Establishing an empirical relationship to predict porosity and hardness of Titanium Oxide (TiO₂) coating deposited by High Velocity Oxy Fuel (HVOF) spraying

R. Sathiyamoorthy*, K. Shanmugam and V. Balasubramanian

Department of Manufacturing Engineering, Annamalai University, Annamalainagar – 608 002, Tamil Nadu, INDIA.

Keywords: HVOF Spray, Titanium oxide (TiO₂), porosity, hardness, response surface methodology (RSM)

Abstract

Thermal sprayed Titanium dioxide (TiO₂) coating could be considered as candidate for the applications in the field of wear resistance, corrosion resistance and photo catalysis. High Velocity oxy Fuel (HVOF) spraying is a flexible and efficient method to deposit TiO₂ coating but the combination of the characteristics of the HVOF process with TiO₂ limits the usefulness of the coating. The HVOF parameters such as Oxygen flow rate, Fuel flow rate, powder feed rate and spray distance plays major role to control the coating properties such as porosity and hardness. In present study, an attempt has been made to develop empirical relationship to predict the porosity and hardness of the TiO₂ coating using response surface methodology (RSM). A central composite rotatable design with four factors and five levels was chosen to minimize the number of experimental conditions. The significant level of both the main effects and the interaction are observed by analysis of variance (ANOVA) approach, student's t-test, coefficient of determination was used to define the desired output variables through developing mathematical models to specify the relationship between the output responses and input variables. The porosity and hardness of the TiO₂ coating obtained within the range is highly influenced by fuel flow rate and spray distance. Further, a linear regression relationship was also established between porosity and hardness of the TiO₂ coating.

Introduction

Titanium dioxide (TiO₂) or Titania is a very important industrial material attracts much research attention owning to their promising application to photocatalytic, electrical, optical and tribological coatings [1-3]. The Titania coating engineered through thermal spray technique has excellent mechanical properties which potentially resist the wear by abrasion, erosion, and sliding [4-5]. Thermal sprayed Titania provide superior performance, life, and reliability to high pressure acid leach hydrometallurgical processing equipments, which employs autoclaves, valves and piping equipment in a severe high temperature acidic slurry environment [6-7]. It is well known that the Titania and other ceramics Al₂O₃, ZrO₂, Cr₂O₃ are processed by Atmospheric Plasma spraying due to high temperature of plasma jet which is necessary to melt the ceramics fully or partially to make coating. However, TiO₂ is ceramic material that has a relatively low melting point (1855°C) and it can be thermally sprayed via High Velocity Oxy Fuel (HVOF) process which is a technique that exhibits relatively low jet temperature (<3000°C) but high velocities. HVOF is a versatile method which can be used to deposit dense, adherent and homogenous coatings with low porosity which is highly difficult to get dense coating through APS system [8-10].

The coating properties such as porosity, Young’s modulus, phase uniformity and hardness determine to a large extent the performance in various applications. During HVOF spraying, the pores and microcracks can be generated from different sources, such as gas entrapment between impinging droplet and the rough surface, inadequate compaction of molten particles, splashing of droplets and micropores that can be result from crystallization of molten particles [11]. Porosity facilitates the crack initiation and propagation through splat boundary leading to exfoliation and delamination of ceramic coating. In case of dense coating, the hardness is high which resist the plastic deformation.

Since the coating properties are concerned about physical and chemical conditions such as pressure, temperature, velocity of flame which is strongly governed by numerous HVOF process parameters. Among those parameters Oxygen flow rate, Fuel flow rate, spray distance and powder particle size considered as primary influencing parameters. In conventional method, effect of some parameters on a process is performed by varying one parameter at a time. It is highly difficult to study one-factor at a time interaction approach which 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 [12]. Researchers across the globe tried to model thermal spraying process using statistical regression techniques. Gill et al. Carried out the 3ª factorial design experiments to establish the variables on the coating quality in relation to the corrosion behavior of HVOF sprayed Ni-based self fluxing alloys coatings [13]. Chang Jiu et al., studied HVOF sprayed TiO₂ coating for photocatalytic applications and reported that fuel flow rate and spray powder had significant influence on phase structure of the coating [14]. Maramossadat et al investigated the HVOF process parameters on properties of nanostructure TiO₂ coating and reported that lower fuel to oxygen ratio preferred for higher percentage of anatase for photo catalytic applications [15]. Forghani et al used 2ª full factorial design to investigate various spraying parameters of TiO₂ coating by
Atmospheric plasma spray on four important properties of coating microhardness, thickness/cycle, deposition efficiency and porosity [16]. Jaworski et al utilized the 2^4 full factorial design to study the effect of operational spray parameters on mechanical properties such as microhardness and critical load of suspension plasma sprayed TiO₂ coating [17]. Recently, Sheng Hong et al used Taguchi method to optimize the process parameters of HVOF and found the important sequence of spray parameters on hardness of nano structured WC-10Co-4 Cr coating.

However, very little information is available from the open literature regarding the influence of HVOF process parameters on microstructural, mechanical behavior of TiO₂ coating. In this study an attempt has been made to develop empirical relationship to estimate porosity and hardness of TiO₂ coating.

Experimental

Identifying the important process parameters

The initial step in the design of experiments is a choice of variables being process parameters. It has been widely recognized in the thermal spray community that there are many hundred parameters, which can potentially influence the properties of coating. It is time consuming and cost expensive to control all parameters. From the literature [18-19] and trial experiments conducted in our laboratory, the predominant factors which are having more influence on spraying process were identified. The typical HVOF spray parameters are as follows:

I. Oxygen flow rate (lpm)
II. Fuel flow rate (lpm)
III. Spray distance (mm)
IV. Powder feed rate (gpm)

Identifying working limits of the process parameters

A large number of spraying trials were conducted on grit blasted 2 mm thick Titanium substrate coupons to determine the feasible working limit of HVOF process parameters by varying one parameter and keeping others constant. The chemical composition of the Titanium substrate is shown in Table 1, the chemical composition of Titanium was found by inductively coupled Plasma-Optical Emission Spectroscopy (ICP-OES). During the trial following observations were made.

(i) Oxygen flow rate is less than 252 lpm, the poor adhesion of coating and less flattening of the particles on coating microstructure was observed (Fig 1a). If the oxygen flow rate exceeds the 268 lpm fragmentation of particles and small solidified particles present in coating (Fig 1b).
(ii) If the fuel flow rate is less than 62 lpm lot of unmelted particles was observed in the coating microstructure (fig 1c). For the fuel flow rate 70 lpm more heat was produced, pores, voids present due to splashing of particles and overheating of substrate was observed (fig 1d).
(iii) If the powder feed rate is 28 gpm, very thin coating was formed due to poor deposition of particles (fig 1e). For the powder feed rate of 48 gpm more unmelted particles remain in the coating (fig 1f).
(iv) If the spray distance is less than 216 mm over heating of substrate and more unmelted particles deposited (fig 1g) whereas the distance is more than 240 mm poor deposition was observed (fig 1h).

Trial experiments are carefully conducted and observed the presence of pores, unmelted particles and coating thickness. From the observation the minimum and maximum limits of process parameters were selected which is presented in table 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Level</th>
<th>Micrograph</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen flow</td>
<td>&lt;252 lpm</td>
<td>1a</td>
<td>Poor adhesion of coating</td>
</tr>
<tr>
<td></td>
<td>&gt;268 lpm</td>
<td>1b</td>
<td>Fragmentation and coating delamination</td>
</tr>
<tr>
<td>LPG Flow</td>
<td>&lt;62 lpm</td>
<td>1c</td>
<td>More unmelted particles along with</td>
</tr>
<tr>
<td></td>
<td>&gt;70 lpm</td>
<td>1d</td>
<td>Melted region</td>
</tr>
<tr>
<td>Powder feed rate</td>
<td>&lt;28 gpm</td>
<td>1e</td>
<td>Poor deposition of particles</td>
</tr>
<tr>
<td></td>
<td>&gt;48 gpm</td>
<td>1f</td>
<td>More unmelted particles</td>
</tr>
<tr>
<td>Spray distance</td>
<td>&lt;216 mm</td>
<td>1g</td>
<td>Dense and thick unmelted particles</td>
</tr>
<tr>
<td></td>
<td>&gt;216 mm</td>
<td>1h</td>
<td>Poor deposition due to loss of coated particles</td>
</tr>
</tbody>
</table>

Figure 1: Microstructural observations during HVOF sprayed Titanium coating trials

Table 1: Chemical composition of commercially pure Titanium (wt %)

<table>
<thead>
<tr>
<th>Element</th>
<th>0.0035</th>
<th>0.0195</th>
<th>0.04425</th>
<th>0.00287</th>
<th>0.03737</th>
<th>Remaining</th>
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<td>Cr</td>
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<td>V</td>
<td></td>
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<tr>
<td>Ti</td>
<td></td>
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</table>
Table 3: The ranges of HVOF spray parameters

<table>
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<tr>
<th>No</th>
<th>Factor</th>
<th>Units</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oxygen Flow Rate (O)</td>
<td>lpm</td>
<td>-2 268</td>
</tr>
<tr>
<td>2</td>
<td>LPG Flow Rate (F)</td>
<td>lpm</td>
<td>62 78</td>
</tr>
<tr>
<td>3</td>
<td>Powder Feed Rate (P)</td>
<td>g/min</td>
<td>28 48</td>
</tr>
<tr>
<td>4</td>
<td>Spray Distance (D)</td>
<td>mm</td>
<td>216 240</td>
</tr>
</tbody>
</table>

Developing the experimental matrix

By considering above conditions, the feasible limits of the parameters were chosen in such a way very good adherent HVOF spray coating was obtained. As the range of individual factor is wide, central composite rotatable four factor five level design matrix has been selected. Central composite rotatable design of second order was found to be the most efficient tool in response surface methodology (RSM) to establish the empirical relationship of the response surfaces using the smallest possible number of experiments without loss of accuracy [20]. Table -3 shows the 30 sets of coded conditions used to form design matrix. First 16 experimental conditions are derived from the design matrix. All the variables at the intermediate (0) level constitute the centre points while the combinations of each process variable at either the lowest (-2) or highest (+2) value with the other four variables of the intermediate levels constitute the star points. Thus 30 experimental conditions allowed the estimation of the linear, quadratic and two-way interactive effects of the variables on porosity and microhardness of HVOF sprayed coating. The method of designing such matrix is dealt elsewhere [21,22]. For the convenience of recording and processing experimental data, the upper and lower levels of the factors have been coded as (-2) and (+2), respectively. The coded values of intermediate values can be calculated using the following relationship:

\[ X_i = 2 \left( \frac{X - (X_{max} + X_{min})}{X_{max} - X_{min}} \right) \]

where \( X_i \) is the required coded value of a variable X and X is any value of the variable from \( X_{min} \) to \( X_{max} \).

Conducting experiments and recording responses

Powder and HVOF spray process

Fused and crushed Titania (TiO\(_2\)) powder feed stock used in this study with size range of 10-45 µm (shown in fig.2). The 25x25x2 mm size Titanium specimens are cut from the as received condition (Optical micrograph is shown in fig.3) and 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: Mitutoyo, Japan; model Surf test 301). In this study 30 coatings were prepared using different combinations of HVOF spraying parameters as prescribed by the experimental design matrix (Table 4). The experiments were conducted in random order to prevent systematic errors from infiltrating the system. HVOF spraying was carried out using equipment supplied by M/S Metallizing Equipment Co. Pvt. Ltd., Jodhpur, India, which utilizes the supersonic jet generated by the combustion of liquid petroleum gas (LPG) and oxygen mixture. LPG fuel gas is cheap and readily available as compared to other fuels used for HVOF spraying.
Porosity and Hardness measurement

Metallographic cross section of the coatings was prepared for the porosity and hardness measurements. The samples were carefully cut by diamond cutting machine at slow speed. Then they were mounted with low viscosity epoxy resin under vacuum environment and polished with diamond paste. The porosity of the coatings was carried out on polished cross section as per ASTM B 276 standard [23] using image analysis software equipped with optical microscope (Make: MEJI, Japan; Model: MIL-7100).

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. The Vickers indentation impressions of TiO$_2$ coatings observed on coating cross sections are shown in fig 4.

| Table 5: Experimental conditions of Vickers indentation |
|---------------------------------|------------------|----------------------------------|
| Experiment No. | Parameter | Vickers’s indentation (HV$_{0.3}$) | Observations |
| Run 2 | O$_2$ flow rate = 264 lpm Fuel flow = 66 lpm Powder feed = 33 gpm Spray distance = 222 mm | Figure 4a | Cracks propagation at the tip of indentation on all directions |
| Run 8 | O$_2$ flow rate = 264 lpm Fuel flow = 74 lpm Powder feed = 43 gpm Spray distance = 222 mm | Figure 4b | No crack initiation and propagation |
| Run 24 | O$_2$ flow rate = 260 lpm Fuel flow = 70 lpm Powder feed = 38 gpm Spray distance = 240 mm | Figure 4c | Severe crack almost all directions |

Figure 4: Microhardness indentation images

Development of predictive model for TiO$_2$ coating

In present study, response surface method was used to predict the response porosity and microhardness of HVOF sprayed coating. Response surface methodology (RSM) is a combination of statistical and mathematical techniques based on a few experiments, which is useful for developing, improving and optimizing HVOF process [24]. To predict the results of experiments with different combinations, second order quadratic model was developed. The responses are function of Oxygen flow rate (O), fuel flow rate (F), Powder feed rate (P), Spray distance (D) and it can be expressed as

\[
\text{Responses} = f(O, F, P, D) \tag{2}
\]

The general form of a quadratic model in several parameters is [25,26] :

\[
Y = b_0 + b_1O + b_2F + b_3P + b_4D + b_{11}O^2 + b_{12}F + b_{13}P + b_{14}D + b_{22}F^2 + b_{23}P + b_{24}D + b_{33}P^2 + b_{34}D + b_{44}D^2 \tag{3}
\]

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

\[
Y = b_0 + b_1O + b_2F + b_3P + b_4D + b_{11}O^2 + b_{12}F + b_{13}P + b_{14}D + b_{22}F^2 + b_{23}P + b_{24}D + b_{33}P^2 + b_{34}D + b_{44}D^2 \tag{4}
\]

Where $b_0$ 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 was developed using these coefficients. The final statistical model to estimate the responses are below:

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 O²+0.33 F²+0.28 P²+0.32 D² vol%
Eqn (5)

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 – 24.9O² - 30.4 F² + 14.5 P²- 19.9 D² HV
Eqn (6)

Checking adequacy of the developed model

Analysis of Variance (ANOVA) technique was used to check the adequacy of the developed empirical relationship. In this investigation the desired level of confidence was considered to be 95%. The relationship may be considered to be adequate provided that (a) the calculated value of the ‘F’ ratio of the model developed should not exceed the standard tabulated value of ‘F’ ratio and (b) the calculated value of the ‘R’ ratio of the developed relationship should exceed the standard tabulated value of ‘R’ ratio for a desired level of confidence. It is found that the model is adequate. The value of probability > F in Table 6 and 7, implied that model is significant. Lack of fit was not significant for all the developed empirical relationship as desired. Fisher’s F test with a very low probability value (p model> F= 0.0001) demonstrates a very high significance. The goodness of fit of the model was checked by the determination coefficient ($R^2$). The coefficient of determination $R^2$ value was greater than 0.99 indicates that less than 1% of the total variations are not explained by the empirical relationship. The value of adjusted determination coefficient also high indicates the high significance of empirical relationships. Adequate precision compares the range of the predicted values at the design point with the average prediction error. At the same time relatively low value of coefficient of variance indicates the improved precision and the reliability of the conducted experiments [25]. The actual value is compared with predicted value as shown in fig. 5, which indicates that high correlation exist between estimated values and predicted values[26-27].

Table 6: ANOVA for the response Porosity

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>P-Value</th>
</tr>
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<td>13.22645</td>
<td>&lt;0.0001</td>
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<tr>
<td>P</td>
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<td>3.592231</td>
<td>16.5128</td>
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</tr>
<tr>
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<td>Total</td>
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<td>20</td>
<td>1.510935</td>
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</table>

Lack of Fit 1.510935 10 0.192434 2.653382 0.3465 insignificant

Table 7: ANOVA for the response Hardness

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<th>Source</th>
<th>Sum of Squares</th>
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Lack of Fit 34.3163 10 3.4533 1.49609 0.3436 Nonsignificant

Figure 5: Predicted Vs Actual graph

Results and Discussion

Perturbation plots

Interaction effects of the HVOF process parameters on coating porosity and microhardness were computed and plotted in the form of perturbation graph as shown in fig 6. The perturbation plot is an important diagrammatic representation, which provides silhouette views of the response surface [28]. This graph shows the response
changes as each factor moves from chosen reference point, with all
other factors held constant at reference value. A steep slope or
curvature in a factor indicates that the response is sensitive to the
factor. Relatively flat line shows insensitivity to change in that
particular factor [29].

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 [30-31]. 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

Porosity and Hardness

From the Analysis of Variance (ANOVA), using F-values, the
predominant factor influencing the porosity and hardness of TiO₂
coating is fuel flow rate and spray distance. The perturbation plot
(fig-6) shows, porosity decreases with increasing the process
parameters, further increase, and the porosity level increases. 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 TiO₂
(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.

Porosity and hardness [32]. 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
splat, 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 [33].

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 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 [34]. 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 [35].
However the low or high oxygen flow produces more unmelted
particles due to cooling of effect happened in 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 [35].

The effect of powder feed rate (curve F) on responses are shown
in fig 6. 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 [36]. 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 [37].

The variations of responses with spray distances (curve D) are
shown in fig 6. 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
[38]. 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 [38, 39].
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 [39]. 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 [40].

Relationship between porosity and hardness

The dependence of hardness with porosity can be related by
fitting the experimental data in straight line (fig 7). The straight
line is governed by the following equation:

\[ \text{Microhardness (HV)} = 1035 - 65.60 \times \text{Porosity} \]  

Eqn (7)
The slope of the estimated regression equation (−65.60) is negative, implying that as porosity decreases, microhardness increases. The coefficient of determination is \( R^2 = 90 \% \), which can be interpreted as the percentage of the total sum square that can be explained by using the estimated regression equation. The coefficient of determination \( R^2 \) is a measure of the goodness of fit of the estimated regression equation [41]. The fitted regression equation line equation (Eq 7) may be used to estimate the mean value of microhardness for the given value of coating porosity and predicting an individual value of coating hardness for a given value of coating porosity level. The confidential interval (CI) and prediction interval (PI) show the precision of regression results. Confidential interval is an interval estimate of the mean value of \( y \) for the given value of \( x \). Prediction interval is an interval estimate of an individual value of \( y \) for a given value of \( x \). For a given value of coating porosity the estimated regression equation provides a point estimate of mean microhardness value. The difference between CI and PI reflects the fact that it is possible to estimate the mean value of microhardness more precisely than individual. The greater width of the PI reflects the added variability introduced by predicting a value of the random variable as opposed to estimating a mean value. From fig 7, it is inferred that the closer the value to \( x \) (2.58%) the narrower the interval.

**Figure 7**: Relationship between porosity and hardness

**Conclusions**

1. Empirical relationships were developed to predict (at 95% confidence interval) the porosity and microhardness of Titania coatings incorporating predominant spray parameters such as fuel flow, oxygen flow, powder feed rate and spray distance.
2. Among the four HVOF process parameters studied in this investigation, fuel flow has the largest effect on the coating characteristics followed by spray distance, oxygen flow rate and powder feed rate.
3. A linear regression equation was developed between porosity and microhardness of HVOF sprayed TiO\(_2\) coating. The developed relationships can be effectively used to predict the coating porosity and microhardness of the TiO\(_2\) coating.

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