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Effects of plasma spray parameters on TiO_2-coated mild steel using design of experiment (DoE) approach

S.M. Forghani[a], M.J. Ghazali[a,*], A. Muchtar[a], A.R. Daud[b], N.H.N. Yusoff[c], C.H. Azhari[a]

[a]*Department of Mechanical & Materials Engineering, Faculty of Engineering & Built Environment, National University of Malaysia, 43600 UKM, Bangi, Selangor, Malaysia*

[b]*School of Applied Physics, Faculty of Science & Technology, National University of Malaysia, 43600 UKM, Bangi, Selangor, Malaysia*

[c]*Maritime Technology Divison, Science and Technology Research Institute For Defence (STRIDE), c/o KD MALAYA 32100 Pangkalan TLDM, Lumut, Perak, Malaysia*

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Abstract

In this study, a design of experiment (DoE) method was utilised to identify the effect of air plasma spray (APS) parameters on several main properties of titanium dioxide (TiO_2) coatings. Titanium dioxide (titania) feedstocks with sizes ranging from 10 μm to 45 μm were sprayed onto the mild steel substrates with different plasma spraying parameters. A 2^4 full factorial design was used to investigate the effects of four varying principal parameters at two levels, namely, the plasma power (20 and 40 KW), the powder feed rate (6 and 22 g/min), the scanning speed (0.2 and 0.5 m/s), and the number of cycles (10 and 20), on four important properties of coatings; microhardness, thickness/cycle, deposition efficiency (DE), and porosity. The results showed that one the most important factor in affecting all responses was the plasma power. It strongly affected the hardness and the porosity which had a primary effect on the thickness/cycle and the DE values. In contrast, the interaction of the powder feed rate and the scanning speed had a negative effects on both thickness/cycle and DE. The number of cycles has no profound effect on the considered responses; it can only be used as a factor to achieve different coating thicknesses. To conclude, a plasma power of 30 kW with a low level of powder feed rate of 6 g/min and 0.5 m/s of scanning speed is most preferable to optimise TiO_2 coating deposition on mild steels.

Keywords: B. Surfaces; C. Mechanical properties; D. TiO_2; E. Structural applications

1. Introduction

1.1. Titania for thermal spraying

Titania (TiO_2) coatings are ceramic products with unique properties that make them good candidates for various fields of applications. They are fairly porous and proportionally ductile, which can be useful under severe working environments. Yilmaz and co-workers found an increase in TiO_2 improves the fracture toughness and lowers the microhardness values of Al_2O_3–TiO_2 coatings [1], whereas Lima et al. studied their superior mechanical properties [2]. Both authors showed that titania coatings provide special combination of hardness, ductility, and wear resistance compared to other hard ceramic coatings, such as Al_2O_3–13% TiO_2 [3]. In biomedical applications, it was found that the bonding between a hydroxyapatite coating and a metallic prosthesis had significantly improved by applying titania [4]. As for the size, Lima and co-workers observed that the nano-sized TiO_2-hydroxyapatite possessed greater biocompatible characteristics [5]. Thus, further studies particularly in optimising the deposition parameters of titania coatings in various applications have to be identified in order to improve the performance.

1.2. Design of experiments (DoE)

In an experimental design, regression models are used to illustrate the relationship between a response and a set of process parameters or factors that affect the response.

*Corresponding author.
E-mail address: mariyam@eng.ukm.my (M.J. Ghazali).

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The regression model is also applied to predict the responses for different process parameters at different levels [6]. The general regression equation to predict the effects of factors on responses is defined as

$$Y = b_0 + \Sigma b_i X_i + \Sigma b_{ij} X_i X_j + \Sigma b_{ijk} X_i X_j X_k + \Sigma b_{ijkl} X_i X_j X_k X_l \quad (1)$$

where Y is the response; b_0 is the mean value of responses of all experiments; b_i is the coefficient of the factor X_i; and b_{ij}, b_{ijk}, and b_{ijkl} are the coefficients of interactions for X_iX_j, $X_iX_jX_k$, and $X_iX_jX_kX_l$ respectively. The values for i, j, k, and l are referred to the number of factors.

Researchers have utilised DoE methods to different thermal spray processes and for different aspects of this field. Steeper and co-workers used a *Taguchi* method to study the effects of plasma processing conditions on properties of alumina-titania coatings [7]. Troczynski and friends applied a response surface methodology (RSM) on plasma spray of WC-12% Co powders to optimise their parameters [8]. In other study, Pierlot and co-workers [9] and Pawlowski et al. [10] had utlised full factorial designs for their thermal spray works.

Various plasma spray operating parameters, such as the plasma power, the gas composition, and the carrier gas flow rates have been the subjects of recent studies. In this study, the effect of four plasma spraying factors, namely; the plasma power, the powder feed rate, the scanning speed and the number of cycles on four basic properties of titania coatings; microhardness, thickness/cycle, deposition efficiency (DE), and porosity were investigated.

2. Experimental

2.1. Powder and plasma spray process

Fused and crushed TiO_2 powder feedstock used in this study was supplied by Starck, Goslar, Germany with a size range of 10–45 μm. Mild steel plates of 40 mm × 20 mm × 6 mm in size were used as substrates. The surface of the substrates was grit-blasted with Al_2O_3 grits of mesh size 40 (420 μm) prior to coating. TiO_2 powder was deposited vertically ($\theta = 90°$) onto the substrates using a Praxair SG-100 plasma torch mounted on a 5-axis ABB industrial robot at a fixed spraying distance of 100 mm.

2.2. Experimental design

The experimental design was carried out using a design expert software (Statistics Made Easy, Version 8.0.4, Stat-Ease, Inc., Minneapolis, MN). By applying a two-level factorial, responses were measured for full combinations of the experimental parameters. A 2^4 full factorial design for four independent variables leading to 16 sets of experiments was chosen. Plasma power (kW) (X_1), powder feed rate (g/min) (X_2), gun scanning speed (mm/s) (X_3), and number of cycles (N) (X_4) were chosen as independent parameters. Selected responses in this study were the microhardness ($HV_{0.3}$) (Y_1), the thickness/cycle (μm) (Y_2), the deposition efficiency (DE%) (Y_3), and the porosity (%) (Y_4). All process parameters including the experimental ranges and the coded levels of the plasma spray formation are shown in Table 1. Two centre points were defined to evaluate the design results.

Table 1
Experimental range and levels including low and high level values of variables.

Variable	Spray process parameter	Low level (−1)	Central point (0)	High level (+1)
X_1	Plasma power (kW)	20	30	40
X_2	Powder feed rate (g/min) (g/min ((g/min)	6	14	22
X_3	Scanning speed (mm/s)	200	350	500
X_4	Number of cycles	10	15	20

2.3. Coating characterisation

Metallography samples were sectioned across the middle of the substrates to ensure relative homogeneity and thickness of the coatings. The samples were then ground and polished prior to the microstructural analyses. The apparent deposition efficiency of the process was determined by the following equation;

$$DE\% = (\text{coating mass}/\text{sprayed powder mass}) * 100 \quad (2)$$

The hardness of the coatings was measured by a Vickers microhardness tester HVS-10 by applying a 300 g (0.3 N) load for 15 s. The hardness test was repeated 10 times for each sample at random locations, and the mean values were obtained.

3. Results

3.1. DoE analysis results

Table 2 shows the complete values of the factors and responses in the experiment. Regression equations were created by ANOVA in the design expert software. The most important effects and their interactions were selected by considering the half-normal probability plots. Fig. 1 shows how these variables were selected. Black points indicate positive effects, whereas grey points indicate negative effects on the considered response. Values positioned away from the straight line and at the right side of the plot are significant modes which were used in the ANOVA calculations.

P-values[1] were also considered as criteria for the significance of the model. The smaller the value of *P*, the more significant the model is. Thus, *P*-values of more than 0.05 were identified as 'non-significant' and 'non-contributing'.

[1]Probability of error.

Table 2
Full 2^4 factorial design for plasma spray parameters (samples 1–18).

Run	X_1	X_2	X_3	X_4	Y_1	Y_2	Y_3	Y_4
					Microhardness ($HV_{0.3}$)	Thickness/cycle (μm)	DE (%)	Porosity (%)
1	1	1	−1	−1	878	31.24	76	2.90
2	1	−1	1	−1	798	75.5	46	4.44
3	−1	1	1	−1	719	63	42	6.58
4	−1	−1	−1	−1	622	15.61	34	11.56
5	−1	−1	1	−1	687	49.72	30	5.88
6	−1	−1	1	1	663	17.92	26	6.02
7	1	−1	1	1	778	35.26	51	4.86
8	1	1	−1	1	831	21.32	69	2.76
9	1	1	1	−1	782	79.86	56	3.53
10	−1	1	−1	−1	692	24.56	57	3.77
11	−1	1	−1	1	695	9.94	56	5.36
12	−1	−1	−1	1	615	13.44	68	5.92
13	1	−1	−1	1	831	12.16	70	4.16
14	1	1	1	1	778	35.61	46	4.82
15	−1	1	1	1	648	29.22	32	5.80
16	1	−1	−1	−1	843	27.84	50	4.80
17	0	0	0	0	864	42.88	62	4.98
18	0	0	0	0	850	37.47	53	3.72

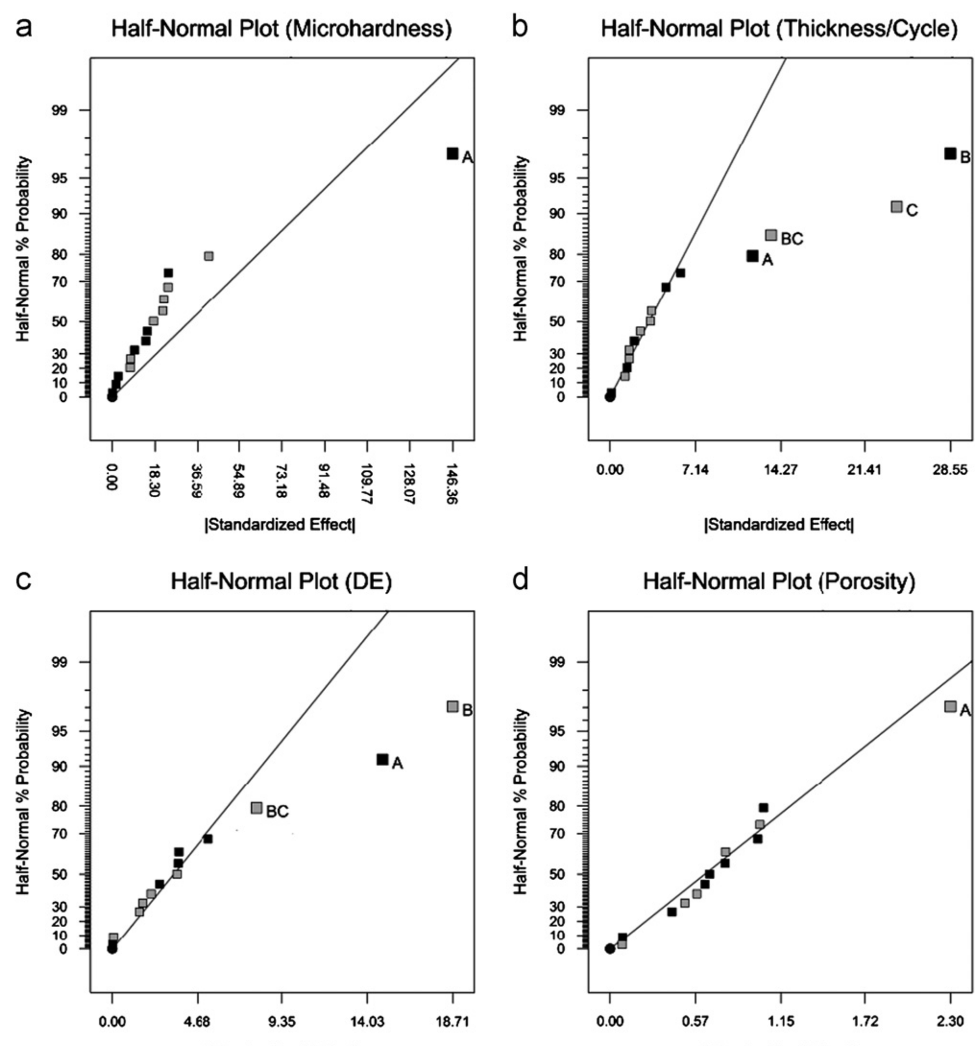

Fig. 1. Half-normal graphs used for selecting the main effects ($A=X_1$, $B=X_2$, $C=X_3$ and $D=X_4$).

Table 3
Results of ANOVA for different responses.

Term	% Contribution	SS[a]	Coefficient	*P*-value*	Std. Dev.	C.V.[b]	Mean value
Y_1 (microhardness)				< 0.0001	51.69	6.86	753.72
b_0			753.72				
X_1	66.72	85688.97	73.18	< 0.0001			
Y_2				< 0.0001	6.37	18.42	34.59
b_0			34.78				
X_1	7.69	568.58	5.96	0.0025			
X_2	44.08	3259.98	14.26	< 0.0001			
X_3	31.30	2315.05	−12.03	< 0.0001			
X_2X_3	9.80	724.69	−6.73	0.0010			
Y_3				< 0.0001	7.01	13.70	51.18
b_0			51.05				
X_1	24.61	884.58	7.44	0.0010			
X_2	38.94	1399.73	−9.35	0.0001			
X_2X_3	7.06	253.99	−3.98	0.0407			
Y_4				0.0134	1.65	32.44	5.09
b_0			5.09				
X_1	32.56	21.07	−1.15	0.0134			

*P-values less than 0.05 indicate that the model terms are significant.
[a]Sum of squares.
[b]Coefficient of variance.

Table 3 shows the contribution percentage, the sum of squares, the coefficients of regression, the P-values, the standard deviations, the coefficients of variance and the mean values.

The final equations in terms of coded factors were

Microhardness ($HV_{0.3}$):

$$Y_1 = +753.72 + 73.18X_1 \quad (3)$$

Thickness/cycle (μm):

$$Y_2 = +34.78 + 5.96X_1 + 14.26X_2 - 12.03X_3 - 6.73X_2X_3 \quad (4)$$

Deposition efficiency (%):

$$Y_3 = +51.05 + 7.44X_1 - 9.35X_2 - 3.98X_2X_3 \quad (5)$$

Porosity (%):

$$Y_4 = +5.09 - 1.15X_1 \quad (6)$$

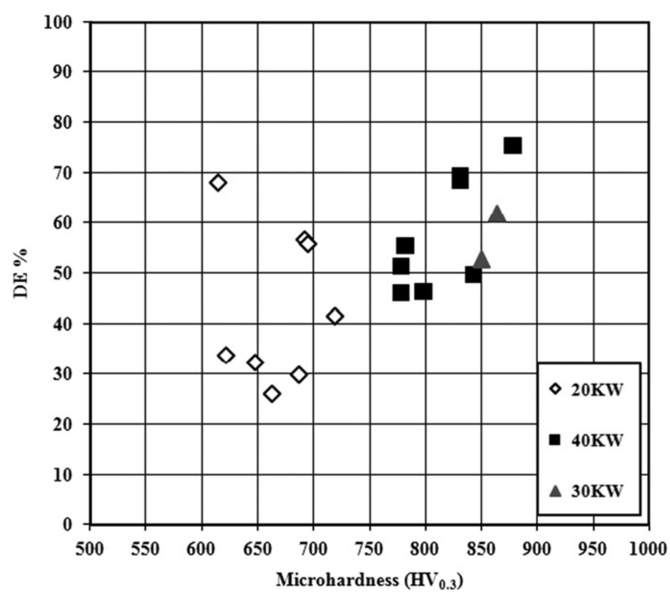

Fig. 2. Microhardness vs. DE%.

4. Discussion

4.1. Microhardness

According to a previous research [10], the microhardness for titania coatings was approximately 850 $HV_{0.3}$. Fig. 1(a) illustrates that one of the most effective factors in determining high microhardness was the power level. The microhardness (Y_1) was directly proportional to the plasma power (X_1), and in this study the microhardness was found to be in the range of 615 $HV_{0.3}$ to 878 $HV_{0.3}$ (refer to Fig. 2). By increasing the plasma power, the impact of titania particles was improved, generating an improved cohesion and lowered the porosity in coatings. Therefore, a denser and harder coating was achieved.

Table 2 shows deposition by using lower power level (20 kW). The microhardness was less than 750 $HV_{0.3}$, whereas all samples deposited by central and high power levels (30 and 40 kW) possessed greater microhardness; which was higher than 750 $HV_{0.3}$. In addition, most of these coatings experienced more than 50% of DE values (refer to Fig. 2). Increased microhardness with an increase of plasma power can be described upon considering that higher plasma power resulted in greater difference in the temperatures of the impacting particles and the substrate. Metal substrates normally have higher coefficients of thermal expansion (CTE) than the ceramic coatings, thus leading to greater amount of stresses. As known, residual stresses have detrimental effects on coating properties, particularly the microhardness. A low level in power may result in high porosity, whereas too much power may lead to high residual stresses, in which both factors gave negative effects on the microhardness. Thus, by using an optimum plasma power of 30 kW, a good combination of low porosity and low residual stresses can be achieved.

4.2. Thickness/cycle

Fig. 3 shows the effect of the powder feed rate on the interaction of the coating thickness/cycle and the DE%. According to Fig. 1(b), the most effective factor on this response was the powder feed rate. By using higher feeding rates, thicker coating layers up to 80 μm can be obtained. The graph demonstrated that by applying a high level of powder feed rate of 22 g/min, the DE of the process can be increased. On the other hand, a low level of powder feed rate increased the DE up to 75%. These figures suggested that an optimum range of thickness/cycle did exist, resulting in higher DE values. In this experiment, 10 out of 11 coatings with a DE higher than 50% had thickness/cycle values between 10 μm and 43 μm.

Fig. 4 illustrates the negative effect of the scanning speed on the thickness/cycle. Obviously, lower scanning speed resulted in thicker coatings as more particles can be deposited on the substrate in a single pass. Samples with the highest thickness/cycle were deposited at the lowest scanning speed (0.2 m/s). Even lowering the scanning speeds may result in thicker layers, the efficiency was far more important. Thus, at high scanning speed, the gun nozzle returned to the spot origin much faster, creating smaller variations in the temperature with smaller residual stresses. As such, high scanning speeds were highly recommended when spraying titania onto metallic substrates.

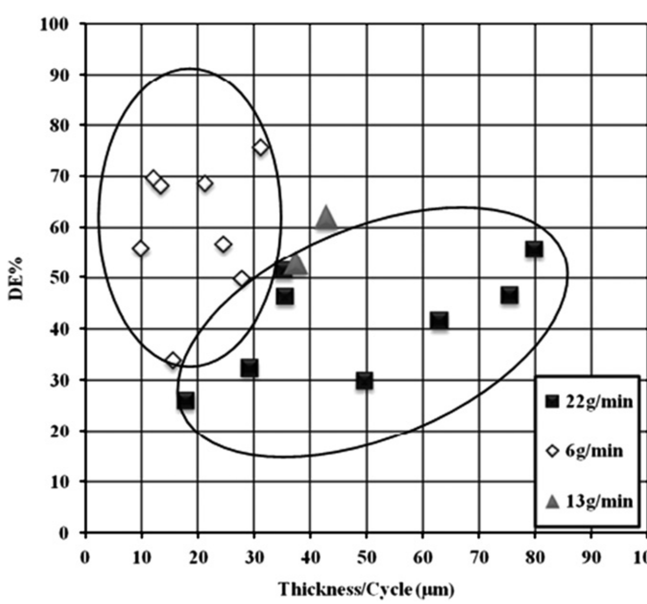

Fig. 3. Thickness/cycle vs. DE% (upon powder feed rate).

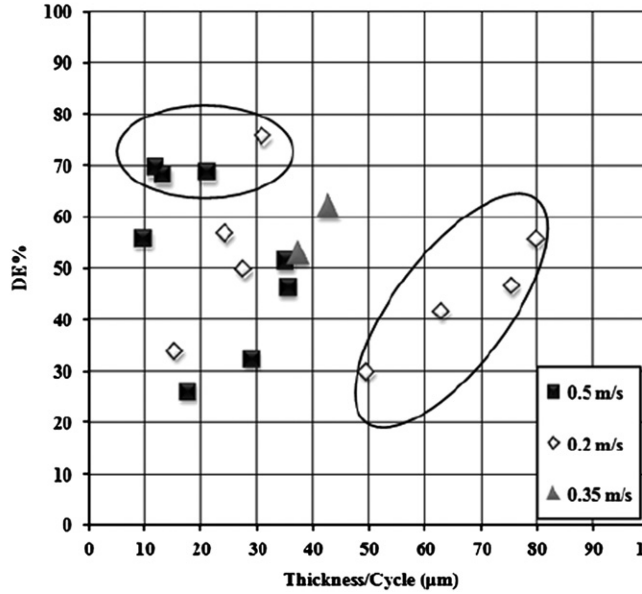

Fig. 4. Thickness/cycle vs. DE% (upon scanning speed).

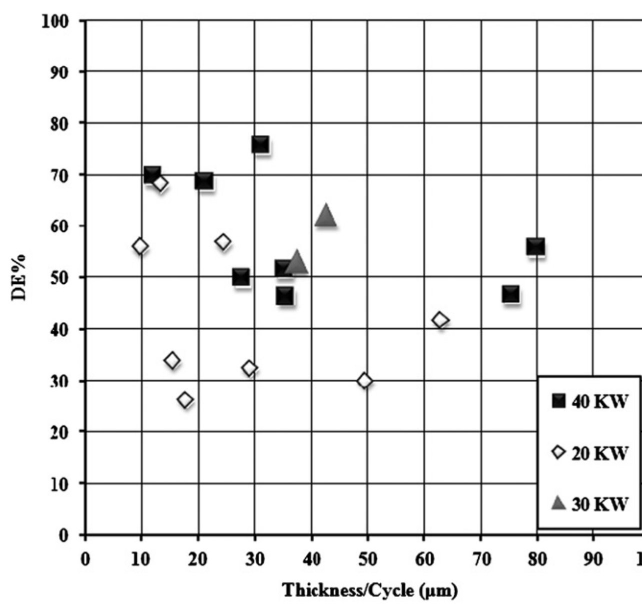

Fig. 5. Thickness/cycle vs. Microhardness (upon plasma power).

Fig. 5 shows that the coatings deposited at central and high power level posses higher DE values than those deposited by low level plasma power. This can be described by the positive role of plasma power on better melting and deposition of particles, therefore, lowering the porosity. Although the thickness/cycle would be reduced, denser and harder coatings can be achieved.

Fig. 1(b) and the regression in Eq. (4) illustrate an important interaction between the powder feed rate and the scanning speed of the thickness/cycle. This interaction is described in Fig. 6. According to the 3-D surface plot, the maximum value of thickness/cycle could be obtained at the maximum value of the feeding rate and the minimum value of the scanning speed.

4.3. Deposition efficiency

Fig. 1(c) depicts that the effective factor on the DE was the powder feed rate and the plasma power. In general, deposited samples at high plasma power have lower DE compared to deposited samples at low powers (refer to Fig. 7). In contrast, the feeding rates seemed to have a harmful effect on the efficiency of the process. By spraying high amounts of feedstock, larger fractions of unmelted or semi-melted particles were obtained. Consequently, larger fractions may weaken the deposition of the coatings. Interaction between the powder feed rate and the scanning speed was also clearly shown in Fig. 8. It was noted that the DE was maximised at a minimum feeding rate of 6 g/min and a maximum scanning speed of 0.5 m/s.

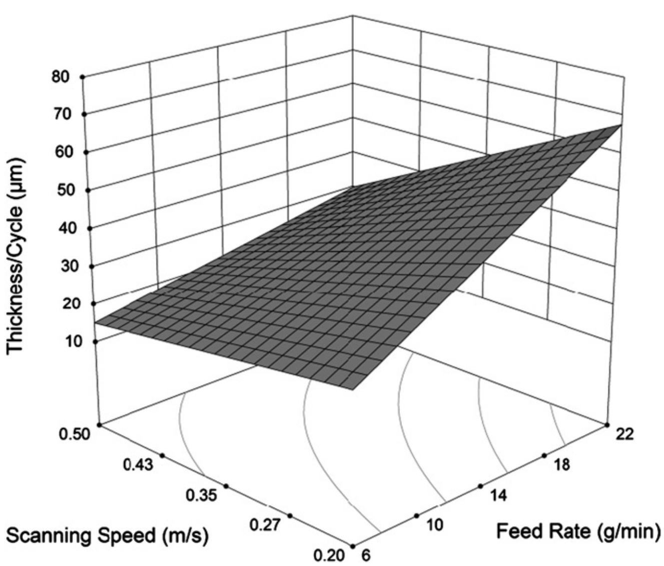

Fig. 6. The effect of the interaction between scanning speed and feeding rate on thickness/cycle.

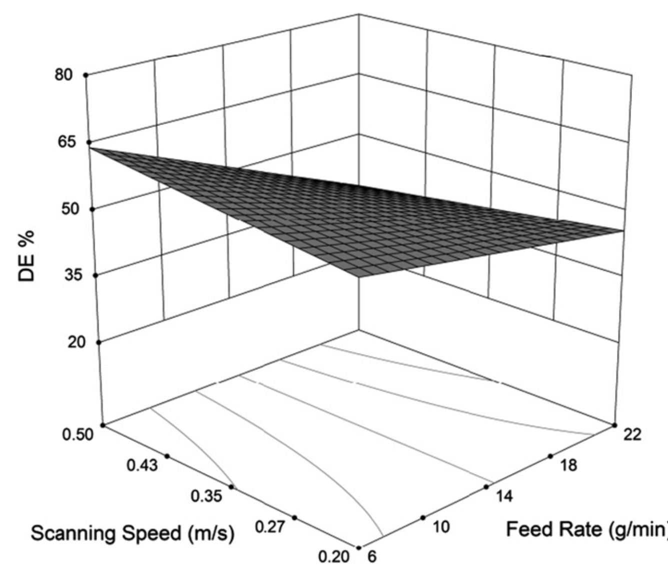

Fig. 8. The effect of the interaction between powder feed rate and scanning speed on DE%.

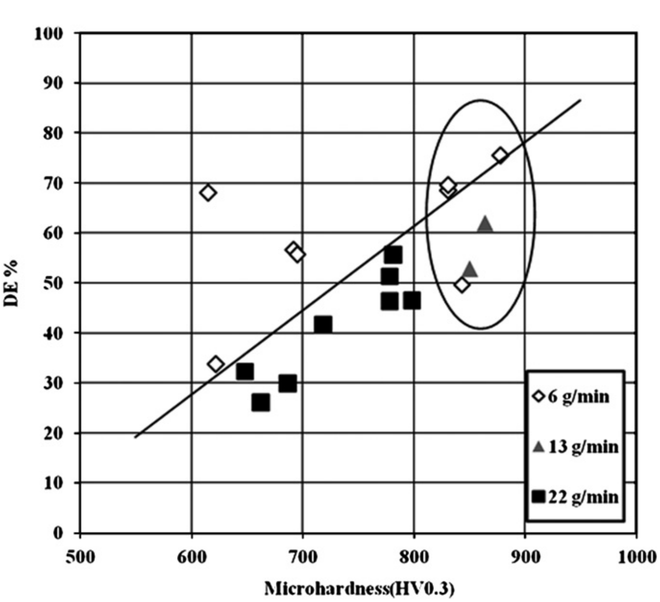

Fig. 7. DE% vs. microhardness (upon powder feed rate).

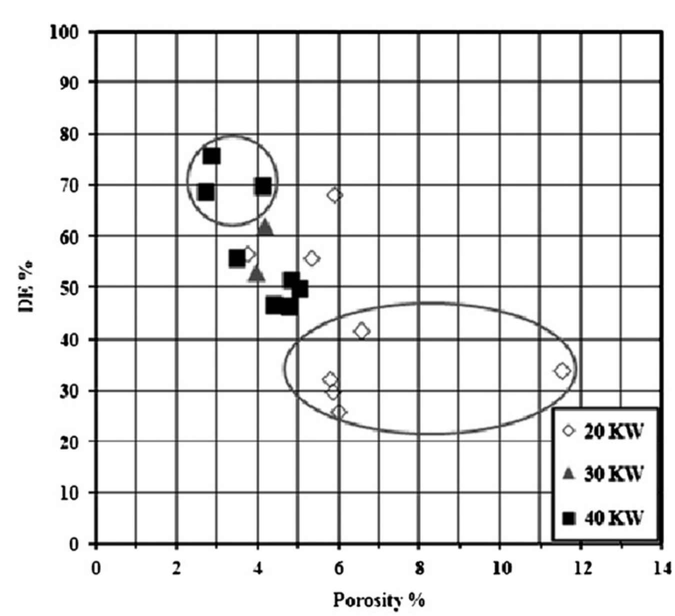

Fig. 9. Porosity vs. DE% (upon plasma power).

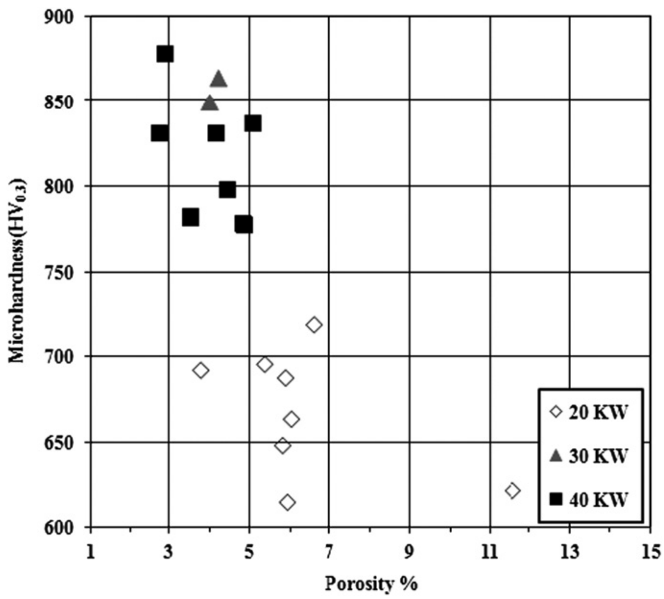

Fig. 10. Porosity vs. microhardness (upon plasma power).

4.4. Porosity

Based on Fig. 1(d), an effective factor in the porosity was the plasma power. A high porosity fraction resulted in a low DE, as shown in Fig. 9. At higher plasma powers of a higher energy level, the temperature of the deposition would be increased. As a result, interlamellar porosities and the fraction of unmelted particles were reduced. Porosity had a tremendous effect on the microhardness of the coatings as lower porosity generates higher density. Fig. 10 exhibits that coatings with microhardness greater than 750 $HV_{0.3}$ were deposited at 30 and 40 kW. In short, by summarizing all results and factors, optimum properties are achieved by using a 30 kW plasma power.

5. Conclusion

- The microhardness and the thickness of the coating were strongly affected by the power of the plasma. High power levels of 30 and 40 kW improved the hardness of the coatings up to 878 $HV_{0.3}$. Higher power also led to higher fractions of melted particles which consequently produce a higher probability of successful deposition.
- Thickness/cycle was highly affected by the powder feed rate. A high scanning speed shortened the deposition time. Thus, a high feed rate with low scanning speed worked best to obtain the optimum thickness/cycle.
- Higher plasma powers resulted in higher fractions of melted particles, which produced denser coatings. However, by using a high level of power (40 kW), a detrimental effect may occur as a result of the residual stresses.
- Number of cycles had no special effect with an exception to achieve desired thicknesses.
- In short, the most preferable parameters of plasma spraying of TiO_2-coated mild steel are at 30 kW with a powder feed rate of 6 g/min, and a scanning speed of 0.5 m/s.

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References

[1] R. Yilmaz, A.O. Kurt, A. Demir, Z. Tatli, Effects of TiO_2 on the mechanical properties of the Al_2O_3-TiO_2 plasma sprayed coating, Journal of the European Ceramic Society 27 (2007) 1319–1323.

[2] R.S. Lima, L. Leblanc, B.R. Marple, Abrasion Behavior of Nanostructured and Conventional Titania Coatings Thermally Sprayed via APS, VPS and HVOF, Osaka, 2004, pp. 1034–1039.

[3] R.S. Lima, B.R. Marple, Superior performance of high-velocity oxyfuel-sprayed nanostructured TiO_2 in comparison to air plasma-sprayed conventional Al_2O_3–13TiO_2, Journal of Thermal Spray Technology 14 (2005) 397–404.

[4] R.B. Heimann, Thermal spraying of biomaterials, Surface and Coatings Technology 201 (2006) 2012–2019.

[5] R.S. Lima, S. Dimitrievska, M.N. Bureau, B.R. Marple, A. Petit, F. Mwale, J. Antoniou, HVOF-sprayed Nano TiO_2-HA coatings exhibiting enhanced biocompatibility, Journal of Thermal Spray Technology 19 (2010) 336–343.

[6] J. Antony, Design of Experiments for Engineers and Scientists, Butterworth-Heinemann, Oxford; Burlinton, MA, 2003.

[7] T.J. Steeper, D.J. Varacalle, G.C. Wilson, W.L. Riggs, A.J. Rotolico, J. Nerz, A design of experiment study of plasma-sprayed alumina-titania coatings, Journal of Thermal Spray Technology 2 (1993) 251–256.

[8] T. Troczynski, M. Plamondon, Response surface methodology for optimization of plasma spraying, Journal of Thermal Spray Technology 1 (1992) 293–300.

[9] C. Pierlot, L. Pawlowski, M. Bigan, P. Chagnon, Design of experiments in thermal spraying: a review, Surface and Coatings Technology 202 (2008) 4483–4490.

[10] L. Pawlowski, The Science and Engineering of Thermal Spray Coatings, 2nd Ed., Wiley, Chichester, England; Hoboken, NJ, 2008.