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EFFECTS OF HIGH VELOCITY OXY-FUEL (HVOF) PROCESS PARAMETERS ON POROSITY AND MICROHARDNESS OF TITANIA COATING

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ABSTRACT

The Titania or Titanium dioxide (TiO_2) coating was produced by High velocity oxyfuel (HVOF) spraying on commercially pure titanium substrate. The titania coating has been considered for wear resistance, corrosion resistance and environmental barrier coating. The Titania is a suitable candidate for titanium to protect from wear and corrosion in oxygen reduced environments due to its coefficient thermal expansion match with titanium substrate. The microstructural and mechanical properties of titania coating could be tailored by controlling parameters involved in the thermal spray system. A design of experiments (DOE) method was used to identify the influence of HVOF spray parameters on coating porosity and microhardness. A central composite rotatable design with four factor and five levels was chosen to minimize the number of experimental condition. The response surface methodology (RSM) was employed to describe effects of process parameters such as spray distance, fuel flow rate, oxygen flow rate and powder feed rate on coating porosity and microhardness. The analysis of results shows the major influencing factors to coating porosity and microhardness are spray distance and fuel flow rate.

Keywords: *Titania, HVOF spraying, Response surface methodology, optimization*

1. Introduction

Titanium dioxide (TiO_2) or Titania is a very important industrial material attracts much research attention owning to their promising application to photocatalytical, electrical, optical and tribological coatings. The titania coating engineered through thermal spray technique has excellent mechanical properties which potentially resist the wear by abrasion, erosion, and sliding [1]. Titania has been used with success in high pressure acid leach hydrometallurgical processing equipments, which employs autoclaves, valves and piping equipment in a severe high temperature acidic slurry environment [2].

However, TiO_2 is ceramic material that has a relatively low melting point (1855° C) and it can be thermally sprayed via HVOF process which is a technique that exhibits relatively low jet temperature (<3000°C) but high velocities [3]. It was observed that the mechanical property of HVOF sprayed titania is superior than APS sprayed coating due to high density and high structural uniformity of the coating achieved because of higher velocity, high degree of melting which gives the near isotropic behavior with respect to mechanical properties like Vickers hardness, Knoop hardness, bond strength and elasticity index[4].

Since the coating properties are concerned the physical and chemical conditions such as pressure, temperature, velocity of flame which is strongly governed by numerous HVOF process parameters among those Oxygen flow rate, Fuel flow rate, spray distance and powder particle size considered as primary influencing parameters. It is highly difficult to study one-factor at a time interaction approach requires prohibitively large numbers of trials. Statistical designs of experiments have been shown to provide efficient approaches to systematically investigate the process parameters of thermal spray. Gill et al. Carried out the 3^3 factorial design experiments to establish the variables on the coating quality in relation to the corrosion behavior of an HVOF sprayed Ni-based self fluxing alloys coatings [5]. Forghani et al used 2^4 full factorial design to investigate various spraying parameters of TiO_2 coating by Atmospheric plasma spray on four important properties of coating microhardness, thickness/cycle, deposition efficiency and porosity [6]. Jaworski et al utilized the 2^3 full factorial design to study the effect of operational spray parameters on mechanical properties such as microhardness and

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critical load of suspension plasma sprayed TiO_2 coating [7].

In this investigation Response surface methodology (RSM) has been applied to study effects of HVOF process parameters such as oxygen flow rate (O), Fuel flow rate (F), powder feed rate (P) and spray distance (D) on porosity and microhardness of Titania coating.

2. Experimental details

2.1. Materials and specimen preparation

Commercially pure titanium (CpTi) plates of 25x25x2 mm size were cut from as received material and used as substrates. Before thermal spraying surfaces were grit blasted by using corundum grits of size 500±320 μm and subsequently cleaned by using acetone in an ultrasonic bath and dried. After grit blasting average surface roughness was measured as 5 μm using surface roughness tester (Make: Mituttoyo, Japan; model Surf test 301).

2.2 Experimental design

In this work, the effect of HVOF spray parameters such as fuel flow rate, oxygen flow rate, powder feed rate and spray distance are investigated using DOE statistical approach. DOE is a statistical method, which is used to perform the experiment work in a planned manner and investigate the interaction effect between various parameters considered. More specifically, Response Surface Methodology (RSM) has been utilized to perform the parametric studies and to develop a statistical model. This model relates the independent variables of HVOF process to the coating porosity and hardness. Also determine optimum process setting to produce coating with low porosity and high hardness.

Table 1 shows the design matrix factors considered and its low high levels. These levels are estimated based on experimental trials carried out in our laboratory. After factor levels are determined the response surface design matrix was created using DESIGN EXPERT State ease 8 software.

2.3 HVOF Spraying

TiO_2 fused and crushed feed stock (AMPRIT) having particle size 10-45μm was used for spraying. The SEM morphology of feedstock is shown in fig-1. In this study 30 coatings were prepared using different combinations of HVOF spraying parameters as prescribed by the experimental design matrix. The experiments were conducted in random order to prevent systematic errors from infiltrating the system.

After coating was developed, the porosity of the coatings was carried out on polished cross section as per ASTM B 276 standard using image analysis software equipped with optical microscope (Make : MEIJI, Japan; Model : MIL-7100) .

The cross sectional morphology of Titania coating at optimized condition was observed with SEM shown in fig 2.

The microhardness measurements was made using Vickers's microhardness tester (Make: Shimnadzu, Japan: Model: HMV – 2T) at 300 g load and 15 s dwell time was used to measure the hardness. The microhardness values were measured at ten random locations on the polished cross section of coating.

3. Results and discussions

Porosity and microhardness of the sprayed TiO_2 coatings on pure titanium was measured and inserted in the created RSM design matrix. The completed design matrix is then analysed with Design expert software and the multivariate model was developed. This model is then utilized to produce the 3D surface plots and the contour plots.

3.1 Development of predictive model for TiO_2 coating

To predict the results of experiments with different combinations, second order quadratic model was developed. The responses are function of Oxygen flow rate (O), LPG flow rate (F), Powder feed rate (P), Spray distance (D) and it can be expressed as

Responses = $f(O, F, P, D)$ Eqn (2)

The general form of a quadratic model in several parameters is:

$$Y = b_o + \sum b_i x_i + \sum b_{ii} x_2 + \sum b_{ij} x_i x_{j\ldots\ldots}$$ Eqn (3)

Table 1-The ranges of HVOF spray parameters

No	Factors	-2	-1	0	1	2
1	Oxygen Flow Rate	252	256	260	264	268
2	LPG Flow Rate - lpm	62	66	70	74	78
3	Powder Feed Rate g/min	28	33	38	43	48
4	Spray Distance (D) mm	216	222	228	234	240

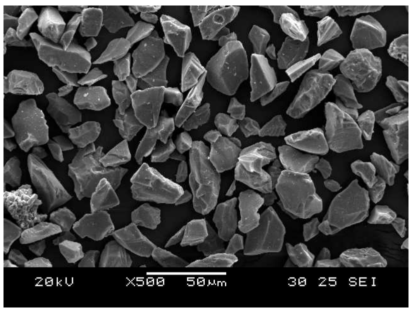

Fig 1 Scanning Electron Micrograph (SEM) of TiO_2 feed stock

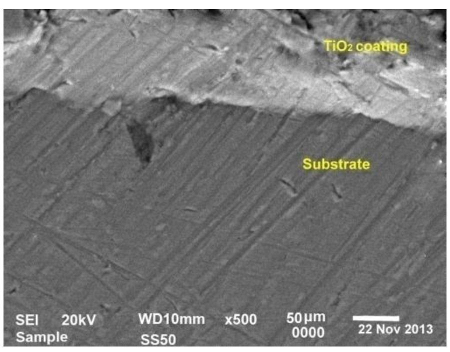

Fig 2 SEM image of TiO_2 coating cross section

For the four factors, the selected polynomial equation can be expressed as

$$Y = b_o + b_1 (O) + b_2(F) + b_3(P) + b_4(D) + b_{11}(O^2) + b_{22} (F^2) + b_{33}(P^2) + b_{44}(D^2) + b_{12}(OF) + b_{13}(OP) + b_{14}(OD) + b_{23} (FP) + b_{24}(FD) + b_{34}(PD) \quad \text{Eqn (4)}$$

Where b_o is a average of responses and b_1, b_2, b_3,........b_{44} are regression coefficients that depend on respective linear, interaction, and square terms of factors. The value of coefficient was calculated using Design Experiment software. After determining the coefficients (at 95% confidence level), the final empirical relationship were developed using these coefficients [8]. The final statistical model to estimate the responses are below:

$$\text{Porosity} = 2.2-0.4O-0.31F+0.39 P+0.43O D +0.28OF +0.13 C O -0.07 DF-0.15 FP +0.23 D P +0.25 D+0.31 O^2+0.33 F^2+0.28 P^2+0.32 D^2 \text{ vol\%} \quad \text{....Eqn (5)}$$

$$\text{Hardness} = 891.8+35.5O+ 27.5F-19.4 P-32.1 D- 8.3 OF – 3.9 OP- 0.81 OD+ 15 FP-17.3 FD-25.2 PD – 24.9O^2- 30.4 F^2 + 14.5 P^2-19.9 D^2 \text{ HV} \quad \text{...Eqn (6)}$$

3.2 Effects of process parameters

From the Analysis of Variance (ANOVA), using F-values (table 2 & 3), the predominant factor influencing the porosity and hardness of TiO_2 coating is LPG flow rate and spray distance. The perturbation plot fig 3(a-b) shows, porosity decreases and hardness increases with increasing the LPG flow rate and spray distance.

3.3.1. Effect of Oxygen flow rate on coating properties

The effect of oxygen flow rate on porosity and hardness is shown in fig 4(a-b). From the graph it can be inferred that oxygen flow rate is important parameter influences the flame temperature and velocity. During HVOF spraying process, the powder particles are heated and accelerated at high speed by the combustible gases. The properties of coating will be depending on the maximum particle temperature and velocity obtained by correct fuel and oxygen ratio. The flame temperature reaches maximum value when oxygen content is enough to produce complete combustion of LPG. For higher oxygen flow rate, there is excess oxygen that act as cooling gas and consequently promotes flame temperature decrease [9]. The increasing oxygen flow rate increases the flame velocity and also particle velocity, reducing the residence time of the particle into the flame and consequently reducing the particle temperature. In case of lower oxygen flow rate the there is an excess LPG that act as cooling gas and consequently decreases flame temperature [10]. However the low or high oxygen flow produces more unmelted particles due to cooling of effect happened in

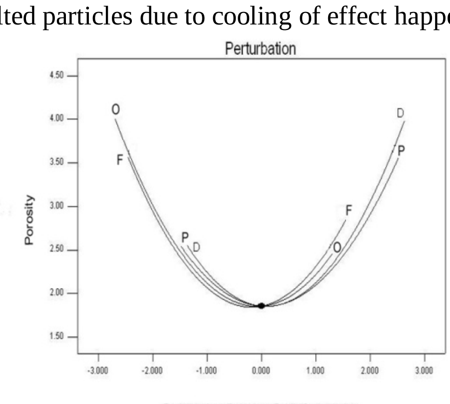

Fig 3a- Perturbation graph for porosity

the flame, this unmelted particles do not adhere in to the substrate or previously deposited layer that is formed by an unmelted particle, the particle rebound may occur and consequently increases porosity level and decreases hardness. The hardness of the titania coating has linear dependence with temperature and velocity of the particles. Higher temperature and velocity enhances the intersplat contact, thereby increasing the cohesive strength of the coating [11].

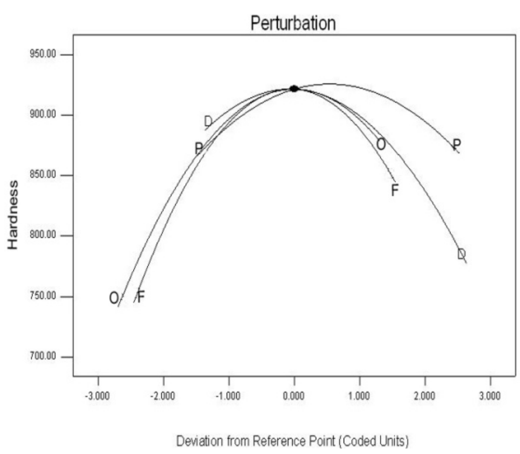

Fig 3b- Perturbation graph for hardness

Table 2 ANOVA Table for porosity

Source	p-value Prob > F	
Model	< 0.0001	significant
Oxygen flow(O)	< 0.0001	
Fuel flow (F)	0.0013	
Powder feed (P)	0.0002	
Spray distance (D)	< 0.0001	
Lack of Fit	0.1465	Not significant
R-Squared	0.925065	
Adj R^2	0.855125	
Pred R^2	0.619694	

Table 3 ANOVA table for Hardness

Source	p-value Prob > F	
Model	< 0.0001	significant
Oxygen flow(O)	< 0.0001	
Fuel flow (F)	<0.0001	
Powder feed (P)	<0.0001	
Spray distance (D)	< 0.0001	
Lack of Fit	0.3436	Not significant
R-Squared	0.996857	
Adj R^2	0.993924	
Pred R^2	0.9853	

3.3.2. Effect of fuel flow rate on coating property

The contour graph and 3D response graph effect of fuel flow rate on responses is presented in fig 5(a-b). From the perturbation graph we could understand that at lower fuel flow rate gave improper melting of particles, which resulted in low hardness and high porosity. At low fuel flow temperature of the flame is insufficient, this is not favours the melting of TiO_2 (melting temperature of the titania is 1855° C) feed stock and particle or droplet deformation at impact of substrate which leads to incomplete filling causes increase of pore and gives low hardness value.

It can be understood that HVOF process was operated under given oxygen pressure and flow, the flame temperature will be increased with the increase in fuel gas flow under present condition. As a result, the melting condition of spray powder was improved with the increase of fuel gas flow [12]. As the more fuel flow rate, increases the flame temperature and velocity of particles. High particle temperature will reduce the viscosity of the droplets, whereas, higher particle velocities will enhance the inter splat contact and reduce coating porosity and increases microhardness. Under very high fuel flow rate, flame temperature and velocity increases drastically. This situation increases the melting of titania particles and gas entrapment upon impact occurs because of the high pressure in the gas layer just prior to impact. During the rapid spreading and quenching of splats, gas escape can be suppressed resulting in escalating gas pressure in the splat centre, which can create the thin cap of a gas bubble, leaving behind a residual hole causing an increase in porosity level and the reduction of hardness values [13].

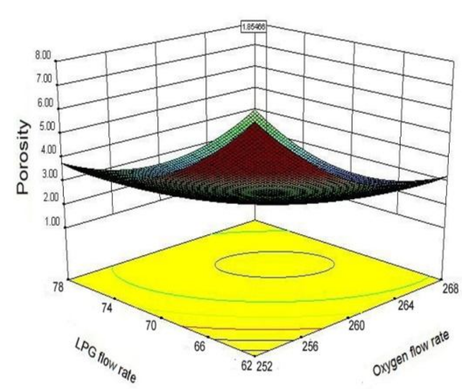

Fig 4a- 3D surface graph of effect of fuel flow and oxygen flow on coating porosity

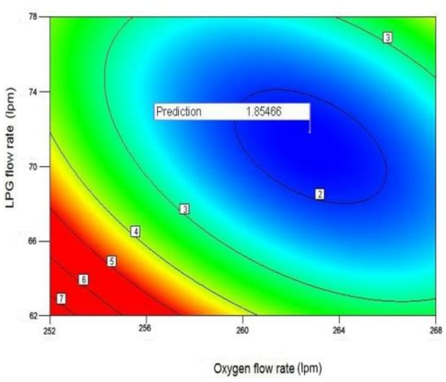

Fig 4b- 2D contour graph of effect of fuel flow and oxygen flow on coating porosity

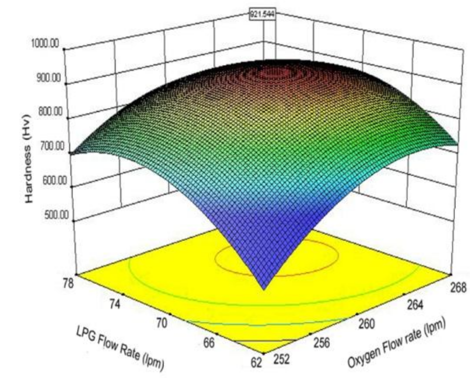

Fig 6a- 3D surface graph of effect of fuel flow and oxygen flow on coating microhardness

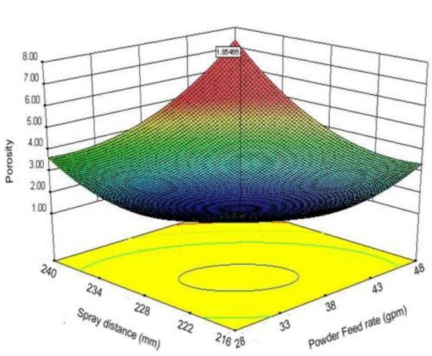

Fig 5a- 3D surface graph of effect of powder feed rate and spray distance on coating porosity

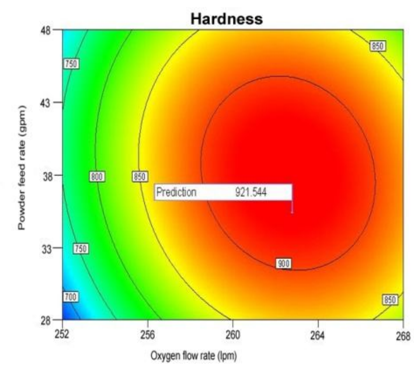

Fig 6b- 2D Contour graph of effect of fuel flow and oxygen flow on coating microhardness

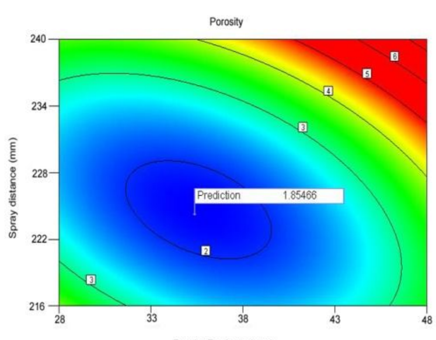

Fig 5b- 2D Contour graph of effect of powder feed rate and spray distance on coating porosity

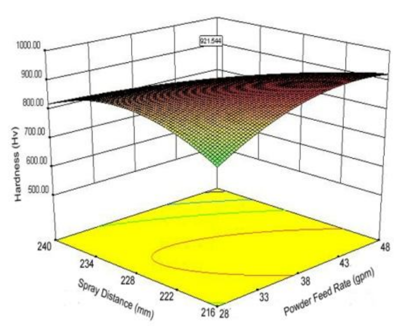

Fig 7a- 3D surface graph of effect of powder feed rate and spray distance on coating microhardness

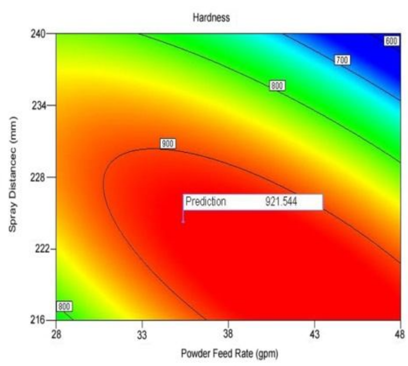

Fig 7b- 2D Contour graph of effect of powder feed rate and spray distance on coating microhardness

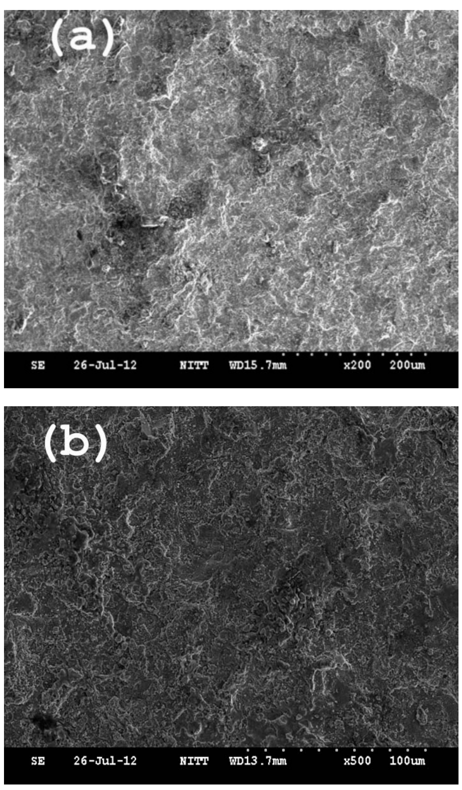

Fig 8 Top surface of TiO_2 coating

3.3.3 Effect of powder feed rate on coating properties

The effect of powder feed rate on responses are shown in fig 6(a-b). Varying powder feed rate affects the number of particles having to share the kinetic and thermal energies of flame, which in turn affects the particle velocity and temperature. When the powder feed rate is extremely low, most of the particles are melted resulting in quench crack that will increase porosity level and decrease hardness. On other hand, the right quantity of powder feed rate, the molten degree of spray particles which will increase the hardness and decrease the porosity [14].

3.3.4 Effect of spray distance on coating properties

The variations of responses with spray distances are shown in fig 7(a-b). It is shown that hardness increases with spray distance reaches maximum and then reduces. A higher spraying distance results in smaller particle velocity towards the substrate producing coating with lower density. Also, by lowering the average impact temperatures of droplets with substrate surface, an increased volume fraction of unmelted particles is produced. Both these effects contribute to a substantial increase in coating porosity. It has been reported that, increasing spray distance the particles were continuously accelerated by a supersonic jet and retarding force worked on particles from entrainment atmosphere. So that the enthalpy of molten ceramic particles is largely lost and particles are decelerated. Under such conditions, the particle striking on substrate will not be flattened to overlap the layers, resulting in higher porosity and reduced hardness value [16]. Lowering spray distance firstly increases deposition rate but problems appear by strongly increasing heat load. Coatings are dense but quenching cracks may form this may promotes porosity thereby reducing hardness. In case of optimum spraying distance, gas jet transfers sufficient temperature and velocity to the particles. The optimum temperature provides more effective packing of splats and better cohesion between splats, hence the decrease in porosity and high hardness was achieved [17].

Based on the response graph, effective factors influencing porosity was LPG fuel flow and spray distance. Flame reaches higher temperature and velocity at optimum fuel flow and spray distance so that TiO_2 particles effectively deposited on the substrate. As a result, interlamellar porosity and fraction of unmelted particles were reduced. The optimized condition of HVOF process variables is oxygen flow rate -262 lpm, fuel flow rate- 72 lpm, powder feed rate-33 gpm and spray distance is 220 mm.

Fig 8(a-b) shows the SEM images of top surface of TiO_2 coating. Fig 8(a) shows the coating produced at higher fuel flow rate, which have some agglomerates having typical size of which solidified before impact with previously deposited coating indicates. At optimum condition surface of the sprayed coating (fig 8b) indicates that the particles are better connected together and the coating seems to be very dense. Porosity had a tremendous effect on the microhardness of the coatings as lower porosity generates higher density [18].

4. Conclusions

1. In this work TiO_2 coating was developed on commercially pure Titanium substrate by HVOF spraying.
2. An empirical relationship was developed to predict the porosity and microhardness of TiO_2 coating on Titanium. The developed relationship can be used to predict the porosity and microhardness of the TiO_2 coating at 95% confidence level.
3. The response surface methodology has been used to demonstrate the influence of HVOF process parameters on coating porosity and microhardness. The major factors influencing porosity and microhardness are Fuel flow rate and spray distance.
4. The minimum porosity level of 1.856 % by volume and maximum hardness of 922 $HV_{0.3}$ could be attained at optimum process condition.

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