

Optimization of sol-gel technique for coating of metallic substrates by hydroxyapatite using the Taguchi method

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In this study, the Taguchi method of design of experiment (DOE) was used to optimize the hydroxyapatite (HA) coatings on various metallic substrates deposited by sol-gel dip-coating technique. The experimental design consisted of five factors including substrate material (A), surface preparation of substrate (B), dipping/withdrawal speed (C), number of layers (D), and calcination temperature (E) with three levels of each factor. An orthogonal array of L₁₈ type with mixed levels of the control factors was utilized. The image processing of the micrographs of the coatings was conducted to determine the percentage of coated area (PCA). Chemical and phase composition of HA coatings were studied by XRD, FT-IR, SEM, and EDS techniques. The analysis of variance (ANOVA) indicated that the PCA of HA coatings was significantly affected by the calcination temperature. The optimum conditions from signal-to-noise (S/N) ratio analysis were A: pure Ti, B: polishing and etching for 24 h, C: 50 cm min⁻¹, D: 1, and E: 300 °C. In the confirmation experiment using the optimum conditions, the HA coating with high PCA of 98.5 % was obtained.

Keywords: *hydroxyapatite; sol-gel; coating; Taguchi method; image processing*

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1. Introduction

Hydroxyapatite (HA) is extensively used for surface coating of clinical biomedical materials due to its excellent biocompatibility and osteoconductivity [1]. Among various techniques for formation of HA coatings (e.g. plasma spraying, sol-gel, pulsed-laser deposition, particle beam irradiation, and electrochemical deposition), the sol-gel method possesses many advantages, including low processing temperature, high crystallinity of coatings, application to complex shapes, modification of coating structure and tailoring the thickness of the coating [2–4]. Dipping into the sol followed by calcining has been employed in many studies as a common procedure for formation of HA coating on metallic substrates [5–7].

The sol-gel parameters such as molarity of precursors solution, sol viscosity, aging time and ag-

ing temperature, which affect the formation of HA coating and thus control the thickness, microstructure and homogeneity of them have been extensively studied in literature, e.g. refs [8, 9]. The uniformity and adhesion of HA coatings on a substrate not only depend on sol-gel parameters, but also correlate to substrate, dip coating and calcination conditions. It is known that the material and surface characteristics of implants could determine the biological response of them. Krechetnikov and Homsy [10] have reported that the stability of sol-gel-derived films was influenced by the roughness of the substrate and a significant thickening of the films was achieved by creating an appropriate surface roughness. The angle and speed of substrate dipping/withdrawal can also be significant [9–11]. In addition, post-dipping factors like drying temperature and time have to be considered. Wang et al. [12] have shown that the hexagonal structure of multilayer HA coatings can be preserved at drying temperatures higher than 500 °C.

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Calcination temperature, time, and atmosphere can intensely influence the purity and crystallinity of the formed films [12–15]. On the other hand, Fathi and Hanifi [15] have reported that increasing the calcination temperature and time could cause decomposition of HA into β -tricalcium phosphate and calcium oxide.

Due to the large number of affecting experimental factors in sol-gel dip-coating technique, preparing a suitable HA coating is challenging and a large number of experiments should be examined. While the practice of conducting the entire experiments is expensive and time consuming, thus it is rational to employ a statistical method to decrease the number of experiments. Taguchi is a robust method that possesses the potential to be employed in this manner [16–18]. While many researchers have employed the Taguchi method to establish the optimal combination of influencing factors in their experiments [19–21], exploiting of this method for achieving a homogeneous HA coating with appropriate properties through sol-gel dip-coating technique has been reported very rarely. Therefore, the aim of this work is to study the influence of various sol-gel dip-coating parameters on the formation of HA coating on different metallic substrates by Taguchi design of experiment (DOE) method. An image processing approach was employed for evaluation of the coverage and homogeneity of coatings. The optimal conditions were obtained using signal-to-noise (S/N) ratio and the contribution rates were analyzed according to the analysis of variance (ANOVA). The effects of various factors on the homogeneity of HA coatings were discussed.

2. Experimental

2.1. Preparation and characterization of hydroxyapatite coatings

316L stainless steel (316L SS), pure titanium (Ti) and Ti–6Al–4V alloy sheets were used as substrates. The sheets were firstly cut into square pieces (10 mm $\times$ 10 mm) and then the pieces were ground up to 1000 grit SiC paper. Some of the pieces were mechanically polished using Al_2O_3

powder to get a shiny surface. The polished substrates were chemically etched in nital (25 vol.% nitric acid in ethanol) for different times. After washing, all of the sheets were dried in an oven at 100 °C before coating.

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Merck, 99.95 %) and phosphorus pentoxide (P_2O_5 , Merck, extra pure) were used as the Ca and P precursors, respectively. The precursors were separately dissolved in ethanol (Merck, 99 %) to form 2 mol L^{-1} “Ca-solution” and “P-solution”. Each solution was stirred vigorously with magnetic stirrer for 4 h to obtain a transparent liquid without any remaining precursor in the container. Before mixing the two solutions, the “P-solution” was refluxed at 60 °C for 24 h. The solutions were mixed with Ca/P molar ratio of 1.67 while vigorous stirring. The transparent mixture was aged in water bath at 60 °C for 1 h to obtain an opaque solution. The prepared sol was kept in a sealed container for 72 h for static aging and then filtered.

The metallic substrates were dipped into the sol, hold for 3 s, and withdrawn out of the sol. The dipping and withdrawal was performed with a fixed speed in the range of 25 – 75 cm min^{-1} . After withdrawal, the coated specimens were dried at 100 °C for 10 min. The dip coating and drying steps were repeated up to four times. Finally the specimens were calcined at 300 – 600 °C for 15 min followed by furnace cooling to the room temperature.

2.2. Taguchi design of experiment (DOE)

The Taguchi experimental design approach was used for design of experiments. The substrate material (A), surface preparation of substrate (B), dipping/withdrawal speed (C), number of layers (D) and calcination temperature (E) were chosen as five controlling factors. For each of these factors, three levels were selected. The factors and their levels used in this study are summarized in Table 1. Normally, in the case of 5 factors with 3 levels, $3^5 = 243$ experiments should be conducted. According to Taguchi’s suggestion, the L_{18} orthogonal array was selected and the number of experiments was reduced to 18. The structure of Taguchi’s orthogonal robust design is given in Table 2. The

Table 1. Main controlling factors and their levels.

Factors	Levels		
	1	2	3
Substrate material (A)	316L SS	Ti	Ti-6Al-4V
Surface preparation of substrate (B)	Polishing and etching for 1 h	Polishing and etching for 24 h	Grinding
Dipping/withdrawal speed [cm min^{-1}] (C)	25	50	75
Number of layers (D)	1	2	4
Calcination temperature [$^{\circ}\text{C}$] (E)	300	450	600

Table 2. Taguchi L_{18} orthogonal array used in this study.

Experiment number	Substrate material (A)	Surface preparation of substrate (B)	Dipping/withdrawal speed (C)	Number of layers (D)	Calcination temperature (E)
1	1	1	1	1	1
2	1	2	2	2	2
3	1	3	3	3	3
4	2	1	1	2	2
5	2	2	2	3	3
6	2	3	3	1	1
7	3	1	2	1	3
8	3	2	3	2	1
9	3	3	1	3	2
10	1	1	3	3	2
11	1	2	1	1	3
12	1	3	2	2	1
13	2	1	2	3	1
14	2	2	3	1	2
15	2	3	1	2	3
16	3	1	3	2	3
17	3	2	1	3	1
18	3	3	2	1	2

specimens were coated according to the experimental conditions suggested by the Taguchi DOE. Each experiment at a specific condition was repeated three times for reduction in errors and obtaining trustworthy S/N ratio.

2.3. Coating characterization

The phase composition of the coatings was characterized using the automated Philips PW3710 X-ray diffractometer (XRD) with Cu K_{α} radiation

source in the range of $2\theta = 20 - 60^{\circ}$. Fourier Transform Infrared (FT-IR) Spectroscopy was used to identify the functional groups of HA coatings. FT-IR measurements were conducted on a Bruker Vector 33 spectrometer in the wave number range of $4000 - 400 \text{ cm}^{-1}$ at a resolution of 2 cm^{-1} . Spectra were measured in the transmission mode. Optical microscope (Olympus BX61) was used to study the surface of coatings. More details on the surface features and chemical composition of the specimens were assessed by a scanning electron

microscope (SEM, Stereoscan S360 Cambridge) equipped with Energy dispersive X-ray (EDX) system operated at an accelerating voltage of 20 kV. The surface of specimens was coated with a thin layer of gold before testing due to their poor conductivity.

2.4. Image processing and evaluation

The image processing was performed on the optical micrographs by a code constructed in MATLAB (MathWorks, Inc., Natick, MA) software. The image processing included four stages: (i) increasing the image contrast; (ii) thresholding the image, (iii) identifying special objects in the modified image; and (iv) calculating the percentage of the area covered by identified objects. Fig. 1 shows the stages of image processing for HA coatings on metallic substrates. First of all, the color image was converted to grayscale in order to improve the quality of the process (Fig. 1b). This image was used as an input for MATLAB script. Then the image contrast was enhanced, as shown in Fig. 1c. The contrasted image was converted to the edge detected black and white one (Fig. 1d). The black and white regions in the image denote the coated and uncoated areas, respectively. Finally, the percentage of coated area (PCA) was calculated.

The experimental results (PCA) were transformed into the Taguchi S/N ratios and optimal parameters were obtained. Statistical ANOVA was performed to determine the rate of contribution of the factors.

3. Results

3.1. HA coating characteristics

Fig. 2 shows the XRD patterns of HA coatings on Ti substrates coated at three different conditions (samples no. 13, 14 and 15 according to Table 2). The diffraction patterns exhibit an intense reflection peak at $2\theta \approx 31.7^\circ$, which represents the characteristic peak of hydroxyapatite phase (211) plane. The other peaks of this phase indexed based on the JCPDS file (JCPDS file card no. 09-432) are also marked. The intensity of the HA diffraction peaks increases from the specimen no. 13 to no. 15, re-

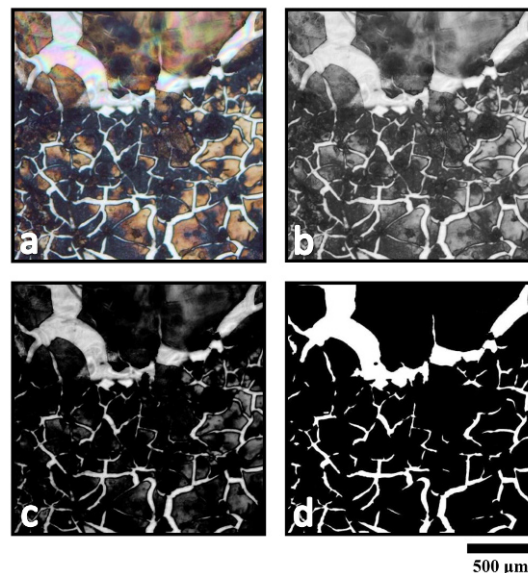


Fig. 1. Stages of image processing: (a) capturing of optical micrograph, (b) converting to grayscale, (c) contrasting, and (d) thresholding the image.

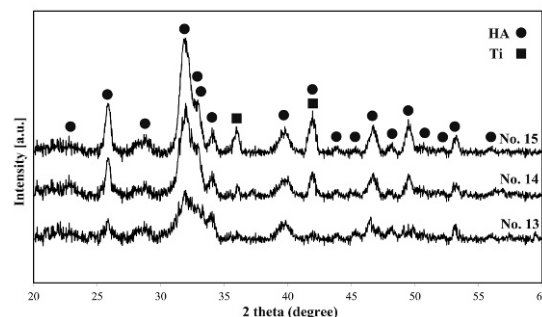


Fig. 2. X-ray diffraction pattern of samples no. 13, 14 and 15.

vealing that higher degree of crystallinity was attained at higher calcination temperature. Although there are some Ti peaks referred to the substrate material in the diffraction patterns, undesirable phases like tricalcium phosphates were not formed during the sol-gel dip-coating processing.

The FT-IR spectra of some selected samples are shown in Fig. 3. A typical structure of HA is characterized by different vibrational modes of the phosphate PO_3^{4-} and hydroxyl OH^- groups [22]. The phosphate group of HA results in four vibrational modes (symmetric stretch (ν_1) at 958 cm^{-1} ; asymmetric stretch (ν_2) at $430 - 460\text{ cm}^{-1}$; bend-

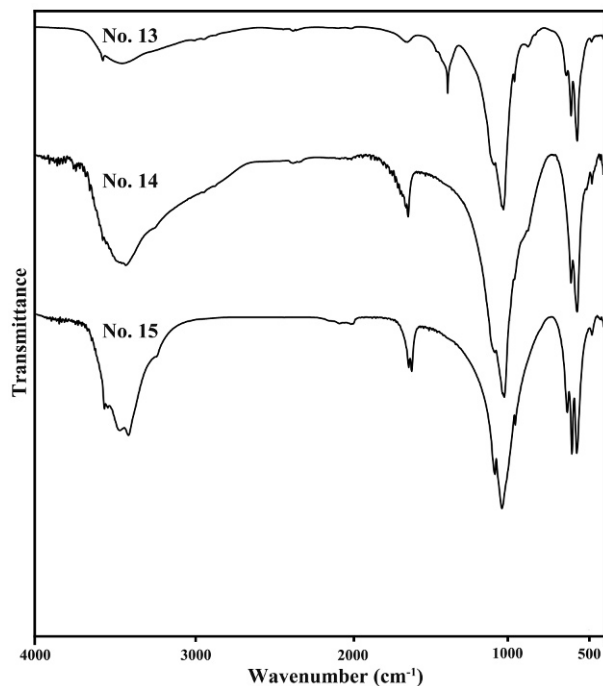


Fig. 3. FTIR spectra of samples no. 13, 14 and 15.

ing (ν_3) at $1041 - 1090 \text{ cm}^{-1}$; bending (ν_4) at $575 - 610 \text{ cm}^{-1}$) and hydroxyl group of HA, has two vibrational modes (stretch at 3570 cm^{-1} and vibrational at 628 cm^{-1}) [22–24]. The FT-IR spectra of all samples demonstrate intensive bands originating from vibrations of phosphate groups. The bands at frequencies of 1041 cm^{-1} and 1090 cm^{-1} are assigned to triply degenerated antisymmetric vibrations (ν_3) of P–O bonds. The bands located at 570 cm^{-1} and 601 cm^{-1} are due to triply degenerated bending vibrations (ν_4) of O–P–O groups. The band at 960 cm^{-1} can be assigned to non-degenerated symmetric vibrations (ν_1) of P–O bonds. The peaks that appeared at 3572 cm^{-1} and 631 cm^{-1} are attributed to the vibrational modes of OH^- groups. Additionally, the presence of peaks in the spectra in the range of $1615 - 1660 \text{ cm}^{-1}$ and $3200 - 3600 \text{ cm}^{-1}$ may be attributed to the existence of lattice water in the samples [22, 25].

Fig. 4 illustrates the surface morphology and corresponding EDS analysis result of the coated Ti substrates. The surface of sample no. 13 is covered by a relatively homogenous coating and no

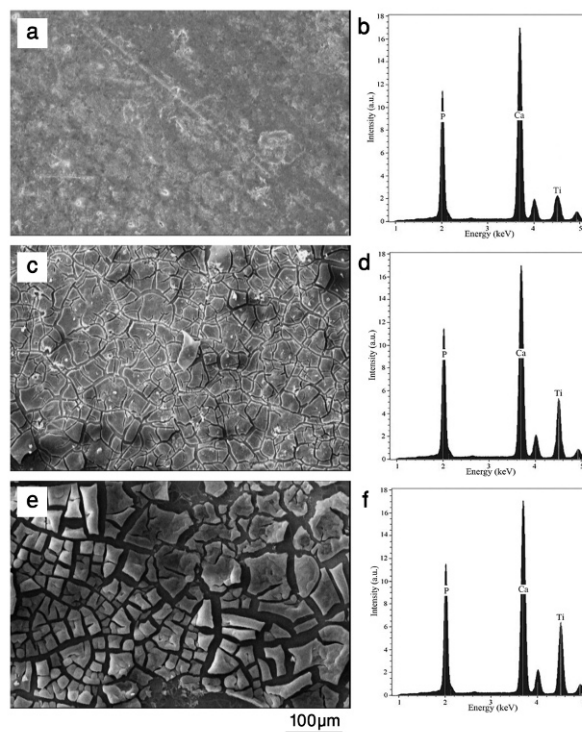


Fig. 4. SEM images (a, c, e) and EDS analysis of samples no. 13, 14 and 15.

cracks are observed as shown in Fig. 4a. Nevertheless, numerous cracks are found in sample no. 14 and no. 15 due to the firing shrinkage during sintering (Figs. 4c, 4e). Clearly, cracking was intensified by sintering at higher temperatures. The EDS analysis reveals that the peaks of Ca and P are dominant (Figs. 4b, 4d, 4f) and the ratio of Ca to P is ~ 1.5 , which is lower than that in the original sol with the Ca to P ratio of 1.67. These results are in agreement with the findings of Wang et al. [26]. The peak of Ti belongs to the substrate.

3.2. S/N analysis

The average percentage of coated area values for the 18 experiment conditions are summarized in Table 3. It is clear that the PCA could be varied from 36.6 to 97.9 %, according to the preparation conditions. The signal-to-noise ratio was used to optimize the coating conditions in the Taguchi method. The objective “bigger-the-better” was used in the analysis of S/N ratio to maximize the PCA value of coatings. Therefore, the S/N ratio

is defined by [27]:

$$\frac{S}{N} = -10 \log \left[\frac{1}{n} \left(\sum_{i=1}^n \frac{1}{y_i^2} \right) \right] \quad (1)$$

where y_i is the value of quality characteristic, which is *PCA* in this case, and n is the number of measurements in each experiment. The calculated S/N ratios are also given in Table 3. Fig. 5 shows the average S/N ratio of the *PCA* for each factor at levels 1 to 3. The optimal factor levels necessary to achieve the highest *PCA* are A_2 , B_2 , C_2 , D_1 and E_1 (A_2 : pure Ti as substrate material; B_2 : polishing and etching for 24 h as surface preparation treatment, C_2 : dipping/withdrawal speed of 50 cm min^{-1} ; D_1 : number of layers of 1; E_1 : calcination temperature of 300°C).

Table 3. Percentage of coated area and S/N ratio for coatings at different processing conditions.

Experiment number	<i>PCA</i> , %	S/N ratio, dB
1	89.3	39.014
2	80.5	38.107
3	36.6	31.248
4	72.3	37.174
5	75.2	37.524
6	89.2	39.006
7	61.8	35.794
8	90.8	39.159
9	72.9	37.167
10	45.4	33.125
11	61.6	35.783
12	97.9	39.817
13	90.9	39.167
14	78.7	37.92
15	65.6	36.324
16	52	34.3
17	95.8	39.628
18	74.9	37.421

3.3. ANOVA

In order to find out the statistical significance of different factors on *PCA*, an analysis of variance was performed. While the equations for calculating

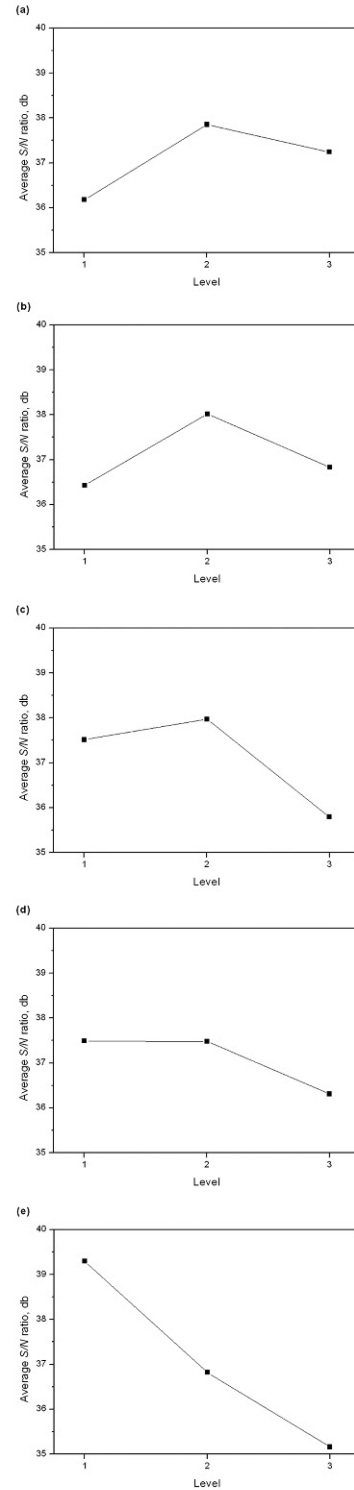


Fig. 5. Average S/N ratio for different levels of the parameters: (a) substrate material, (b) surface preparation of substrate, (c) dipping/withdrawal speed, (d) number of layers, and (e) calcination temperature.

the variance can be found in [19, 27], the main ones used in this study are briefly presented here. The correction factor (CF) is defined as:

$$CF = \frac{T^2}{N} \quad (2)$$

where N is the total number of experiments and T is the total of all results and given by:

$$T = \sum_{i=1}^n \sum_{j=1}^R y_{ij} \quad (3)$$

where n is the number of columns in the defined matrix and R is the number of repetitions. The total sum of squares (SS_T) can be calculated as:

$$SS_T = \sum_{i=1}^n \sum_{j=1}^R y_{ij}^2 - CF \quad (4)$$

Sum of squares for parameter i (SS_i) can be obtained as follows:

$$SS_i = \left(\frac{y_{i1}^2}{N_{i1}} + \frac{y_{i2}^2}{N_{i2}} + \frac{y_{i3}^2}{N_{i3}} \right) - CF \quad (5)$$

where y_{i1} , y_{i2} and y_{i3} are the values of results of each level (1, 2, 3) of parameter i and N_{i1} , N_{i2} and N_{i3} are repetition number of each level of parameter i . Error sum of squares (SS_e) is calculated by:

$$SS_e = SS_T - \sum SS_i \quad (6)$$

Variance of parameter i (V_i) and variance for errors (V_e) are achieved by:

$$V_i = \frac{SS_i}{DF_i} \quad (7)$$

$$V_e = \frac{SS_e}{DF_e} \quad (8)$$

where DF_i is the degree of freedom for parameter i and equals to the number of levels of that parameter-1 and DF_e is the degree of freedom for error term and given by:

$$DF_e = DF_T - \sum DF_i \quad (9)$$

where DF_T is the total degree of freedom which is the number of experiments - 1. F ratio for parameter i is achieved by:

$$F_i = \frac{V_i}{V_e} \quad (10)$$

Table 4. ANOVA results for HA coatings on metallic substrates.

		DF	SS	V	F	ρ (%)
Substrate material (A)		2	8.576	7.624	4.288	8.155
Surface preparation of substrate (B)		2	8.214	7.262	4.107	7.768
Dipping/withdrawal speed (C)		2	15.842	14.89	7.921	15.928
Number of layers (D)		2	5.523	4.571	2.761	4.889
Calcination temperature (E)		2	51.999	51.047	25.999	54.603
Error		7	3.331	—	0.475	8.657
Total		17	93.487	—	—	100.00

The percentage contribution for parameter i (ρ_i) is calculated as follows:

$$\rho_i(\%) = \frac{SS_i - DF_i \times V_e}{SS_T} \times 100 \quad (11)$$

The results of ANOVA are summarized in Table 4. It is apparent that the F -ratios of parameters A, B, C, and E were all greater than $F_{0.05,2,17} = 3.59$. Factor D (number of layers), with an F -ratio value lower than $F_{0.05,2,17}$, was not an effective parameter. Calcination temperature has the highest values of sum of squares, variance, F -ratio and contribution percentage. Therefore, it is the main contributing factor on PCA of HA films on substrates with percentage contribution of 54.6 %. After calcination temperature, dipping/withdrawal speed contributes 15.9 % to the PCA , nearly double of the contribution of substrate material and its surface treatment.

3.4. Prediction and confirmation of the optimum conditions

The final step in the Taguchi method is to conduct confirmation experiments in order to examine the quality characteristics using the optimal levels of the parameters. The predicted S/N ratio using the optimal level of the design parameters can be

calculated as [28]:

$$\left[\frac{S}{N}\right]_{predicted} = \left[\frac{S}{N}\right]_m + \sum_1^n \left(\left[\frac{S}{N}\right]_i - \left[\frac{S}{N}\right]_m \right) \quad (12)$$

where $[S/N]_m$ is the total mean S/N ratio, $[S/N]_i$ is the mean S/N ratio for parameter i at the optimal condition, and n is the number of the main design parameters. Therefore, Eqn. 12 can be written as:

$$\begin{aligned} \left[\frac{S}{N}\right]_{predicted} = & \left[\frac{S}{N}\right]_m + \left(\left[\frac{S}{N}\right]_{A2} - \left[\frac{S}{N}\right]_m \right) \\ & + \left(\left[\frac{S}{N}\right]_{B2} - \left[\frac{S}{N}\right]_m \right) + \left(\left[\frac{S}{N}\right]_{C2} - \left[\frac{S}{N}\right]_m \right) \\ & + \left(\left[\frac{S}{N}\right]_{D1} - \left[\frac{S}{N}\right]_m \right) + \left(\left[\frac{S}{N}\right]_{E1} - \left[\frac{S}{N}\right]_m \right) \end{aligned} \quad (13)$$

In this study, three confirmation experiments were carried out to evaluate the performance of experimental trials conducted for *PCA* under optimal conditions (A = pure Ti, B = polishing and etching for 24 h, C = 50 cm min⁻¹, D = 1, and E = 300 °C). Table 5 shows the comparison of the predicted *PCA* with the experimental results using the optimal conditions. As it can be seen, there is a good agreement between the predicted and experimental results.

Table 5. Results of the prediction and confirmation experiment for *PCA*

	Levels	<i>PCA</i>	<i>S/N</i> ratio (dB)
Prediction	A ₂ , B ₂ , C ₂ , D ₁ , E ₁	99.97	42.257
Confirmation	A ₂ , B ₂ , C ₂ , D ₁ , E ₁	98.53	41.996

4. Discussion

The ANOVA revealed that the calcination temperature was the most significant factor influencing the *PCA* of hydroxapatite coatings on metallic substrates, as shown in Table 4. The optimum temperature for calcination of HA was found to be 300 °C according to the S/N analysis. As shown in Fig. 5e, S/N ratio was reduced by an increase in the calcination temperature. This can

be attributed to the promotion of microcracks and peeling of coatings at higher calcination temperatures (Fig. 4). It is well known that the calcination temperature can significantly affect the crystallinity of HA films and powders derived by sol-gel method. As it is observable from the XRD patterns (Fig. 2), HA peaks in the sample calcinated at 600 °C are sharper than the one sintered at 300 °C revealing the higher crystallinity of the coating calcinated at higher temperature. On the other hand, the lower amount of water in the structure of HA coatings at higher calcination temperatures are observed (Fig. 3). As the amorphous calcium phosphate transforms to crystalline HA at higher calcination temperature, a considerable shrinkage occurs and internal stresses are created in the film on cooling cycle causing microcracks [29]. Microcracking resulted in the poor adhesion of the HA coating and peeling, therefore *PCA* was reduced.

Although dipping/withdrawal speed and number of coating layers could alter the thickness of HA coating, the role of dipping speed on *PCA* was found to be more significant than the number of layers according to the ANOVA (see Table 4). The effects of these factors on the *PCA* can be explained by their role on the mechanism of coating formation before calcination. In dip coating operation, a substrate is immersed in a sol solution and withdrawn; therefore, a liquid layer remains on the substrate with a defined thickness. During the drying step, the solvent evaporates out of the sol, therefore the concentration of the solutes increases. The solutes begin to precipitate and the precipitates reunite together to form grains. By progressing the drying step, the grains will disconnect and some isolated regions form if the sol volume or concentration of the solute is not high enough [12]. The relationship between the thickness of coating (t) and withdrawal speed (U) can be predicted by [29]: $t = AU^m$, where the values of exponent m range from 0.1 to 1. Therefore, at a low dipping/withdrawal speed of a substrate, very thin layer is obtained that can be disintegrated after drying and calcination steps. On the other hand, dipping/withdrawal at a high speed results in a thick and continuous coating that is more susceptible to cracking due to the excessive drying and calcina-

tion strain [30]. Consequently, there is an intermediate dipping/withdrawal speed ($\sim 50 \text{ cm min}^{-1}$) that results in a uniform and crack-free coating with a high S/N ratio of PCA (Fig. 5c). It is pertinent to note that an excessive cracking with a minimum value of PCA was obtained by coating at the highest dipping/withdrawal speed (75 cm min^{-1}) and calcination temperature (600°C), which demonstrates the synergic effect of these two factors (see Table 3). Similar observation has been reported by Balamurugan et al. [30]. By repeating the dipping process, the as-dried layer partially redissolves into the sol coated on it. During the drying process, new precipitates combine firmly with the as-dried layer to form only a new layer without a division surface in it [12]. After repeating dipping and drying steps for several times, the final coating forms. Therefore, by increasing the number of layers, thicker coatings will be formed that have more susceptibility to cracking and peeling after calcination. Consequently, the S/N ratio was decreased by an increase in the number of layers, as shown in Fig. 5d.

The substrate type and its surface treatment had a slight and an approximately equal contribution on PCA of HA coatings. This could suggest that HA coatings formed through sol-gel dip-coating technique have the potential to be deposited on different biocompatible metallic substrates. It is known that the surface roughness is necessary for a good adherence of coating to the substrate through sol-gel dip-coating procedure. In fact, the cavities on the surface of a substrate act as reservoirs for the sol solution during dip-coating. Therefore, the thickness of coating at different areas of the substrate surface can be altered. While the thicker-coated areas are more susceptible to cracking, the grinded substrates containing deep and nonuniform cavities on their surfaces showed low PCA values. Nevertheless, the formation of relatively uniform cavities throughout the surface of substrates via etching for 24 h resulted in the highest S/N ratio of PCA , as shown in Fig. 5b.

5. Conclusions

Metallic biocompatible sheets were coated by hydroxyapatite through sol-gel dip-coating tech-

nique at different conditions. The Taguchi robust design method with L_{18} orthogonal array was applied for the optimization of experimental conditions. Experimental results were evaluated using ANOVA. The findings are summarized as follows:

- The optimum levels of the control factors in order to obtain the maximum percentage of coated area were: A_2 (substrate material, pure Ti), B_2 (surface preparation of substrate, polishing and etching for 24 h), C_2 (dipping/withdrawal speed, 50 cm min^{-1}), D_1 (number of layers, 1), and E_1 (calcination temperature, 300°C).
- Calcination temperature was the most significant factor affecting the PCA with a percentage contribution of 54.6 %.
- The confirmation test results at optimal conditions were in good agreement with the prediction of the Taguchi design approach.

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