Optimization of plasma spray process variables to attain the minimum porosity and maximum hardness of the LZ/YSZ thermal barrier coatings utilizing the response surface approach

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Abstract

Lanthanum zirconate (LZ) has emerged as a novel thermal barrier coating (TBC) material because of its higher temperature phase stability, and low sintering ability than the current standard yttria-stabilized zirconia (YSZ). In order to combine the advantages, LZ and YSZ feedstock powders are blended with predetermined weight ratios (50:50) as composite coatings. The leading issue in developing the composite coating using the atmospheric plasma spray method (APS) is finding the optimum range of input parameters to attain the desired coating properties. This issue can be resolved by developing empirical relations to find the porosity and microhardness of the coating by the atmospheric plasma spray method (APS). Spray parameters such as input power, spray distance, and powder feed rate are vital in determining the coating quality. Three variables and five levels of central composite rotatable design (CCD) to reduce the overall run of the experiment were utilized in the research. The empirical relations were predicted to find the porosity and microhardness of the specimens with APS process parameters, and the empirical relations were examined through ANOVA. Optimizing the plasma spray parameters was done using response surface methodology (RSM), which provides the minimum porosity and maximum hardness. It is validated using surface response graphs, contour plots, and overlay plots. As a result, the input power has the greatest impact on the coating properties among the three variables, and the standoff distance and powder feed rate are the subsequent important spray parameters.

1. Introduction

Thermal barrier coatings (TBC) are extensively utilized for aerospace gas turbines, automotive engines, aircraft, chemicals, and energy applications. The concern is mainly centered on increasing the engine’s effectiveness by extending the working temperatures and enhancing the life of the substrate [1]. In the study of TBC material, efficiency, and lifetime are crucial parts that must be agreed upon to achieve any development. Simply, the TBC system consists of at least three parts, namely, plasma-sprayed zirconia-based top layer coating, NiCrAlY superalloy-based intermediate bond layer, and substrate. The thermal barrier coating is bonded to the superalloy via a bond coat and substrate [2].

Commonly, engine parts for hot region gas turbines composed of a nickel-based alloy super alloy called Inconel 718 were used as a substrate. This superalloy is the most widely used material for the manufacturing of high-temperature components such as turbine rotors, nozzle guide vanes, and exhaust assemblies. 7–8 weight percentage of YSZ is normally employed as the current state of art TBCs top coat material. YSZ is comparatively easy to use because of its higher temperature phase stability; good mechanical and thermal properties in gas turbine operating conditions. Despite that, the working temperatures of YSZ are limited to 1200 °C due to phase transition and sintered at high temperatures [3].

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In order to establish advanced gas turbines, the operational temperatures must be improved without compromising the properties of TBCs. Nowadays, pyrochlore oxides are of great attention to researchers. Recently, lanthanum zirconate (LZ) has emerged as a novel thermal barrier coating (TBC) material because of its high-temperature phase stability (nearly 2000 °C) and lower sintering ability than the current standard YSZ [3–7]. However, LZ has much more challenging properties due to a lower coefficient of thermal expansion (CTE) and poor toughness compared to YSZ, and it cannot be applied directly to the NiCrAlY bond coat due to a mismatch between the thermally grown oxide layer (TGO). In order to combine the advantages, LZ and YSZ coating powders are blended with different compositions for enhancing the coating life in composite layer coatings. The author demonstrated this briefly in a previously published paper about composite and multi-layer coating architecture [8]. The majority of the compositions are not capable of satisfying the above-mentioned properties [9].

Nevertheless, coating for high-temperature applications is developed by utilizing the following techniques: HVOF spray, EP-PVD, and D-GUN to develop the TBC [10–12]. Among the techniques, plasma spray has been extensively accepted in several industries owing to its affordable price, high degree of flexibility, very versatile, highly automated process, and the performance of coating developed for high operating temperatures. The plasma spraying method produces higher hardness with reduced porosity compared to the other thermal spray techniques. The exponential growth of research on plasma spray over thermal spray always increases.

The phase consistency, thermal stability, and sintering ability of composite coatings could be enhanced through the blending of 50 wt% LZ with YSZ powder at elevated temperatures [13]. The LZ/YSZ composite coating reduces the coefficient of thermal expansion different from the topcoat and bond coat, and it improves the toughness and hardness of the top coat. The results showed that the hardness is correlated to its porosity and composition [14]. The thermal cycle studies of LZ/YSZ coatings with various proportions (50:50 & 25:75) reveal that the composite coatings with buffer layers provide enhanced microstructural properties during the thermal cycling experiments [15]. The microstructural properties and phase stability of the various depositions and amongst weight percentage of 50% 8YSZ + 50% LZ composite deposit demonstrated the lowest corrosion deterioration of the other deposit [16]. According to the literature survey [13–17], a large number of coatings were carried out with different weight proportions of LZ: YSZ (25:75, 50:50, 75:25). Hence, YSZ (Metco 204 NS), LZ blended with an equal weight percentage of its composite coatings (50% YSZ + 50% LZ) were selected for optimizing the process parameters for the plasma spray method.

From the literature study, no investigation was carried out on optimizing the plasma spray parameters of LZ + YSZ blended composite coatings. The leading issue in the production of composite coatings using the APS is finding the optimum input parameters to attain the desired coating properties. The author proposed that it the essential provide a possible working limit of plasma spray deposition for further research. An effort was undertaken to achieve the optimum spray parameters to attain higher hardness with reduced porosity in the composite coatings by RSM. Since the mechanical properties of LZ decrease with increasing porosity, it is important to control the porosity by tuning the APS process parameters [11].

High-quality lanthanum zirconate powder needs to be synthesized with good flowability. The requirements of powder are sphere shape and size distribution. Powder flowability is important in feeding stock in the APS method. Better purity and homogenous composition can improve phase consistency and corrosion performance, extending the coating lifetime. Henceforth, with the aforementioned aspects in mind, an experiment was performed to synthesize, spray deposition, and optimize the process variables in TBCs using the APS method.

2. Experimental investigation

This study was intended to meet the target goals in the following order: synthesis of coating LZ powders; preparation of substrate and coating materials for plasma spray deposition; evaluating the porosity and hardness; identification of key parameters of the plasma spray process; determination of the high and low levels of the selected parameters; choosing the appropriate matrix of experimental design; conducting the experimentation according to the design matrix; developing the empirical relations to estimate the above responses with RSM; and optimization through mathematically and graphically.

2.1. Synthesis of lanthanum zirconate powders

The LZ powders utilized in this investigation were synthesized by the solid-state method [9, 18, 19]. The raw materials for the synthesis of LZ, lanthanum oxide (La2O3, 99.9%, molecular weight—325.81 g mol⁻¹), and zirconium oxide (ZrO2, 99.5%, molecular weight —123.22 g mol⁻¹) powders were employed. SEM micrograph and EDS analysis of La2O3 powder and ZrO2 powder, as illustrated in figures 1 and 2. It demonstrated that both particles have a sphere-shaped and angular structure. The x-ray diffraction patterns
reveal that lanthanum oxide demonstrates a cubic phase, whereas zirconium oxide demonstrates tetragonal and monoclinic phases, with irregular morphology and particles in the submicron size range, as can be seen in figure 3. The stoichiometric ratios of La$_2$O$_3$ and ZrO$_2$ were calculated by a balanced chemical equation as shown below,

$$\text{La}_2\text{O}_3 + 2\text{ZrO}_2 \rightarrow \text{La}_2\text{Zr}_2\text{O}_7$$

So, $\%$ of La$_2$O$_3$ = $\left(\frac{325.8}{572.24}\right) \times 100 = 56.93\%$ and $\%$ of ZrO$_2$ = $\left(\frac{246.44}{572.248}\right) \times 100 = 43.06\%$.

Thus, the mixture of La$_2$O$_3$ and ZrO$_2$ in the molar ratio of 1:2 (weight percentage 56.93% and 43.06%, respectively) was utilized and the powder was blended in a ceramic crucible for 30 min. The blended powders (for 250 grams) with mixing media such as zirconia balls (20 nos., 10 mm in diameter) were blended using ball milling (Make: VB Ceramics, Chennai, India; Model: VBCRC Planetary Ball Mill) using a vial made up of tungsten carbide to prevent impurity at 300 rpm for 12 h. The weight percentage of ball-to-powder was kept constant at 10:1, and blended powders were extracted from the vial after 4 h.

A hydraulic pellet press is used to compact these ceramic powders into pellet shapes using a hydraulic pellet press (Make: VB Ceramics, Chennai, India; Model: VBCRC Press) using a five-tonne load and a five-minute dwelling duration. Then the pellet was sintered at 1400 °C for 5 h in the open-air environment using a box furnace (Make: VB Ceramics, Chennai, India; Model: VBHTSF-1400MF12) and this confirmed that the pellets had completely sintered. Then the sintered pellet was crushed in a ceramic crucible and sieved into different sizes of mesh to fulfill the size specification of the plasma process. The powder was sieved with specific mesh sizes several times.
The SEM morphology of sintered lanthanum zirconate powders (LZ) is shown in figure 4(a). It represents a spherical or ellipse shape with an average particle mean size of 17 μm measured using a laser scattering particle size distribution analyzer (Make: Horiba Ltd, Japan; Model: Partica LA-960) that meets the powder size requirement of the APS process. In a single LZ particle, a porous surface is evident. After that, the sintered powders were exposed to XRD analysis to verify the LZ structure as shown in figure 4(b). It reveals the distribution of the LZ powder and narrow peak widths, suggesting high crystalline in the LZ powder.

2.2. Plasma spray deposition
Nickel-based Inconel 718 super alloy with 4mm thickness was used as substrate (Next Gen Steel & Alloys, India). The composition of the substrate is as follows: Nb-4.87, Al-0.34, Ti-0.81, Ta-0.002, C-0.05, Mn-0.12, Cu-0.15, Co-0.2, P-0.006, S-0.01, Si-0.21, B-0.001 in wt% according to the test report of the material, confirmed to Inconel 718 with respect to elements specified by optical emission spectrometry. The Inconel substrate is cut into a dimension of 100 × 25 × 4 & 10 × 10 × 4 mm through a wire-cut EDM (Make: JK Machines, India. Model: ECO 25) facility available at the Government College of Technology, Coimbatore, India. The optical micrograph of the substrate is made up of columnar and equiaxed grains. The cross-sectional surface of the substrate was grit blasted, employing 500 + 320 μm corundum grit to enhance the adhesive behavior, and then treated through an ultrasonic cleaner using acetone and dried before plasma was sprayed.

Commercial grade NiCrAlY (Amdry 962, Oerlikon Metco) with the composition of Ni-Balance, Cr-22, Al-10, and Y-1 in wt% powder with a particle size of −106 + 53 microns was selected as the typical feedstock powder for a bond coat in this investigation. SEM micrograph and EDS analysis with the elemental distribution of NiCrAlY powder as shown in figures 5(a)–(b). It has a globular shape due to gas atomization and includes a
huge number of small particles. The bond coat thickness was about 150 microns and coated by the APS method (Make: Ion Arc Technologies, India; Model: APSS-II) available at AUM Surface Pvt. Ltd, Bangalore, India.

A spray-dried and dense YSZ powder (Metco 204NS, Oerlikon Metco) with a composition of ZrO₂-balance, Y₂O₃−8 wt% with a particle size of −125 + 11 microns was used as the topcoat feedstock. The SEM micrograph of the feedstock demonstrates some particles with satellites and the EDS findings of YSZ powder for the top coat show the presence of zirconia and yttria as major elements, with no other traceable elements seen in figures 5(c)–(d).

The feedstock powder was mixed with 50 wt% of LZ and 50 wt% of YSZ through the ball mill method. Then the composite LZ and YSZ samples were sprayed on the bond coat by the APS method as a topcoat layer. Plasma spraying has been performed with a 40 kW IGBT-based plasmatron APS system. A digital micrometer (Make: Mitutoyo, Japan; Model: IP 65) assessed the thickness of the bond coat layer as 150 microns and the topcoat layer as 350 microns to attain a total thickness of 500 ± 15 microns and completed the spray run as shown in LZ/YSZ composite coating architecture illustrated in figure 6(a). The bond layer and top layers demonstrate the typical microstructure of an APS-deposited coating. The roughness was evaluated by a surface roughness tester (Make: Mitutoyo, Japan; Model: SJ-410) as per ASTM D7127–17 and the average roughness was five microns. Photographs of uncoated, bond coated, and as-coated multilayer specimens as shown in figures 6(b)–(d).

2.3. Coating properties evaluation
The porosity was measured using an optical microscope (Make: Chennai Metco Pvt Ltd, Chennai, India; Model: Vertimet Pro MV06) on the polished cross-section with image analyzing software (Metaision V 3.0) based on ASTM B 276 [20]. Initially, 200 μm square regions have been picked on the refined cross section and the image has been examined. The same technique has been performed on five different sites to evaluate the average porosity. The porosity analysis for the as-sprayed samples was deposited as per the design matrix. The microstructure porosity analysis and binary images of experimental conditions are listed in table 1. The porosity ranges from 4% to 26%. Typically, the APS LZ/YSZ coatings have a porosity of 3%–27% [18, 21, 22].

Using a Vickers microhardness tester, the hardness measurement was performed (Make: Mitutoyo, Japan; Model: Autovick, HM-200 system D). The hardness was evaluated employing a load of 300 grams and a duration of 15 seconds at 10 different regions of the coating. The hardness indentation images for experimental
conditions are summarized in table 1. It shows that the hardness decreases as the porosities increase, owing to the presence of pores, splats, and cracks. The same microstructural properties of APS deposits were observed by many researchers [21–26].

2.4. Identification of key process parameters
According to the literature [27] and the previous research work [18, 21–23], the key parameter for plasma spray that has a more significant impact on the characteristics of the coating was determined as input power, standoff distance, and the powder feed rate.

2.5. Identification of work limits of parameter
A huge number of trials are carried out to find out the possible working limits of the aforementioned APS process variables, as can be seen in figure 7. The below explanations have been presented during the experiments based on literature, microstructural examination, and practical and theoretical understanding of process knowledge.

(i) If the input power was less than 26 kW, the coating would have been poorly adhered as a result of poor melting of particles, thus increasing the pore size after that delamination occurred. When the power level has been increased by more than 34 kW, porosity reduces because the enthalpy of the ionized flames has increased. Thus, enhancing the flow and compactness during the formation of the coating [24].

(ii) If the standoff distance was below 102 mm, substrate deformation and coating delamination would occur. If the standoff distance extended beyond 132 mm, the melted particles were not able to attain the substrate and re-solidification occurred. This led to poor adhesion to the coating, resulting in porosity and a lower hardness value.

(iii) The minimum feed rate attainable was 20 gpm (limited to the feedstock system). If the powder feed rate is greater than 40 gpm, a significant portion of the feedstock powders remains unmelted and particles get clogged in the injecting port.

![Figure 6](image_url)

Figure 6. (a) Composite coating architecture Photograph of (b) uncoated (c) bond coated (d) as-coated multilayer specimen.
3. Development of empirical relationships

After considering all these factors, the parameter limits for the APS have been identified. Response surface methodology (RSM) is utilized to find the relations between the input variables and outcomes such as porosity and hardness. Due to the extensive range of variables, the experimental circumstances have been maximized using three variables, and five levels of central composite rotatable design (CCD) to reduce the overall run of the experiment. The optimization of the APS process parameters was carried out through Design Expert V 13.0 statistical software [21–25]. The APS coating parameter range is listed in table 2 and the experimental design matrix for the 20 deposits for the coating with various combinations of APS process parameters and their responses is listed in table 3. The higher and lower levels of the factors were \( +1.682 \) and \( -1.682 \). The coded values of any intermediate level are calculated by equation (3).

### Table 1. Porosity and hardness images for experimental conditions.

| Exp. No | Experiment conditions | Microstructure of porosity analysis | Binary images of the porosity analysis | Hardness indentation | Observation |
|---------|------------------------|------------------------------------|--------------------------------------|---------------------|-------------|
| 1.      | P=28 kw S=108 mm F=24 gpm | ![Microstructure image] | ![Binary image] | ![Hardness image] | Porosity= 16 %. Vol. Diagonal Length = 59.2 \( \mu \)m Hardness Vickers= 667 HV |
| 2.      | P=32 kw S=108 mm F=24 gpm | ![Microstructure image] | ![Binary image] | ![Hardness image] | Porosity= 5 %. Vol. Diagonal Length = 37.4 \( \mu \)m Hardness Vickers= 1015 HV |
| 3.      | P=28 kw S=126 mm F=24 gpm | ![Microstructure image] | ![Binary image] | ![Hardness image] | Porosity= 22%. Vol. Diagonal Length = 64.5 \( \mu \)m Hardness Vickers= 620 HV |
| 4.      | P=32 kw S=126 mm F=24 gpm | ![Microstructure image] | ![Binary image] | ![Hardness image] | Porosity= 7%. Vol. Diagonal Length = 39.8 \( \mu \)m Hardness Vickers= 1007 HV |
| 5.      | P=28 kw S=108 mm F=36 gpm | ![Microstructure image] | ![Binary image] | ![Hardness image] | Porosity= 16%. Vol. Diagonal Length = 50.2 \( \mu \)m Hardness Vickers= 822 HV |
| 6.      | P=32 kw S=108 mm F=36 gpm | ![Microstructure image] | ![Binary image] | ![Hardness image] | Porosity= 10%. Vol. Diagonal Length = 41.5 \( \mu \)m Hardness Vickers= 950 HV |
| 7.      | P=28 kw S=126 mm F=36 gpm | ![Microstructure image] | ![Binary image] | ![Hardness image] | Porosity= 26%. Vol. Diagonal Length = 67.4 \( \mu \)m Hardness Vickers= 557 HV |
| 8.      | P=32 kw S=126 mm F=36 gpm | ![Microstructure image] | ![Binary image] | ![Hardness image] | Porosity= 18%. Vol. Diagonal Length = 54.6 \( \mu \)m Hardness Vickers= 731 HV |
| 9.      | P=26 kw S=117 mm F=30 gpm | ![Microstructure image] | ![Binary image] | ![Hardness image] | Porosity= 21%. Vol. Diagonal Length = 62.5 \( \mu \)m Hardness Vickers= 641 HV |
| 10.     | P=34 kw S=117 mm F=30 gpm | ![Microstructure image] | ![Binary image] | ![Hardness image] | Porosity= 5%. Vol. Diagonal Length = 35.6 \( \mu \)m Hardness Vickers= 1054 HV |
Where, $Y_i$-coded value of Y variable, Y-any variable value between $Y_{\text{mini}}$ and $Y_{\text{maxi}}$, $Y_{\text{mini}}$- small range and $Y_{\text{maxi}}$- high range of the variables.

The second most effective method in RSM to build an empirical relation between the response surfaces by the least feasible number of tests was conducted in the central composite rotatable design without compromising accuracy. The output response ($Y$), such as porosity level ($PL$) and hardness ($HV$), is represented by the input power ($P$), standoff distance ($S$), and powder feed rate ($F$), written as responses $Y = f(P, S, F)$. The direct and interactive impacts of all components are the empirical connections. The polynomial chosen is shown in the following.

$$Y_i = 1.682 \frac{[2Y - (Y_{\text{maxi}} + Y_{\text{mini}})]}{[Y_{\text{maxi}} - Y_{\text{mini}}]}$$  \hspace{1cm} (3)$$

Table 1. (Continued.)

|   | P=30 kw | S=102 mm | F=30 gpm |
|---|---------|-----------|-----------|
|11.|         |           |           |
|12.| P=30 kw | S=132 mm  | F=30 gpm  |
|13.| P=30 kw | S=117 mm  | F=20 gpm  |
|14.| P=30 kw | S=117 mm  | F=40 gpm  |
|15.| P=30 kw | S=117 mm  | F=30 gpm  |
|16.| P=30 kw | S=117 mm  | F=30 gpm  |
|17.| P=30 kw | S=117 mm  | F=30 gpm  |
|18.| P=30 kw | S=117 mm  | F=30 gpm  |
|19.| P=30 kw | S=117 mm  | F=30 gpm  |
|20.| P=30 kw | S=117 mm  | F=30 gpm  |

Where, $Y_i$-coded value of Y variable, Y-any variable value between $Y_{\text{mini}}$ and $Y_{\text{maxi}}$, $Y_{\text{mini}}$- small range and $Y_{\text{maxi}}$- high range of the variables.

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$$Y = a_0 + \sum a_i x_i + \sum a_{ij} x_i^2 + \sum a_{ij} x_i x_j$$  \hspace{1cm} (4)$$

Table 1. (Continued.)

|   | P=30 kw | S=117 mm | F=30 gpm |
|---|---------|-----------|-----------|
|21.|         |           |           |
|22.|         |           |           |
|23.|         |           |           |
|24.|         |           |           |
|25.|         |           |           |

Where, $Y_i$-coded value of Y variable, Y-any variable value between $Y_{\text{mini}}$ and $Y_{\text{maxi}}$, $Y_{\text{mini}}$- small range and $Y_{\text{maxi}}$- high range of the variables.
For three factors, the selected polynomial was written as below.

\[
\text{Responses} = a_0 + a_1(P) \\
+ a_2(S) + a_3(F) + a_{12}(PS) + a_{13}(PF) \\
+ a_{23}(SF) + a_{11}(P)^2 + a_{22}(S)^2 + a_{33}(F)^2
\]  

(5)

Here, \(a_0\) is the average response, and \(a_1, a_2, a_3, \ldots a_{33}\) are the regressive coefficient. In this expression, no substantial impact can be made on the responses of all the variables (primary and interacting factors).

Significant factors have been determined using ANOVA test results and are listed in tables 4 and 5. The developed empirical relationships are presented below.

\[
\text{Porosity level (vol.\%)} = +4.35 - 5.35(P)
\]
Table 3. DOE matrix and outcomes.

| Exp. condition | Actual values | Outcomes |
|---------------|---------------|----------|
|               | Power (kW)    | Stand-off distance (mm) | Powder feed rate (gpm) | Porosity (Vol. %) | Hardness (HV) |
| 1             | 28            | 108       | 24              | 16             | 667         |
| 2             | 32            | 108       | 24              | 5              | 1015        |
| 3             | 28            | 126       | 24              | 22             | 620         |
| 4             | 32            | 126       | 24              | 7              | 1007        |
| 5             | 28            | 108       | 36              | 16             | 822         |
| 6             | 32            | 108       | 36              | 10             | 950         |
| 7             | 28            | 126       | 36              | 26             | 557         |
| 8             | 32            | 126       | 36              | 18             | 731         |
| 9             | 28            | 117       | 30              | 21             | 641         |
| 10            | 34            | 117       | 30              | 5              | 1054        |
| 11            | 30            | 102       | 30              | 11             | 928         |
| 12            | 30            | 132       | 30              | 23             | 698         |
| 13            | 30            | 117       | 20              | 8              | 887         |
| 14            | 30            | 117       | 40              | 16             | 731         |
| 15            | 30            | 117       | 30              | 4              | 1113        |
| 16            | 30            | 117       | 30              | 5              | 1094        |
| 17            | 30            | 117       | 30              | 4              | 1117        |
| 18            | 30            | 117       | 30              | 5              | 1113        |
| 19            | 30            | 117       | 30              | 4              | 1114        |
| 20            | 30            | 117       | 30              | 4              | 1113        |

Table 4. ANOVA result for porosity level.

| Source         | Sum of squares | Df | Mean square | F Value | p-value | prob > F |
|----------------|----------------|----|-------------|---------|---------|----------|
| Model          | 1063.86        | 9  | 118.21      | 106.15  | < 0.0001 | significant |
| A-power        | 324.00         | 1  | 324.00      | 290.94  | < 0.0001 |          |
| B-SOD          | 156.10         | 1  | 156.10      | 140.17  | < 0.0001 |          |
| C-feed rate    | 81.97          | 1  | 81.97       | 73.60   | < 0.0001 |          |
| AB             | 4.50           | 1  | 4.50        | 4.04    | 0.0722  |          |
| AC             | 18.00          | 1  | 18.00       | 16.16   | 0.0024  |          |
| BC             | 12.50          | 1  | 12.50       | 11.22   | 0.0074  |          |
| A²             | 136.19         | 1  | 136.19      | 122.30  | < 0.0001 |          |
| B²             | 320.34         | 1  | 320.34      | 287.65  | < 0.0001 |          |
| C²             | 125.75         | 1  | 125.75      | 112.92  | < 0.0001 |          |
| Residual       | 11.14          | 10 | 1.11        |         |         |          |
| Lack of Fit    | 9.80           | 5  | 1.96        | 7.35    | 0.0236  | Not significant |
| Pure Error     | 1.33           | 5  | 0.2667      |         |         |          |
| Cor Total      | 1075.00        | 19 |             |         |         |          |
| Std Dev.       | 1.06           |    |             |         |         |          |
| Mean           | 11.50          |    |             |         |         |          |
| CV%            | 9.18           |    |             |         |         |          |
| R²             | 0.9896         |    |             |         |         |          |
| Adjusted R²    | 0.9803         |    |             |         |         |          |
| Predicted R²   | 0.9214         |    |             |         |         |          |
| Adeq. Precision| 28.1195        |    |             |         |         |          |

\[
\text{Hardness(HV)} = +1110.09 + 138.41(P) - 67.43(S) \\
-37.21(F) + 12.52(PS) - 63.79(PF) - 52.66(SF) \\
-97.94(P^2) - 112.38(S^2) - 113.79(F^2)
\]
3.1. Testing the adequacy of the developing relations

ANOVA values of output responses such as porosity and hardness were listed in tables 4 and 5. The method for analyzing ANOVA statistics has been published in the literature [28–30]. The probability value is greater than F and below 0.0500 in the empirical relations, which implies the empirical model is significant. The R² value was determined as 0.9972 and 0.9979 for porosity and hardness. This means that 99.72 and 99.79 percent of the experimental data agree with the existing empirical relationship. The R² value should be close to one, implying that the developed statistical model is more appropriate. The predicted R² accords in good agreement with the adjusted R². Figure 8 demonstrates that the result is strongly related to the experimentation data.

4. Results and discussion

4.1. Perturbation plots

The proposed empirical relations could efficiently determine the responses by replacing the process parameter variables. Based on the obtained regression equations (6) and (7), the main and interaction result of the spray parameter was predicted and exhibited as the perturbation plots indicated in figure 9.

4.2. Effect of power on porosity and hardness

The effects of power on coating properties were illustrated as curve A in figure 9. The coating structure is probably associated with input power. Due to lower power, the energy density of the ionized flames is poor. Thus, the coating was improperly adhered as a result of poor melting of particles, thus increasing the pore size after that delamination occurred. When the power level has been enhanced, the heavier particles are melted or partially melted, whereas the evaporated smaller particles remain finite, leading to enhanced overall coating performance, adhesion, and surface hardness during the formation of coatings [31]. Furthermore, particles that are flattened and solidified efficiently on the substrate will minimize porosity and improve surface hardness. Even though the power level has been increased beyond a certain level, there won’t be much of an impact on the coatings. It leads to a reduction in the porosity because the enthalpy of the ionized flames is increased and particles are prone to melting with the elevated plasma energy level, as shown in figure 9(a). This increases flow and compactness in the formation of coatings. Ramachandran et al [18] demonstrated that power has the greatest impact on the coating qualities and characteristics.

The effect of unmelted particles would raise the roughness and reduce the hardness due to the lower particle cohesiveness, and it would subsequently raise the porosity, as can be seen in figure 9(b). As the porosity increases, the stiffness of the coating decreases, lowering the hardness values. Owing to elevated pressure in the gas layer before the impingement, gas entrapment occurs at very high-power levels. Gas escape can be prevented by the rapid spread and quenching of splats, leading to an increase in gas pressure in the splat center. This could result

### Table 5. ANOVA result for hardness.

| Source | Sum of squares | Df | Mean square | F Value | p-value prob | > F |
|--------|----------------|----|-------------|---------|--------------|-----|
| Model  | 7.321 × 10⁵    | 9  | 81345.24    | 104.91  | < 0.0001     | significant |
| A-power| 2.169 × 10⁵    | 1  | 2.169 × 10⁵ | 279.77  | < 0.0001     |
| B-SOD  | 62756.47       | 1  | 62756.47    | 80.94   | < 0.0001     |
| C-feed rate | 19112.53 | 1  | 19112.53    | 24.65   | 0.0006       |
| AB     | 903.13         | 1  | 903.13      | 1.16    | 0.3058       |
| AC     | 23436.13       | 1  | 23436.13    | 30.23   | 0.0003       |
| BC     | 23005.13       | 1  | 23005.13    | 29.67   | 0.0003       |
| A²     | 1.245 × 10⁵    | 1  | 1.245 × 10⁵ | 160.57  | < 0.0001     |
| B²     | 1.805 × 10⁵    | 1  | 1.805 × 10⁵ | 232.85  | < 0.0001     |
| C²     | 1.851 × 10⁵    | 1  | 1.851 × 10⁵ | 238.75  | < 0.0001     |
| Residual | 7753.66    | 10 | 775.37      |         |              |
| Lack of Fit | 7408.32 | 5  | 1481.66     | 21.45   | 0.0022 Not significant |
| Pure Error | 345.33  | 5  | 69.07       |         |              |
| Cor Total | 7.399 × 10⁵  | 19 |             |         |              |
| Std Dev. | 27.85        |    |             |         |              |
| Mean    | 898.60        |    |             |         |              |
| Coefficient of variation (CV %) | 3.10 |    |             |         |              |
| R²      | 0.9895        |    |             |         |              |
| Adjusted R² | 0.9801 |    |             |         |              |
| Predicted R² | 0.9165 |    |             |         |              |
| Adeq. Precision | 27.0040 |    |             |         |              |
in an increase in porosity and a decrease in hardness by forming a thin cap around a gas bubble and leaving a residual hole [32]. Due to the evaporation of particulates, extremely large power levels resulted in a reduction in coating performance.

4.3. Effect of standoff distance on porosity and hardness
The variations of output variables with stand-off distances were demonstrated in curve B in figure 9. With a small standoff distance, poor adhesion occurs due to overheating of the powders and the formation of fine layers due to internal stresses built-up within the coatings. It leads to the chance of melted powders splashing out with fragmentation and quenching the cracks, which results in higher porosity [33]. When at optimum standoff distance, the surface has a relatively homogenous structure with impact material undergoing flattening without cracks and demonstrating great adhesion. Optimal particle temperature led to more efficient splat packing and improved splat cohesiveness, and subsequently, hardness also increased with reduced porosity [22]. From the findings, the optimum standoff was maintained between the nozzle and base materials for melting and
accelerating the powder and it is crucial to find a multi-objective optimum strategy to achieve the desired properties.

When the standoff was extended further, the melted particles were not able to attain the substrate, the enthalpy of the melted powder was mostly dropped, and the particles lead to decelerating in a long flight path due to their interaction with the air. It leads to particles being flattened poorly on the substrate, resulting in a porous structure and lower hardness. According to figure 9(a), as the standoff distance increases, the porosity increases as well. The hardness improves as the standoff reaches a maximum and then begins to decrease, as can be seen in figure 9(b). Zhao et al [34] demonstrated that the standoff is the second important factor that influences the porosity of the coatings, with reasonably accurate porosity being able to be attained by turning the standoff distance.

4.4. Effect of powder feed rate on porosity and hardness

The effect of feed rate upon coating properties is demonstrated in curve C in figure 9. The number of particles sharing the flame kinetic and thermal energy changes as the powder feed rate changes, affecting particle velocity and temperature. At a lower feed rate, a smaller quantity of material is supplied to the feedstock, and the powder is vaporized and highly melted, which leads to quenching cracks, resulting in good splat formation, reduced microhardness, splashing, and lower porosity level. The thickness of coatings may be affected by the particle feed rate. Henceforth, a higher feed rate may achieve the optimum thickness [35]. At a higher powder flow rate, a significant portion of the feedstock powder remains unmelted and particles are clogged in the injecting port. It might also lead to unmelted particles being chipped off from the top layer, lowering the splatter flattening ratio and subsequently reducing the splat flattening ratio and resulting in porosity [36]. The finding reveals that the coating efficiency and hardness are improved at an optimum level and the coating quality is excellent when most of the particles are melted, as shown in figure 9(b). It is obvious that the porosity is unaffected by the powder feed rate compared to the other parameters.

Nevertheless, because of the large number of particles in the feedstock, the great deviations from the spray path are caused by a change in the input powder conditions as well as a lot of chances for particle collisions that affect the impacting particle paths [37]. Too many small and large particles will float to the top of the flames or infiltrate the lowest area, owing to insufficient velocity and temperature. Nevertheless, such particles will penetrate the coating or adhere to it. Moreover, in-flight processing of powders to developing APS coatings should be achieved at a higher feed rate to make the most effective use of the storage of thermal energy in the plasma [38]. When the particles exceed the optimum level, they interact with one another, and the momentum and temperature of plasma flames drop as the mass of particles increases. The ionized gas is dramatically cooled in that area because the particle paths are so near to the spray path. A higher feed rate will result in a lower plasma temperature [22]. The effects of properties demonstrated that the predicted result is strongly related to the experimentation results.

5. Process optimization

The multi-objective optimization technique is utilized to achieve a result. In this research, a numerical and graphical approach was utilized to find the porosity and hardness of the APS coatings. Since the inverse relationship between the porosity and hardness in APS coatings was well established, the optimum condition for enhancing the hardness with reduced porosity was achieved through setting constraints on output parameters and operating parameters. The three-dimensional response surface graph was a graphical representation of regression equations, and it demonstrated the porosity and hardness of the coatings, as can be seen in figures 10(a)–(f).

The three-dimensional graphs were plotted at various operating parameters to analyze the effect of the trend in response to porosity and hardness. It is feasible to find, graphically, a better agreement, that is, to define the makings of the desired variables for both responses at the same time. The porosity falls and rises with the increase in spray parameters such as power, feed rate, and standoff distance, as shown in figures 10(a)–(c). The minimal porosity is found in the valley of the response surface curves. The response curves are utilized to calculate the output response of porosity in all areas of the investigated area. The power has a major impact on the hardness of the coating, as shown in figures 10(d)–(f).

Meanwhile, the graphical optimization with output parameters requires describing zones that need to match the suggested criteria instantaneously, by overlaying the crucial output response on a contour plot. Thus, searching visually for the optimal solution becomes feasible. When working with multiple output responses, it is better to initiate with numerical optimization. If not, identifying a suitable zone could be challenging. In graphical optimization, the region of possible zones in the factor space is depicted. Shaded areas are those that do not meet the optimization conditions [22, 39]. The final step is overlapping the specified regions of output
responses to develop the interesting zone. The overlay plot of output response variables of porosity and hardness for predicted values can be seen in figures 11(a)–(b). The thin grey color represents formulations with high hardness and low porosity.

5.1. Validation of optimization procedures
The validation experimentation was performed using graphical optimizations with the optimized APS spray parameters at an input power of 30 kW, a standoff of 117 mm, and a powder feed rate of 30 gpm as recommended. The validated response values are consistent with the predicted values, and only a slight variation occurred, as per the graphical overlay plot shown in figure 11. Three further validation experiments were carried out to correlate the experimentation value with the predicted value of the optimum parameter in order to

Figure 10. Response graph for porosity and hardness.
validate the model. The mean experimentation results are presented in table 6. The study revealed that the optimum deposition parameters for minimum porosity and maximum hardness of APS sprayed composite coatings were about 4 vol. % and 1117 HV0.3 respectively.

5.2. The porosity-hardness relationship in composite coatings
As demonstrated in figure 12, there is a relation between porosity and hardness. The hardness and porosity of the composite coating were based on the experimentation records derived. The experimental values are closely matched with a straight line. The regressive equation is utilized to represent the straight line.

\[
y = -25.397x + 1190.7
\]

The slope of the equation \((-25.397)\) is negative, showing that hardness increases as porosity are reduced. The determination coefficient \(R^2 = 0.9372\). It could be stated as a percent of the overall sum of squares using equation (8). The determination coefficient \(R^2\) is a measure of the fit-goodness of the regression equation, and

| Responses     | Numerical optimization | Graphical optimization | Validation |
|---------------|------------------------|------------------------|------------|
| Porosity (vol. %) | 4.35396               | 4.14467               | 4          |
| Hardness (HV)   | 1110.09               | 1116                  | 1117       |

Figure 11. Graphical optimization (overlay plot).

Figure 12. Relationship between porosity and hardness.

Table 6. Results of responses achieved using optimized processing conditions.
that equation is used to calculate the mean and individual values of hardness with respect to porosity. According to figure 12, the $R^2$ is about 0 and 1, indicating that the empirical relations obtained from experimental conditions are correct. As a result, this $R^2$ implies that the regression model is capable of predicting porosity and hardness.

5.3. Microstructure analysis of optimized coating

The cross-section of SEM micrograph, XRD analysis, optical micrograph of porosity analysis, and hardness indentation image of the composite TBCs samples under optimum conditions are illustrated in figures 13(a)–(d). The two feedstock powders, LZ (white) and YSZ (grey) are blended together as a splat formation in the top layer, resulting in small cracks and pores in the composite coating. The as-sprayed top layer exhibits no delamination or spallation, indicating that the primary deposition was of excellent quality. Every surface and interface has uneven roughness, and there is no TGO layer between the top coat and the bond coat. [14].

6. Conclusions

- This research was performed to synthesize LZ and spray deposit with 50 wt% LZ blended with 50 wt% YSZ, and the APS method was utilized to optimize the process parameters of the composite coating.

- Empirical relations were established to predict (95% confidence level) the porosity and hardness of LZ/YSZ coatings incorporating plasma sprayed variables including input power, standoff distance, and powder feed rate.

- According to ANOVA results, plasma input power has the greatest impact on coating properties among the three variables, and standoff distance and powder feed rate are the subsequent important spray parameters assessed in this research.
• The porosity and microhardness of the LZ/YSZ coatings have been incorporated into a regression equation. If the porosity of the composite coating is specified, this equation could be utilized to estimate the hardness of plasma sprayed coatings.

• The input power of 30 kW, the standoff distance of 107 mm, and the powder feed rate of 30 gpm were the optimum deposition parameters for minimum porosity and maximum hardness of APS sprayed composite coatings.

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**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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**References**

[1] Guo X, Lu Z, Jung Y G and Zhang J 2021 Novel Lanthanum Zirconate-based Thermal Barrier Coatings for Energy Applications (Switzerland AG: Springer Nature) (https://doi.org/10.1007/978-3-030-58695-9)

[2] Vašen V, Bakán E, Mack D E and Guillon O 2022 A perspective on thermally sprayed thermal barrier coatings: current status and trends I. Therm. Spray Technol. 31 1–14

[3] Zhang J, Guo X, Jung Y G, Li L and Knapp J 2017 Lanthanum zirconate based thermal barrier coatings: a review Surf. Coat. Technol. 323 18–29

[4] Guo X, Lu Z, Park H Y, Li L, Knapp J, Jung Y G and Zhang J 2019 Thermal properties of La2Zr2O7: double-layer thermal barrier coatings Adv. Appl. Ceram. 118 91–7

[5] Wang L, Di Y, Wang H, Li X, Dong L and Liu T 2019 Effect of lanthanum zirconate on high temperature resistance of thermal barrier coatings Trans. Indian Ceram. Soc. 78 212–8

[6] Ramachandran C S, Balasubramanian V, Ananthapadmanabhan P V and Viswabaskaran V 2012 Influence of the intermixed interfacial layers on the thermal cycling behaviour of atmospheric plasma sprayed lanthanum zirconate based coatings Ceram. Int. 38 4081–96

[7] Guo X, Li L, Park H M, Knapp J, Jung Y G and Zhang J 2018 Mechanical properties of layered La2Zr2O7 thermal barrier coatings J. Therm. Spray Technol. 27 581–90

[8] Mathanbabu M, Thirumalaikumaramasy D, Thirumal P and Ashokkumar M 2021 Study on thermal, mechanical, microstructural properties and failure analyses of lanthanum zirconate based thermal barrier coatings: a review Mater. Today Proc. 46 7948–54

[9] Viswanathan V, Dwivedi G and Sampath S 2015 Multilayer, multi material thermal barrier coating systems: Design, synthesis, and performance assessment J. Am. Ceram. Soc. 98 1769–77

[10] Rucharsky J and Panda A 2017 Plasma and thermal spraying Springer Sci. Rev. (https://doi.org/10.1007/978-3-319-46273-8)

[11] Lashmi P G, Ananthapadmanabhan P V, Unnikrishnan G and Aruna S T 2020 Present status and future prospects of plasma sprayed multilayered thermal barrier coating systems J. Eur. Ceram. Soc. 40 2731–45

[12] Bernard B, Quet A, Bianchi L, Joulia A, Malé A, Schick V and Rémy B 2017 Thermal insulation properties of YSZ coatings: suspension plasma spraying (SPS) versus electron beam physical vapor deposition (EB-PVD) and atmospheric plasma spraying (APS) Surf. Coat. Technol. 318 122–8

[13] Lui G, Kim I S, Song D, Park H M, Kim J S, Song T and Zhang J 2020 Sintering behavior and phase transformation of YSZ-LZ composite coatings Ceram. Int. 46 13077–13

[14] Guo X, Lu Z, Jung Y G, Li L, Knapp J and Zhang J 2016 Thermal properties, thermal shock, and thermal cycling behavior of lanthanum zirconate-based thermal barrier coatings Metall. Mater. Trans. E 3 64–70

[15] Song D, Paik U, Guo X, Zhang J, Woo T K, Lu Z, Jung S H, Lee J H and Jung Y G 2016 Microstructure design for blended feedstock and its thermal durability in lanthanum zirconate based thermal barrier coatings Surf. Coat. Technol. 308 40–9

[16] Yugewaran S, Kobayashi A and Ananthapadmanabhan P V 2012 Initial phase hot corrosion mechanism of gas tunnel type plasma sprayed thermal barrier coatings Mater. Sci. Eng. 177 536–42

[17] Liu Y Y, Wang X Z, Javed A, Zhu C and Liang G Y 2016 The effect of sintering temperature on the microstructure and phase transformation in tetragonal YSZ and LZ/YSZ composites Ceram. Int. 42 2436–65

[18] Ramachandran C S, Balasubramanian V and Ananthapadmanabhan P V 2012 Synthesis, spheroidization and spray deposition of lanthanum zirconate using thermal plasma process Surf. Coat. Technol. 206 3017–35

[19] Ganesan B, Hariharan P and Dhineshakaran D 2021 Hot corrosion studies of nanostructured gadolinium zirconate thermal barrier coatings Ceram. Int. 47 25959–72

[20] ASTM B276-05 2010 Standard Test Method for Apparent Porosity in Cemented Carbides, American Society for Testing and Materials Pennsylvania
[21] Karthikeyan S, Balasubramanian V and Rajendran R 2014 Developing empirical relationships to estimate porosity and microhardness of plasma-sprayed YSZ coatings Ceram. Int. 40 3171–83
[22] Ramachandran C S, Balasubramanian V and Ananthapadmanabhan P V 2011 Multi objective optimization of atmospheric plasma spray process parameters to deposit yttria-stabilized zirconia coatings using response surface methodology J. Therm. Spray Technol. 20 590–608
[23] Thirumalaikumarasamy D, Shanmugam K and Balasubramanian V 2012 Influences of atmospheric plasma spraying parameters on the porosity level of alumina coating on AZ31B magnesium alloy using response surface methodology Prog. Nat. Sci.: Mater. Int. 22 468–79
[24] Keshavamurthy R, Navyeeta B E, Ramesh T and Shashikumara N K 2021 Optimization of Processing Parameters for Plasma Sprayed Lanthanum Zirconate TBCs on Nickel Based Superalloy Adv. Sci. Technol. 106 90–6
[25] Mathivanan K, Thirumalaikumarasamy D, Ashokkumar M, Deepak S and Mathanbabu M 2021 Optimization and prediction of AZ91D stellite-6 coated magnesium alloy using box behnken design and hybrid deep belief network J. Mater. Res. Technol. 15 2953–69
[26] Moskal G 2007 The porosity assessment of thermal barrier coatings obtained by APS method J. Achiev. Mater. Manuf. Eng. 20 483–6
[27] Pawlowski I. 2008 The science and engineering of thermal spray coatings John Wiley & Sons
[28] Murugan K, Ragupathy A, Balasubramanian V and Sridhar K 2014 Optimizing HVOF spray process parameters to attain minimum porosity and maximum hardness in WC–10Co–4Cr coatings Surf. Coat. Technol. 247 90–102
[29] Oktém H, Erzurumlu T and Kurtaran H 2005 Application of response surface methodology in the optimization of cutting conditions for surface roughness J. Mater. Process. Technol. 170 11–6
[30] Shahi A S and Pandey S 2008 Modelling of the effects of welding conditions on dilution of stainless steel claddings produced by gas metal arc welding procedures J. Mater. Process. Technol. 196 339–44
[31] Ramaiah K, Betthahali Eswaregowda N, Tambrallimath V and Kuppahalli P 2021 Optimization of Deposition Parameters in Plasma Spray Coatings Coatings Modeling and Optimization in Manufacturing: Toward Greener Production by Integrating Computer Simulation (GmbH: Wiley) 217–35
[32] Montavon G, Godet C, Sampath S, Herman H and Berndt cc 1997 Quality control of the intrinsic deposition efficiency from the controls of the splat morphologies and the deposit microstructure J. Therm. Spray Technol. 6 153–66
[33] Kucuk A, Berndt cc, Senturk U, Lima R S and Lima C R C 2000 Influence of plasma spray parameters on mechanical properties of yttria stabilized zirconia coatings. i: four point bend test Mater. Sci. Eng. A 284 29–40
[34] Zhao Y, Peyraut F, Planche M P, Ilavsky J, Liao H, Lasalle A, Allimant A and Montavon G 2019 Experiments, statistical analysis, and modeling to evaluate the porosity influence in SPS coatings J. Therm. Spray Technol. 28 76–86
[35] Kuroda S, Dendo T and Kitahara S 1995 Quenching stress in plasma sprayed coatings and its correlation with the deposit microstructure J. Therm. Spray Technol. 4 75–84
[36] Liu Y, Nakamura T, Srinivasan V, Vaidya A, Gouldstone A and Sampath S 2007 Non-linear elastic properties of plasma-sprayed zirconia coatings and associated relationships with processing conditions Acta Mater. 55 4667–78
[37] Vardelle M, Vardelle A, Fauchais P, Li K I, Dussoubs B and Themelis N 2001 Controlling particle injection in plasma spraying J. Therm. Spray Technol. 10 267–84
[38] Fauchais P 2004 Understanding plasma spraying J. Phys. D: Appl. Phys. 37 R86
[39] Montgomery D C 2017 Design and Analysis of Experiments John Wiley & Sons