness of deposition film (Y_1) and deposited mass (Y_2) separately. A regression model and statistical analysis were applied using DPS software based on the uniform design experimental data as shown in Table 3. The regressed equations are expressed as follow:

$$Y_1 = 228.65x_4 - 0.49x_2{}^2 - 29.15x_4{}^2 + 3.05x_1x_3 + 0.72x_2x_3 - 140.30 \tag{2}$$

$$Y_2 = 40.02x_4 + 0.49x_3{}^2 + 23.77x_1x_4 - 0.04x_2x_3 - 4.06x_3x_4 - 55.48 \tag{3}$$

The correlation indices of the regression analysis results are shown in Table 4, in which the statistical terminologies are defined as follows: R_a is the adjust correlation coefficient, F is the overall F-statistic, P is the probability, S is the residual standard deviation and Durbin-Watson is the Durbin-Watson statistic. If the value of R_a is close to 1, the value of P is

less than 0.05 and the value of Durbin-Watson is close to 2; this means the result of regression analysis has statistical significance. The comparison of the results of the uniform design of experiments with the value calculated from the regressed equation is shown in Table 5. The relative error of Y_1 and Y_2 are both less than 0.5%, which shows that the regressed equations from uniform design are reliable and credible to analyse and predict the relationship between Y and X.

From equations (2) and (3), the optimal parameters of uniform design for roughness and deposited mass of nanofilms were obtained as shown in Table 6. Note that the regressed equations obtained from the results of the uniform design are valid only within the chosen ranges of the investigated process parameters [16]. According to the Table 6, the optimal roughness is 583.9 nm when the nanofluid concentration, deposition time and applied voltage all achieve maximum values and suspension pH is 3.92. This result is consistent with Ref [6, 27], which shows that the zeta potential of the Al_2O_3 will achieve max when pH is around 4. While the optimal deposited mass is 424.4×10^{-4} g/cm^2 when the nanofluid concentration, deposition time, and suspension pH all achieve maximum values and the applied voltage is 5 V. The result reveals that applied voltage and suspension pH have different influence on the roughness and deposited mass. As the goal is to obtain the optimal roughness and deposited mass at the same time, the problem becomes one of multiobjective nonlinear optimization. Considering the higher priority of roughness, which is the key factor influenceing the boiling heat transfer [2, 3], one approximate solution was given as ($X_1 \sim X_4$, 2 15 23 3) (see section 5.2 for detailed explanation), while the optimal roughness and deposited mass are 561.8 nm and 172.5×10^{-4} g/cm^2, respectively.

Table 4 The correlation indices of the quadratic polynomial stepwise regression analysis

Dependent variables	R_a	Overall F	P	S	Durbin-Watson
Y_1	0.9999	31133.96	0.0043	0.9666	2.41
Y_2	0.9998	99999.85	0.0024	0.0463	2.05

Table 5 Comparison of the results of the uniform design with the value calculated from the regressed equations

Exp.No.	Y_1			Y_2		
	Experimental result	Value from equation	Relative error (%)	Experimental result	Value from equation	Relative error (%)
1	78.5	78.9	-0.50	4.7	4.6	0.15
2	282.1	281.6	0.14	45.3	45.3	-0.06
3	444.3	444.1	0.07	157.1	157.1	-0.01
4	487.3	487.8	-0.10	106.3	106.3	0.02
5	351.3	351.2	0.03	27.6	27.5	0.09
6	119.9	119.5	0.32	4.3	4.3	-0.42
7	215.1	215.3	-0.16	266.2	266.2	0.00

Table 6 Optimal parameters of uniform design

No.	wt%, X_1 (%)	Time, X_2 (min)	Voltage, X_3 (V)	pH, X_4 (~)	Roughness, Y_1 (nm)	Deposited mass, Y_2 (10^{-4} g/cm^2)
1	2	15	23	3.92	583.9	~
2	2	15	5	7	~	424.4

In order to assess the validity of the equations and the predictions, a verification experiment was conducted under the optimal conditions mentioned above. A dense layer of Al$_2$O$_3$ nanofilm has been deposited compactly and uniformly on the substrate with few pores and no obvious cracks can be observed as shown in Fig 5. The roughness and deposited mass of the verification sample are 520.9 nm and 161.6×10^{-4} g/cm^2, with relative errors of 7.2% and 6.3% compared to the theoretical calculate, respectively. Combined with the AFM and SEM images shown in Fig 5(b) and Fig 5(c), the conclusion could be reached that, within the range of the experiments, the optimal Al$_2$O$_3$ nanofilm is obtained with process parameters of: nanofluid concentration of 2 wt%, deposition time of 15 mins, voltage of 23 V and suspension pH of 3.

5.2. Sensitivity discussion

Firstly, coefficient standardization analysis was carried out here to find out which of the independent variables has the greatest effect on the dependent variables. The standardized regression coefficient refers to the number of standard deviations a dependent variable will change, per standard deviation increase in the predictor variable b, as defined by the following formula:

$$b_i = \beta_i \frac{S_x}{S_y} \tag{4}$$

Where β_i is the constant coefficient of each X, S_x and S_y are standard deviation of X and Y.

Figure 6 shows the results of standardized regression coefficient about roughness Y_1 and deposited mass Y_2 based on equations (2) and (3). The suspension pH, X_4 and X_4^2 significantly influence the roughness of nanofilms, Y_1, while the other factors have less impact. There is a strong positive correlation between the factor of X_4, X_3^2, X_1X_4 and deposited mass of nanofilm, Y_2, the biggest effect of which is X_3X_4 while the smallest is X_2X_3. The same conclusion as before can be drawn i.e. that the applied voltage X_3 and suspension pH X_4 are key parameters and correlated with each other to control the quality and quantity of Al_2O_3 nanofilms through the EPD process.

Next, sensitivity analyses of the effect of the four main influencing conditions controlling the EPD process were given in the following sections. In the analysis, the basic value of each independent variables was setting as the optimal data ($X_1 \sim X_4$, 2 15 23 3). When one process parameter is varied, whereas other parameters are kept constant.

5.2.1 Effect of nanofluid concentration, X_1

Figure 7 shows the roughness Y_1 and deposited mass Y_2 of nanofilms versus the nanofluid concentration X_1. Within the chosen ranges of X_1, when nanofluid concentration increases from 0.5 wt% to 2 wt%, the roughness of nanofilm increases from 456.5 nm to 561.8 nm and the deposited mass increases from 65.5×10^{-4} g/cm^2 to 172.5×10^{-4} g/cm^2. The results indicate that the roughness and mass increase linearly with the concentration. The same conclusion could be obtained from equations (2) and (3) , where the coefficient of X_1 in the equations is $3.05X_3$ and $23.77X_4$, respectively. This means there is a positive correlation between X_1 and Y.

From the result of sizer analysis for 2 wt% nanofluid shown in Fig 2, most of the particles are existed in the state of slight aggregation. As good separation of particles is the key point for EPD process and the concentration is the main factor to separation, the concentration of nanofluid should be within limits in the present technology condition for distribution. Hence the maximum concentration of 2 wt% was selected as the optimal parameter for EPD.

5.2.2 Effect of deposition time, X_2

The roughness Y_1 and deposited mass Y_2 of nanofilms with variation of the deposition time X_2 is shown in Fig 8. Within the chosen ranges of X_2, when deposition time increases from 3 mins to 15 mins, the roughness of nanofilms increases from 468.9 nm to 561.8 nm and the deposited mass decreases from 183.5×10^{-4} g/cm^2 to 172.5×10^{-4} g/cm^2. It can be seen that the roughness increases with a decreasing rate of growth, and the mass decreases slightly

with the deposition time. Combining the coefficients of X_2, the equation of Y_1 can be converted into $Y_1 = -0.49(x_2 - 0.73x_3)^2 + f(x_1, x_3, x_4)$, it is clear that when X_2 equals to $0.73X_3$, Y_1 will get the highest value. However, as the value of X_3 was restricted to 23, X_2 have to take the maximum value of 15 to make Y_1 to be optimized within the limition of the chosen ranges. And there is a negative correlation between X_2 and Y_2, where the coefficient of X_2 in the equation (3) is -0.04X_3. That means applied voltage, X_3 have a negative correlation with deposition time, X_2. The higher the voltage, the less the deposition time should be to get higher mass of deposited nanofilms.

Because the water electrolysis process occurs together with electrophoretic deposition, hydrogen bubbles at the cathode may remove a small part of Al_2O_3 nanofilms causing its mass to decrease. Nevertheless, as the loss of mass is not too high (11×10^{-4} g/cm^2) and considering the priority of roughness, the maximum deposition time of 15 mins was preferred.

5.2.3 Effect of applied voltage, X_3

Figure 9 shows the roughness Y_1 and deposited mass Y_2 of nanofilms versus the applied voltage X_3. Within the chosen ranges of X_3, when applied voltage increases from 5 V to 23 V, the roughness of nanofilms increases from 257.6 nm to 561.8 nm and the deposited mass first decreases from 155.6×10^{-4} g/cm^2 to 124×10^{-4} g/cm^2, and then increases from 124×10^{-4} g/cm^2 to 172.5×10^{-4} g/cm^2. The results indicate that the roughness increases linearly with voltage and the mass has a minimum value at 13 V. The coefficient of X_3 in the equation (2) is $(3.05X_1 + 0.72X_2)$, which shows a positive correlation between X_3 and Y_1. Combining the

coefficients of X_3, the equation of Y_2 can be converted into $Y_2 = 0.49(x_3 - (0.04x_2 + 4.14x_4))^2 + f(x_1, x_4)$. Thus, within the range explored, the maximum voltage of 23 V gives the highest roughness and mass.

One possible explanation for these findings is that applied voltage controls the current of the EPD field, which is the key factor for the quality and quantity of electrophoretic deposition nanofilms. The motion of macroparticles inside the suspension is more intense under the higher voltage, which is helpful for the increase of roughness and mass of nanofilms. But the water electrolysis process is strengthened at the same time. So the increase or decrease of mass depends on both the EPD and the water electrolysis processes, which may have opposing effects. Thus, the maximum applied voltage of 23 V was selected as the preferred parameter for EPD.

5.2.4 Effect of suspension pH, X_4

The roughness Y_1 and deposited mass Y_2 of nanofilms versus the suspension pH X_4 is shown in Fig 10. Within the chosen ranges of X_4, when suspension pH increases from 1 to 7, the roughness of nanofilms increases from 337.6 nm to 586.3 nm and then decreases from 586.3 nm to 310.3 nm, while the deposited mass decreases from 184.1×10^{-4} g/cm^2 to 149.2×10^{-4} g/cm^2. The results indicate that the roughness has a maximum value and the mass decreases linearly with the increase of suspension pH. Combining the coefficients of X_4, the equation of Y_1 can be converted into $Y_1 = -29.15(x_4 - 3.92)^2 + f(x_1, x_2, x_4)$, it is clear that when X_4 equals to 3.92, Y_1 will attain the highest value. The coefficient of X_4 in the equation (2) is -5.82, which shows a negative correlation between X_4 and Y_2.

The pH influences the concentration of charged ions, which together with the applied voltage then affects the current of the EPD field. The lower the suspension pH, the higher is the current, which enhances the accumulation of nanoparticles around the cathode. However, the reaction is too violent and the evolution of hydrogen also intensified at low pH which is not perfect to get the dense and high roughness layer of the nanofilm. Consequently, the optimal suspension pH should be determined based on the trade-off between higher roughness and higher deposited mass. In our case, the suspension pH of 3 was selected as the preferred parameter for EPD as shown in Fig 10, as it gives a good balance between maxima of roughness and deposited mass.

6. Conclusions

This work has explored the optimal combination of process parameters for EPD based on the UD method, with the goal of obtaining rough and dense Al_2O_3 nanofilms for applications such as heat transfer and boiling enhancement. A series of tests with four main influencing conditions were carried out based on the UD experimental design. A regression model and statistical analysis were applied to the results. Sensitivity analyses of each main parameter on the roughness and deposited mass of Al_2O_3 films were also performed. Through the experiments and theoretical analysis, the main findings and conclusions are as follows:

- The roughness and mass increase linearly with the concentration; the roughness increases with a decreasing rate of growth, and the mass decreases slightly with the deposition time; the roughness increases linearly and the mass has a minimum value as at a voltage of 13 V; the roughness has a maximum value at pH of 4 and the mass decreases linearly as the

suspension pH increases.

- Within the range of the uniform design of these experiments, the preferred combination of process parameters is: nanofluid concentration of 2 wt%, deposition time of 15 mins, applied voltage of 23 V and suspension pH of 3; while the roughness and deposited mass are 520.9 nm and 161.6×10^{-4} g/cm^2 respectively. A verification experiment was carried out at these conditions and gave values of roughness and deposited mass within 8% error of the expected ones as determined from the UD approach.

- The rough and dense layer of Al_2O_3 nanofilm was deposited compactly and uniformly on the substrate under the optimal combination of EPD process parameters.

We have shown how the uniform design method is useful for the efficient optimization of an EPD process, requiring only 7 tests compared to 49 tests with the orthogonal design method. In future studies, we will carry out more experiments using UD to explore further this and other EPD processes under wider parameter ranges to explore the mechanism of EPD and to identify the role of each parameter. The uniform design method is recommended for researchers to achieve optimised nanocoatings and nanostructures without requiring excessive experimental effort, even when several process parameters have to be optimised.

Acknowledgements

References

1. White, S.B., A.J. Shih, and K.P. Pipe, *Boiling surface enhancement by electrophoretic deposition of particles from a nanofluid.* International Journal of Heat and Mass Transfer, 2011. 54(19): p. 4370-4375.

2. Ciloglu, D. and A. Bolukbasi, *A comprehensive review on pool boiling of nanofluids.* Applied Thermal Engineering, 2015. 84(0): p. 45-63.

3. Yeom, H., K. Sridharan, and M.L. Corradini, *Bubble dynamics in pool boiling on nanoparticle-coated surfaces.* Heat Transfer Engineering, 2015. 36(12): p. 1013-1027.

4. Besra, L. and M. Liu, *A review on fundamentals and applications of electrophoretic deposition (EPD).* Progress in Materials Science, 2007. 52(1): p. 1-61.

5. Deen, I. and I. Zhitomirsky, *Electrophoretic deposition of composite halloysite nanotube–hydroxyapatite–hyaluronic acid films.* Journal of Alloys and Compounds, 2014. 586, Supplement 1: p. S531-S534.

6. F. Q. Tang, et al., *Electrophoretic deposition of aqueous nano-gamma-Al_2O_3 suspensions*, Mater. Res. Bull., 2002. 37: p. 653-660.

7. F. Q. Tang, T. Uchikoshi and Y. Sakka, *Electrophoretic deposition behavior of aqueous nanosized zinc oxide suspensions*, J. Am. Ceram. Soc., 2002. 85: p.2161-2165.

8. F. Q. Tang, et al., *Effect of polyethylenimine on the dispersion and electrophoretic deposition of nano-sized titania aqueous suspensions*, J. Europ. Ceram. Soc., 2006. 26: p. 1555-1560.

9. Chang, H. and C. Wei, *Fabrication of CuO nanofilm preparation by electrophoretic deposition.* NSTI Nanotech 2007, Technical Proceedings, 2007. 4: p. 370-373.

10. Santillán, M., et al., *Characterization of TiO_2 nanoparticle suspensions for electrophoretic deposition.* Journal of Nanoparticle Research, 2008. 10(5): p. 787-793.

11. Kishida, S., et al., *Coating of γ-Al_2O_3 on the stainless steel substrate by electrophoretic deposition method.* Journal of Environmental Sciences, 2009. 21(SUPPL. 1): p. S112-S115.

12. Tian Hai-yan, et al., *Distribution of Nano-particles in Nano-Al_2O_3/Ni Composite Coatings Prepared by Electrophoretic.* Materials for Mechanical Engineering, 2009(06): p. 14-17+21 (Chinese).

13. Miao, L., S. Cai, and Z. Xiao, *Preparation and characterization of nanostructured ZnO thin film by electrophoretic deposition from ZnO colloidal suspensions.* Journal of Alloys and Compounds, 2010. 490(1): p. 422-426.

14. Firouzdor, V., et al., *Electrophoretic deposition of diffusion barrier titanium oxide coatings for nuclear reactor cladding applications.* Applied Surface Science, 2013. 282: p. 798-808.

15.   Firouzdor, V., et al., *Development of titanium diffusion barrier coatings for mitigation of fuel–cladding chemical interactions.* Surface and Coatings Technology, 2013. 219: p. 59-68.

16.   Liang, Y.-z., K.-t. Fang, and Q.-s. Xu, *Uniform design and its applications in chemistry and chemical engineering.* Chemometrics and Intelligent Laboratory Systems, 2001. 58(1): p. 43-57.

17.   Fang, K.T., *The Uniform Design: Application of Number-Theoretic Methods in Experimental Design.* 1980.

18.   Fang, K.T., et al., *Uniform Design: Theory and Application.* Technometrics, 2000. 42(3): p. 237-248.

19.   Li, J.F., et al., *Uniform design method for optimization of process parameters of plasma sprayed TiN coatings.* Surface and Coatings Technology, 2003. 176(1): p. 1-13.

20.   Lin, J., et al., *Optimization of culture conditions and medium composition for the marine algicidal bacterium Alteromonas sp. DH46 by uniform design.* Journal of Ocean University of China, 2013. 12(3): p. 385-391.

21.   Fang, K.T. and Y. Wang, *Number-Theoretic Methods in Statistics.* 1994, London: Chapman and Hall.

22.   Tang, QY. and Feng, MG, *Practical Statistics and DPS Data Processing System.* 1997, China (Beijing): Agricultural Press.

23.   Ghadimi, A., R. Saidur, and H.S.C. Metselaar, *A review of nanofluid stability properties and characterization in stationary conditions.* International Journal of Heat and Mass Transfer, 2011. 54(17–18): p. 4051-4068.

24.   L. Besra, et al., *Experimental verification of pH localization mechanism of particle consolidation at the electrode/solution interface and its application to pulsed DC electrophoretic deposition (EPD)*, J. Europ. Ceram. Soc., 2010. 30: p. 1187-1193.

25.   Y. Sakka and T. Uchikoshi, *Forming and Microstructure Control of Ceramics by Electrophoretic Deposition (EPD)*, KONA Powder Particle J., 2010, 28: p. 74-90.

26.   F. Q. Tang, T. Uchikoshi and Y. Sakka, *Electrophoretic deposition of aqueous nano-sized zinc oxide suspensions on a zinc electrode*, Mater. Res. Bull., 2003. 38: p. 207-212.

27.   Leiva, K., et al., *Effect of Mo content in Mo(x)/³-Al$_2$O$_3$ catalysts over the conversion of 2-methoxyphenol as lignin-derivates components.* Journal of the Chilean Chemical Society, 2013. 58: p. 1947-1951.

Figure Captions

Fig. 1   Schematic of EPD set up

Fig. 2   Particle size distribution of the 2 wt% nano suspension

Fig. 3   Photographs and SEM images of the disc samples: (a) smooth disc before EPD, (b)

   sample 4, (c) sample 7

Fig. 4   Three-dimensional AFM images of the disc samples: (a) smooth disc before EPD, (b)

   sample 4, (c) sample 7

Fig. 5   The verification sample with ($X_1 \sim X_4$, 2 15 23 3): (a) Photograph, (b) AFM, (c) SEM

Fig. 6   Standardized regression coefficient of variables: (a) Y_1, (b) Y_2

Fig. 7   Variation of roughness Y_1 and deposited mass Y_2 with nanofluid concentration X_1

Fig. 8   Variation of roughness Y_1 and deposited mass Y_2 with deposition time X_2

Fig. 9   Variation of roughness Y_1 and deposited mass Y_2 with applied voltage X_3

Fig. 10   Variation of roughness Y_1 and deposited mass Y_2 with suspension pH X_4