

LOW-POROSITY AND LOW-OXIDATION 316L STAINLESS-STEEL COATINGS DURING HVOF SPRAYING: NUMERICAL SIMULATION AND EXPERIMENT

PREVLEKE IZ NERJAVNEGA JEKLA 316L Z MAJHNO POROZNOSTJO IN DOBRO ODPORNOSTJO PROTI OKSIDACIJI, IZDELANE S HVOF POSTOPKOM NAPRŠEVANJA; EKSPERIMENT IN NUMERIČNA SIMULACIJA

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316L stainless-steel coatings with low porosity and low oxidation were successfully produced via High-Velocity Oxygen-Fuel (HVOF) spraying of 10–50 µm feedstock powder, combining numerical simulation and experimental validation. A gas-solid coupled multiphase flow model incorporating oxidation kinetics, employing Computational Fluid Dynamics (CFD), was developed to simulate the HVOF spraying process. The study delved into the effects of oxygen/fuel (O/F) ratio, reactant flow rate, and spraying distance on the gas flow field parameters (pressure, temperature, and velocity) and particle in-flight behaviors (temperature, velocity, and oxidation status). Furthermore, Response Surface Methodology (RSM) was utilized to quantitatively analyze the sensitivity of these parameters on the oxide layer's thickness. The optimum spraying parameters (OSPs) predicted by the simulation results were determined: 2.7 for the O/F ratio, 0.025 kg/s for the reactant flow rate, and 350 mm for the spraying distance. Subsequently, HVOF spraying experiments based on the OSP yielded 316L stainless-steel coatings with a porosity of 0.18 %, an oxide content of 0.52 w/%, and excellent mechanical properties. This work provides valuable insights for the production of 316L stainless-steel coatings with minimal porosity and low oxidation through HVOF spraying.

Keywords: 316L stainless-steel coating; HVOF; Numerical simulation; RSM; Oxidation behavior

Avtorji članka so uspešno izdelali tanke plasti nerjavnega jekla 316 L s postopkom naprševanja prašnih delcev velikosti od 10 µm do 50 µm v plinskem toku kisika in goriva (HVOF; High-Velocity Oxygen-Fuel). Izdelane plasti so imele majhno poroznost in nizko stopnjo oksidacije. V tem članku opisujejo izvedbo numerične simulacije postopka, združene s praktičnimi preizkusi. Za simulacijo procesa naprševanja s postopkom HVOF so avtorji razvili model večfaznega toka plina in trdnih delcev, ki vključuje kinetiko oksidacije in temelji na računalniški dinamiki tekočin (CFD; angl.: Computational Fluid Dynamics). V raziskavi so avtorji članka ugotavljali vpliv razmerja med kisikom in gorivom (O/F; angl.: oxygen/fuel), pretoka reagentov in razdalje brizganja na parametre tokovnega polja plina (tlak, temperatura in hitrost) ter na obnašanje delcev med letom (temperatura, hitrost in stopnja oksidacije). Poleg tega so za kvantitativno analizo občutljivosti teh parametrov glede na debelino oksidne plasti uporabili metodologijo odziva površine (RSM; angl.: Response Surface Methodology). Določili so optimalne parametre naprševanja (OSP; angl.: optimal spraying parameters) na podlagi rezultatov simulacije: razmerje O/F 2,7, pretok reagentov 0,025 kg/s in razdalja brizganja 350 mm. Naknadni optimalni preizkusi brizganja HVOF z uporabo parametrov OSP so privedli do izdelave nanosov iz nerjavnega jekla 316L s poroznostjo 0,18 %, vsebnostjo oksidov 0,52 mas. % in odličnimi mehanskimi lastnostmi. S to raziskavo so avtorji podali dragocena spoznanja o postopku HVOF naprševanja za izdelavo nanosov iz nerjavnega jekla 316L z minimalno poroznostjo in majhno stopnjo oksidacije.

Ključne besede: prevleke iz nerjavnega jekla 316L, naprševanje s HVOF postopkom, numerična simulacija, metodologija odziva površine, obnašanje med oksidacijo

1 INTRODUCTION

Critical components are frequently exposed to harsh service environments in the fields of marine engineering, petrochemical transportation, and power generation due to severe corrosion and mechanical wear.^{1–3} Fortunately, surface-engineering technology provides a cost-effective solution to extend the service life of these components by fabricating high-performance protective coatings on low-cost substrates. 316L stainless-steel coatings have

become the preferred choice due to their superior corrosion resistance, excellent wear resistance, and relatively low preparation costs.^{4,5} Therefore, dense, pure, and well-bonded 316L coatings hold great potential for engineering applications in harsh environments.

To construct high-quality 316L coatings, researchers have extensively explored various deposition techniques, including laser cladding,^{6–8} cold spray,^{9–11} and atmospheric plasma spray (APS).^{12,13} However, establishing a balance between coating quality and process efficiency remains a challenge due to the distinct limitations of each method. Although laser cladding offers metallurgical bonding, its excessive heat input often induces substrate melting and coarse grain growth, resulting in high

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dilution rates that compromise coating purity.^{6–8} Conversely, while cold spray effectively avoids oxidation, relying solely on mechanical interlocking makes it difficult to eliminate the internal porosity in high-yield-strength materials like 316L, and the deposition efficiency remains relatively low.^{10,11} Traditional APS, dominated by high flame temperatures, inevitably leads to severe in-flight oxidation and elemental burnout.¹³ In contrast, HVOF spraying, characterized by a high particle kinetic energy and moderate thermal output, is regarded as the most promising route for fabricating dense and adherent 316L coatings.^{14–17} Significant efforts have been dedicated to optimizing this process. Totemeier et al.¹⁸ confirmed that HVOF-sprayed 316L coatings exhibit superior wear resistance compared to sintered samples due to their refined microstructure. To further enhance a coating's quality, Palanisamy et al.¹⁹ employed RSM to minimize the porosity and maximize the microhardness through experimental parameter optimization. However, the inherent contradiction between particle melting and oxidation remains a critical bottleneck. Kuroda et al.²⁰ revealed that the in-flight oxidation of stainless-steel particles is extremely sensitive to combustion parameters, particularly the oxygen-fuel ratio, with the oxide content fluctuating dramatically even under high-velocity conditions. Moreover, Dobler et al.²¹ highlighted a persistent trade-off: reducing flame temperature to suppress oxidation often leads to insufficient particle deformation and compromised bonding strength. Crucially, existing literature mainly focuses on empirical parameter screening, lacking a quantitative understanding of the “semi-molten” critical state needed to minimize oxidation while ensuring density. This highlights the urgent need to introduce a numerical simulation to bridge this gap.

With the rapid development of CFD, numerical simulation has become a powerful tool for resolving the complex two-phase flow fields and particle in-flight behaviors in HVOF.^{22,23} Early studies primarily focused on the effects of gun geometry and gas parameters on the gas-phase characteristics, successfully predicting particle velocity and temperature distributions under different operating conditions.^{24–27} In terms of oxidation mechanism, Zeoli et al.²⁸ pioneered the establishment of a particle oxidation kinetic model suitable for thermal spray processes by coupling the particle in-flight parameters captured by a numerical simulation into the Mott-Cabrera theory, realizing the quantitative estimation of oxide layer growth on in-flight droplets. On this basis, recent studies further applied this theory to high-speed spray processes,^{29,30} successfully achieving numerical tracking and experimental validation of the dynamic evolution of oxide layers in complex flow fields. However, existing simulations are mostly limited to model validation, lacking a quantitative decoupling of the competitive influence of process parameters on “particle melting” and “oxide growth,” as well as guidance for process mapping.

In this study, the HVOF spraying process of 316L stainless steel was systematically investigated by integrating a numerical simulation with an experimental validation. Using CFD, a multiphase flow model was developed for both the HVOF gun and the external flow field. The study rigorously analyzed the impacts of the oxygen-fuel ratio, reactant flow rate, and spraying distance on gas-phase dynamics and particle in-flight behaviors – specifically temperature, velocity, and oxidation status. Additionally, RSM was utilized to quantitatively characterize the interactive effects of these process parameters on the particle's oxide-layer thickness. Based on the optimization analysis, the OSPs were identified, offering a robust theoretical foundation and essential data support for producing low-oxide, high-performance 316L stainless-steel coatings.

2 NUMERICAL SIMULATION AND EXPERIMENTAL METHODS

2.1 Numerical simulation

2.1.1 Gas-phase model

To simulate the viscous, turbulent, and compressible reactive flows during HVOF spraying, the model employs the Navier–Stokes equations governing mass, momentum, energy, and species conservation. Closed by the ideal gas law, these steady-state equations are solved using Favre (mass-weighted) averaging in Cartesian tensor form: Continuity equation:

$$\frac{\partial(\bar{\rho}\tilde{u}_j)}{\partial x_j} = 0 \quad (1)$$

Momentum equation:

$$\frac{\partial(\bar{\rho}\tilde{u}_j\tilde{u}_i)}{\partial x_j} = \frac{\partial\bar{p}}{\partial x_i} + \frac{\partial}{\partial x_j}((\bar{\tau}_{ij})_{\text{eff}}) + S_{\text{mom},p} \quad (2)$$

Energy equation:

$$\frac{\partial}{\partial x_i}[\tilde{u}_i(\bar{\rho}\tilde{h}_i + \bar{p})] = \quad (3)$$

$$= \frac{\partial}{\partial x_i} \left[\left(\lambda + \frac{c_p\mu_t}{Pr_t} \right) \frac{\partial\tilde{T}}{\partial x_j} + \tilde{u}_i((\bar{\tau}_{ij})_{\text{eff}}) \right] - \sum_{k=1}^{N_s} \tilde{J}_k \tilde{h}_k + S_{\text{heat},p}$$

$$(\bar{\tau}_{ij})_{\text{eff}} = \mu_{\text{eff}} \left(\frac{\partial\tilde{u}_i}{\partial x_j} + \frac{\partial\tilde{u}_j}{\partial x_i} \right) - \frac{2}{3} \mu_{\text{eff}} \frac{\partial\tilde{u}_l}{\partial x_l} \delta_{ij} \quad (4)$$

Species transport:

$$\frac{\partial}{\partial x_j}(\bar{\rho}\tilde{Y}_k\tilde{u}_j) = \frac{\partial}{\partial x_j}[\bar{J}_k] + \bar{\omega}_k; \quad k=1, \dots, N_s-1 \quad (5)$$

In the gas-solid coupled model, particle effects are incorporated via source terms. The momentum source term $S_{\text{mom},p}$ is:

$$S_{\text{heat},p} = -\rho_p C_p \frac{dT_p}{dt} \quad (6)$$

The heat source term $S_{\text{heat},p}$ is derived as:

$$S_{\text{mom},p} = -\frac{18}{24} \frac{C_D \rho_g}{d_p} (\vec{U}_g - \vec{U}_p) |\vec{U}_g - \vec{U}_p| \quad (7)$$

2.1.2 Turbulence model

Turbulence is modeled using the realizable k - ε model, which improves upon the standard model with a new turbulent viscosity formula and dissipation rate transportation equation^{31,32}:

Turbulent kinetic energy:

$$\frac{\partial}{\partial x} (\rho \nu k) = \frac{\partial}{\partial x} \left[\left(\mu + \frac{\mu_t}{\sigma_k} \right) \frac{\partial k}{\partial r} \right] + N_k + N_b - \rho \varepsilon + Y_M + S_k \quad (8)$$

Turbulence dissipation rate:

$$\frac{\partial}{\partial t} (\rho \varepsilon) + \frac{\partial}{\partial r} (\rho \nu \varepsilon) = \frac{\partial}{\partial r} \left[\left(\mu + \frac{\mu_t}{\sigma_\varepsilon} \right) \frac{\partial \varepsilon}{\partial r} \right] + \rho C_1 S_\varepsilon - \rho C_2 \frac{\varepsilon^2}{k + \sqrt{\nu \varepsilon}} + C_{1\varepsilon} \frac{\varepsilon}{k} C_{3\varepsilon} N_b + S_\varepsilon \quad (9)$$

Turbulent viscosity:

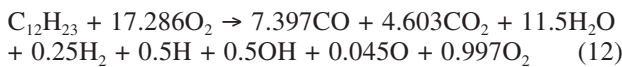
$$\mu_t = \rho C_\mu \frac{k^2}{\varepsilon} \quad (10)$$

Dynamic viscosity:

$$C_\mu = \frac{1}{A_0 + A_s U \frac{k}{e}} \quad (11)$$

2.1.3 Combustion model

Kerosene ($C_{12}H_{23}$) combustion is modeled using a global reaction scheme:



The eddy dissipation model (EDM) governs the reaction rates, prioritizing turbulent mixing over Arrhenius kinetics.³¹ The net production rate of species i in reaction r is determined by the smaller value of the following two expressions:

$$R_{i,r} = \nu_{i,r} M_{w,i} A \rho \frac{\varepsilon}{k} \min \left(\frac{Y_R}{\nu_{R,r} M_{w,R}} \right) \quad (13)$$

$$R_{i,r} = \nu_{i,r} M_{w,i} A B \rho \frac{\varepsilon}{k} \left(\frac{\sum_p Y_p}{\sum_j \nu_{j,r} M_{w,j}} \right) \quad (14)$$

2.1.4 Particle phase dynamics

The discrete phase model (DPM) tracks particle motion and temperature using a Lagrangian approach. The particle motion equation is³³:

$$m_p \frac{dV_p}{dt} = \frac{1}{8} \rho_g A_p C_D (\vec{U}_g - \vec{U}_p) |\vec{U}_g - \vec{U}_p| + \vec{F} \quad (15)$$

where the drag coefficient is:

$$C_D = \begin{cases} \frac{24(1 + 0.15 \text{Re}_p^{0.687})}{\text{Re}_p}, & \text{Re}_p \leq 10^3 \\ 0.44, & \text{Re}_p \geq 10^3 \end{cases} \quad (16)$$

where the Reynolds number Re_p is defined as:

$$\text{Re}_p = \rho_g \frac{|\vec{U}_g - \vec{U}_p|}{\mu_g} \quad (17)$$

The single-particle energy balance is:

$$m_p C_p \frac{dT_p}{dt} = A_p h_c (T_g - T_p) \quad (18)$$

where

$$h_c = \frac{Nu_\lambda}{d_p} \quad (19)$$

$$Nu = 2.0 + 0.6 \text{Pr}^{0.33} \text{Re}^{0.5} \quad (20)$$

Unlike decoupled models, which assume negligible particle influence, this study accounts for a higher particle loading to capture gas-particle interactions, comparing coupled and decoupled solutions.

2.1.5 Oxidation Models

The heat-transfer process in spherical coordinates is described by the following equation:

$$\frac{\partial T}{\partial t} = \frac{\alpha}{\psi(T)} \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) \quad (21)$$

where the function $\psi(T)$ is defined as³⁴:

$$\psi(T) = \begin{cases} \text{if } T_g \leq T \leq T_L & 1 + \frac{H_{sf} (T_K - T_L)^{\frac{1}{(1-\beta)}}}{C_p (1-\beta) (T_K - T)^{\frac{(2-\beta)}{(1-\beta)}}} \\ \text{else} & 1 \end{cases} \quad (22)$$

Assuming infinite diffusion (equilibrium) in the liquid phase and zero diffusion in the solid, the boundary conditions for Equation (22) at the particle's surface and center are defined as follows:

$$\left. \frac{\partial T}{\partial r} \right|_{r=0} = 0 \quad k_s \left. \frac{\partial T}{\partial r} \right|_{r=R} = h(T_g - T_R) \quad (23)$$

To evaluate the convection coefficient, the Ranz and Marshall equation is used as:

$$Nu_u = (2 + 0.6 \text{Re}^{1/2} \text{Pr}^{1/2}) \quad (24)$$

where Nu_u is the non-dimensional Nusselt number, defined as:

$$Nu_u = \frac{h_d}{k_g} \quad (25)$$

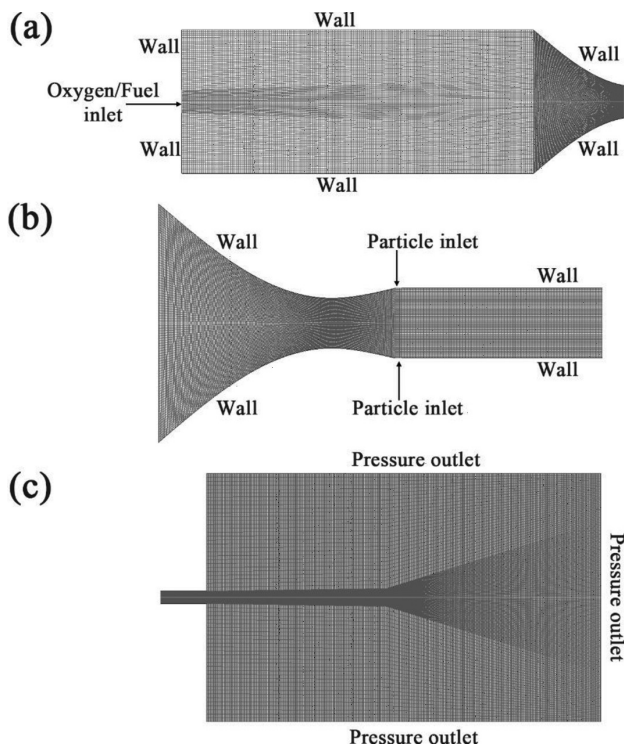


Figure 1: Meshing of the calculation domain for: a) combustion chamber, b) Laval nozzle and barrel and c) free jet region

Particle oxidation initiates upon encountering sufficient oxygen in the surrounding gas flow. According to the Mott-Cabrera theory,³⁵ this process is fundamentally dictated by ion transport across the oxide film, enabling the oxide layer's growth to be computed as follows:

$$\frac{dx}{dt} = 2A_0 \exp\left(-\frac{Q}{k_b T_R}\right) \exp\left(\frac{K_0 \sqrt{P_{O_2}}}{k_b T_R}\right) \quad (26)$$

For the oxidation of 316L stainless steel, $A_0 = 5 \times 10^6 \text{ Ås}^{-1}$, $Q = 1.5 \text{ eV}$ and $K_0 = 0.149 \text{ eVtorr}^{-0.5}$.³⁰

2.1.6 Boundary setting and meshing

As depicted in **Figure 1**, a 2D axisymmetric computational domain models the HVOF spray gun. To guarantee computational accuracy, the generated mesh—comprising 121,326 cells, 258,327 faces, and 121,796 nodes—features targeted local refinement across critical regions: the combustion chamber, the Laval nozzle, and the free jet zone.

2.1.7 Numerical method

Numerical simulations were executed using the commercial CFD software ANSYS Fluent, utilizing a double-precision, pressure-based solver for the steady-state, 2D axisymmetric governing equations. To accurately resolve the high-speed combustion dynamics, the SIMPLE algorithm was applied for pressure-velocity coupling, while the ideal gas law was incorporated to account for fluid compressibility.

2.2 Experimental method

Commercial 316L stainless-steel powder (10–50 μm ; density: 7.9 g/cm^3 ; specific heat: $457 \text{ J/(kg}\cdot\text{K)}$; solidus/liquidus: $1675 \text{ K}/1708 \text{ K}$ ^{36,37}) was deposited onto grit-blasted, preheated SS400 substrates ($100 \times 40 \times 5 \text{ mm}$) using a JP-5000 HVOF system. The operational parameter window encompassed an oxygen-to-fuel (O/F) ratio of 2.5–3.2, a reactant flow rate of $0.023\text{--}0.030 \text{ kg/s}$, a spraying distance of $300\text{--}400 \text{ mm}$, and a constant particle mass flow rate of 0.0005 kg/s . Real-time in-flight particle dynamics were monitored using a Spray Watch system. Coating microstructures were examined via a Quanta 600 SEM. Porosity was quantified through gray-scale contrast analysis using Image-Pro Plus 6.0 software, and oxygen content was measured with a LECO TC-436 analyzer. Furthermore, mechanical properties were evaluated using an HMV-G 20ST Vickers microhardness tester and a PosiTest AT pull-off adhesion tester (ASTM D4541-02), while phase composition was determined via X-ray diffraction (XRD).

3 RESULTS AND DISCUSSION

3.1 Numerical simulation

3.1.1 Effects of the O/F ratio on spraying

To evaluate how the O/F ratio affects the HVOF thermodynamics, centerline gas-phase parameters were analyzed. As shown in **Figure 2** (a, c and e), gas pressure peaks in the combustion chamber and drops sharply at the Laval nozzle throat, efficiently converting potential energy into kinetic energy. This accelerates the gas to supersonic speeds at the exit, sustaining a high-velocity plateau in the free jet region. Notably, quantitative analysis reveals that an O/F ratio of 2.7 maximizes both the gas temperature and velocity. Specifically, it reaches a peak combustion temperature of 3140.87 K (in the combustion chamber) and a maximum jet velocity of 2248.29 m/s (at the entrance of the jet core). Although the profiles for $\text{O/F} = 2.7$ and $\text{O/F} = 2.8$ appear visually similar, CFD data confirms that the absolute peak values under the 2.7 condition are slightly higher than those at 2.8 (which peak at 3121.09 K and 2223.78 m/s , respectively). Furthermore, the sustained local peaks within the jet core region—where particles undergo crucial heating and acceleration—consistently remain highest at the 2.7 ratio. Deviating from this optimal ratio visibly reduces the thermal and kinetic energy densities, thereby weakening the particle propulsion. Furthermore, while the O/F ratio mainly influences pressure within the combustion chamber (Figure 2a), it dictates temperature and velocity throughout the entire flow domain. Despite minor downstream fluctuations in the free jet region, the overall number of Mach cones remains stable.

Figure 3 (a–e) illustrates gas velocity contours across various O/F ratios. As the pressurized gas accelerates through the nozzle, periodic "Mach cones" consistently

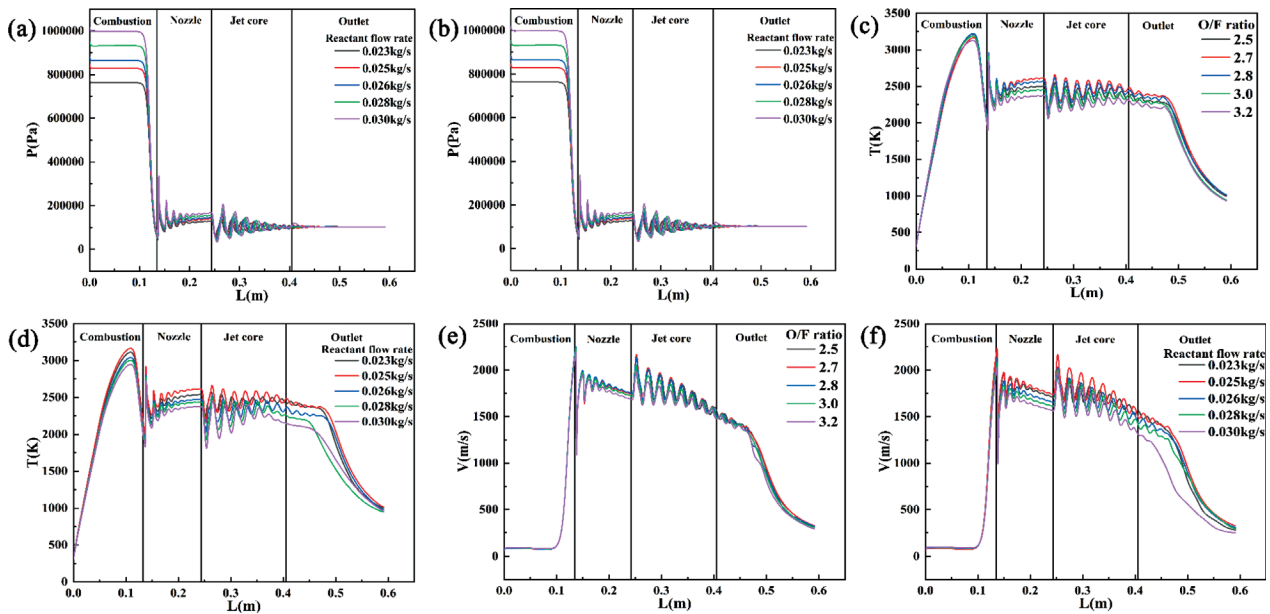


Figure 2: Effects of the O/F ratio and reactant flow rate on the gas phase (a, b) pressure, (c, d) temperature, and (e, f) velocity.

emerge in the supersonic free jet region. Notably, an O/F ratio of 2.7 yields the most numerous and distinct Mach cones alongside an elongated, concentrated jet core. This indicates that the combustion efficiency has reached its optimal level.

This optimized flow field directly influences particle dynamics (Figure 4). For 30 μm 316L particles (Figure 4a, 4c), only an O/F ratio of 2.7 drives their peak temperature precisely between the solidus and liquidus. This

ensures the dominant particles achieve the ideal "semi-molten" state, avoiding both insufficient melting and overheating. Furthermore, just prior to impacting the substrate, particles across the entire 10–50 μm size range consistently achieve their maximum axial temperatures and velocities under this specific O/F condition (Figure 4b, 4d).

Regarding surface oxidation (Figures 5a–5c), the process unfolds across three spatial stages—combustion chamber, nozzle, and free jet region—due to the JP-5000 gun's unique axial powder feeding mode.²¹ When the O/F ratio exceeds 2.7, local oxygen partial pressure within the nozzle rises sharply (Figure 5a). Consequently, these high-oxygen conditions (O/F = 2.8 and 3.0) trigger higher instantaneous peak oxidation rates (Figure 5b). As shown in the cumulative curves (Figure 5c), oxide layer growth primarily occurs in the free jet region. Here, the internal "oxygen-lean" environment transitions abruptly into an "oxygen-rich" zone due to external air entrainment at the nozzle exit, causing a dramatic oxidation surge. Overall, oxide layer thickness correlates positively with the O/F ratio. Although an O/F of 2.7 produces a slightly thicker oxide layer than fuel-rich conditions (e.g., O/F = 2.5), the increment is marginal and highly controllable. Thus, balancing both melting requirements and oxidation suppression, an O/F ratio of 2.7 emerges as the optimal parameter: it guarantees the necessary "semi-molten" state while preventing excessive oxide formation.

3.1.2 Effects of the reactant flow rate on spraying

Similar to the O/F ratio, reactant flow rate significantly influences gas-phase dynamics (Figures 2b, 2d, 2f). Gas pressure peaks in the combustion chamber – increasing proportionally with the flow rate (Figure 2b) –

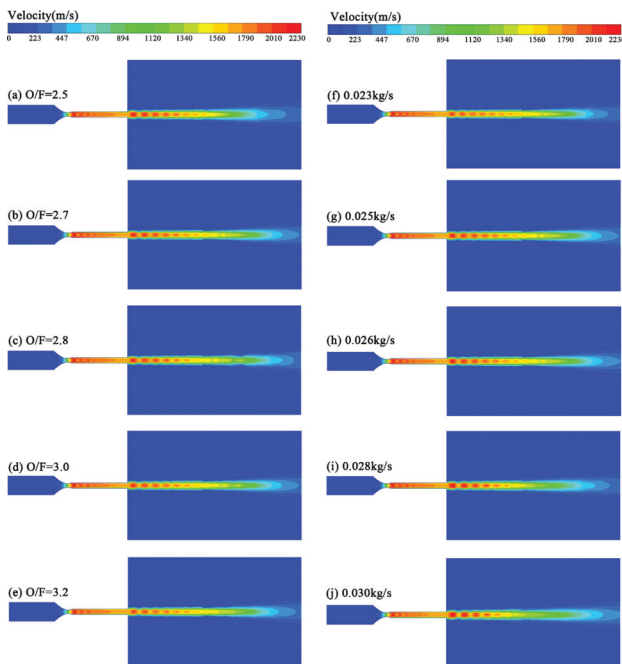


Figure 3: Contours of the gas phase velocity at different O/F ratios: a) 2.5, b) 2.7, c) 2.8, d) 3.0, and e) 3.2; and at different reactant flow rates: f) 0.023 kg/s, g) 0.025 kg/s, h) 0.026 kg/s, i) 0.028 kg/s, and j) 0.030 kg/s.

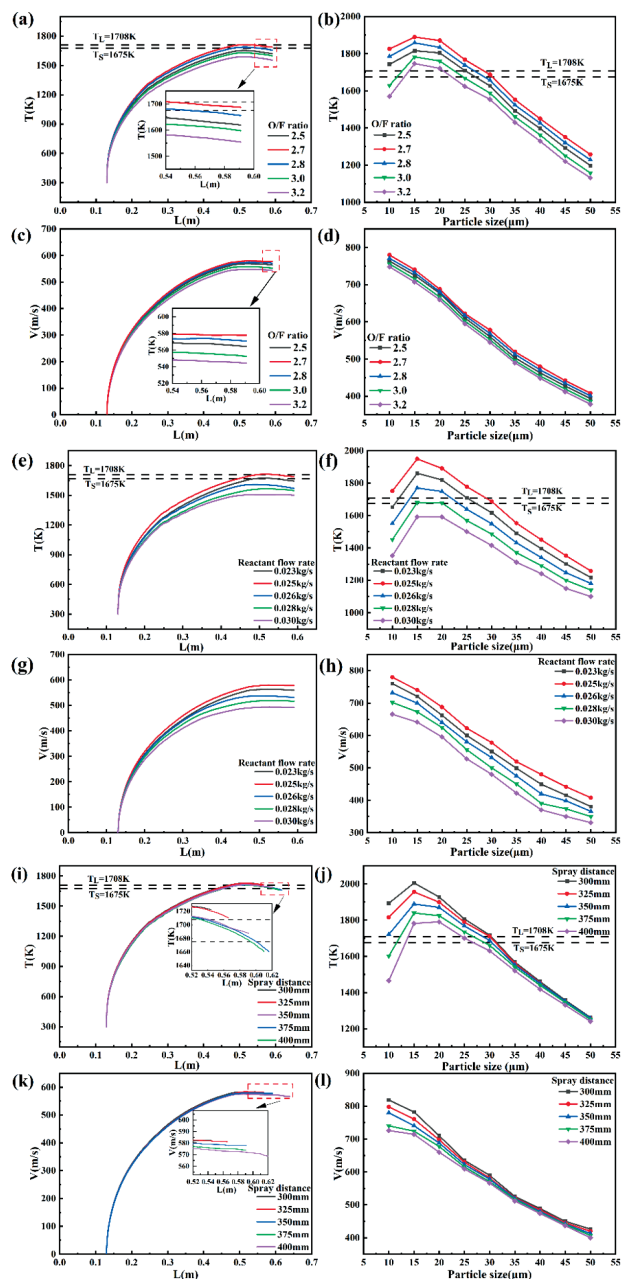


Figure 4: Evolution of particle temperature, predicted particle axial temperature, particle velocity, and predicted particle axial velocity under different process parameters: (a–d) effects of the O/F ratio; (e–h) effects of the reactant flow rate; and (i–l) effects of the spraying distance.

and drops sharply at the Laval nozzle throat, efficiently converting potential energy into supersonic kinetic energy. Notably, an optimal flow rate of 0.025 kg/s maximizes both the centerline gas temperature and velocity (Figure 2d, 2f). Deviations from this optimal value fail to sustain the maximum thermal and kinetic outputs across the domain. Furthermore, this optimal rate yields the most numerous and distinct Mach cones in the free jet region (Figures 3f–3j), indicating peak combustion efficiency and a highly stable flow field structure. This

optimized flow field directly dictates the particle dynamics (Figure 4). For 30-μm 316L particles (Figure 4e, 4g), velocity and temperature increase with flow rates up to 0.025 kg/s, but decline at higher rates. Critically, only at exactly 0.025 kg/s does the peak temperature of these dominant particles fall precisely between the 316L solidus and liquidus lines. This guarantees they enter the ideal "semi-molten" critical state essential for ultra-low porosity coatings, preventing both "un-molten" and "fully-molten" behaviors. Additionally, prior to substrate impact, particles across the entire 10–50-μm range consistently exhibit their highest axial temperatures and velocities under this 0.025 kg/s condition (Figures 4f, 4h), providing the substantial kinetic energy required for dense coating formation.

Figure 5(d–f) illustrates particle oxidation dynamics under varying reactant flow rates. Constrained by the JP-5000 gun's unique axial feeding mode, the system maintains an "oxygen-lean internal, oxygen-rich external" distribution, causing a sharp step-change in oxidation at the nozzle exit. Specifically, variations in flow rate do not alter the low oxygen partial pressure inside the combustion chamber and nozzle (Figure 5d); particles only encounter a high-oxygen environment upon entering the free jet region via atmospheric entrainment. The superposition of this sudden oxygen influx and high temperatures concentrates the peak oxidation rates strictly at the nozzle exit (Figure 5e). At this juncture, flow-rate-induced fluctuations in particle temperature directly dictate the magnitude of these instantaneous peaks. Consequently, cumulative oxide layer growth undergoes non-linear acceleration primarily within the free jet stage (Figure 5f), correlating positively with the reactant flow rate. Ultimately, a flow rate of 0.025 kg/s provides the optimum balance: it guarantees the critical "semi-molten" state while effectively suppressing excessive oxide formation.

3.1.3 Effects of spraying distance on particle in-flight behavior

Figure 4(i–l) illustrates the influence of spray distance (300 to 400 mm) on particle dynamics. Prior to impact, both axial temperature and velocity of 10–50 μm particles decline as spray distance increases, with smaller particles (< 20 μm) exhibiting the greatest sensitivity (Figures 4j, 4l). Specifically, at a distance of 300 mm, particles smaller than 30 μm fully melt during flight. As the trajectory extends, particles gradually cool; notably, at exactly 350 mm, 30 μm particles achieve the ideal "semi-molten" state just prior to impact (Figure 4j). Distances exceeding 350 mm lead to solid-state impacts. Furthermore, while smaller particles maintain higher axial velocities at any fixed distance, the overall velocity decay across varying distances is relatively minor (Figure 4l). Consequently, a 350-mm spray distance ensures 30-μm particles strike the substrate in a semi-molten

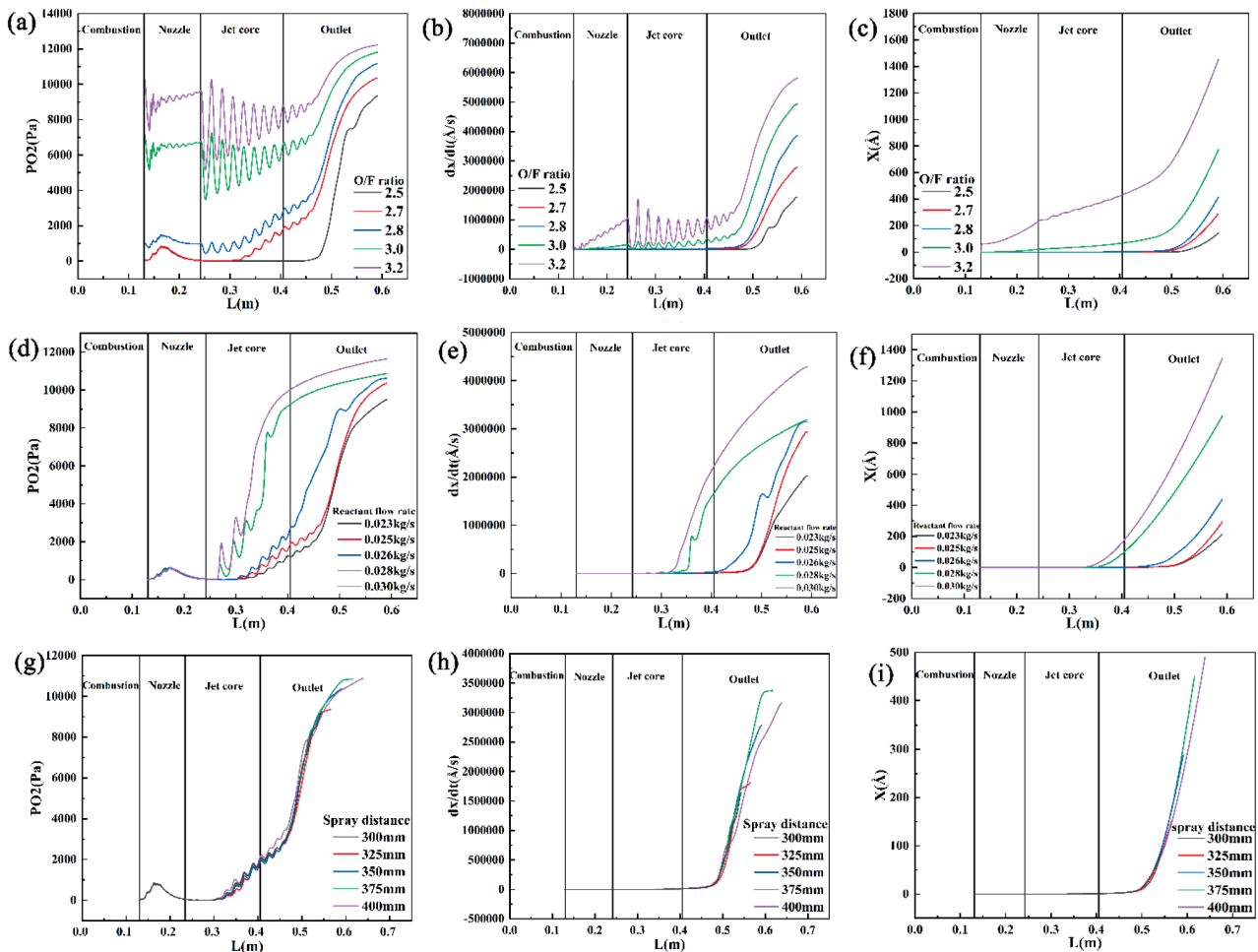


Figure 5: Evolution of gas phase oxygen partial pressure, oxidation rate, and oxide layer thickness under different parameters: (a–c) effects of the O/F ratio; (d–f) effects of the reactant flow rate; and (g–i) effects of the spraying distance

state with substantial kinetic energy, promoting high coating density.

Correspondingly, **Figure 5(g–i)** details the oxidation behavior across these distances. Regardless of the distance setting, oxygen partial pressure abruptly surges from a low level at the nozzle exit to a high level in the free jet region (**Figure 5g**). Extending the spray distance fundamentally elongates the particles' flight trajectory through this high-oxygen zone. Intense oxidation concentrates in the initial free jet segment, driven by the superposition of high temperatures and elevated oxygen levels (**Figure 5h**). Although this oxidation rate gradually decays as ambient air mixing cools the particles, it consistently remains above the effective reaction threshold. Consequently, cumulative oxide layer thickness strictly follows a "distance equals time" law (**Figure 5i**): prolonged residence in the oxygen-rich atmosphere leads to a monotonic increase in oxide thickness. Particularly beyond 350 mm, oxide accumulation surges without a significant reduction in the curve's slope. Therefore, restricting spray distance is crucial for minimizing high-oxygen exposure. Balancing both optimal melting and

oxidation suppression, 350 mm emerges as the ultimate balance point, securing the critical "semi-molten" state while effectively preventing excessive oxide formation.

3.2 Sensitivity analysis of process parameters via RSM

3.2.1 Model development and statistical validation

In this study RSM was employed specifically to evaluate and rank the effects of process parameters on the particle oxide layer thickness. As a robust statistical tool, RSM utilizes a second-order polynomial model to effectively capture non-linear relationships and visually map complex factor interactions.³⁸

To systematically evaluate the interactive effects of process parameters on particle oxide layer thickness, a 15-run Box-Behnken Design (BBD) was executed. The three independent variables were investigated at three levels (coded as -1, 0, and 1): reactant flow rate F (0.020, 0.025, and 0.030 kg/s), O/F ratio R (2.3, 2.7, and 3.1), and spraying distance L (300, 350, and 400 mm). The complete experimental matrix and corresponding response outcomes are detailed in **Table 1**.

Table 1: RSM random scheme and results

Order number	<i>F</i> (kg/s)	<i>R</i>	<i>L</i> (mm)	<i>X</i> (Å)
1	0.025	2.3	300	55.2
2	0.025	3.1	300	903.7
3	0.025	2.3	400	484.5
4	0.025	3.1	400	1333.5
5	0.020	2.3	350	181.6
6	0.020	3.1	350	1025.3
7	0.030	2.3	350	1311.7
8	0.030	3.1	350	2259.1
9	0.020	2.7	300	28.2
10	0.020	2.7	400	409.5
11	0.030	2.7	300	1110.3
12	0.030	2.7	400	1539.6
13	0.025	2.7	350	288.7
14	0.025	2.7	350	288.6
15	0.025	2.7	350	288.3

A multiple regression analysis was conducted based on the randomized test scheme and the results listed in **Table 1** to quantify the relationship between the design factors and the outputs. The derived response surface function for the oxide layer thickness (*X*) is given by:

$$X = 9588 - 5311.2R + 3.454L - 354899F + 1096.8R \times R + 8200625F \times F - 0.4133R \times L - 18.47L \times F \quad (27)$$

Table 2 summarizes the Analysis of Variance for oxide layer thickness. Statistically, the F-value dictates the intensity of a factor’s influence, while the P-value determines its significance (significant if *P* < 0.05, highly significant if *P* < 0.001). Based on F-values, the parameters impact oxidation in the following order: spraying distance *L* (115.29) < O/F ratio *R* (5043.69) < reactant flow rate *F* (5501.52). Correspondingly, the linear terms (*R*, *L*, *F*), quadratic terms (*R*², *F*²), and the *R*×*L* interaction exhibits highly significant effects, whereas the *L*×*F* interaction remains significant. The established model

Table 2: Analysis of variance test results for oxide layer thickness

Source	Freedom	Seq ss	Distribution	Adj SS	Adj MS	F value	P value
Model	7	1076474	99.99%	1076474	153782	10558.69	<0.0001
Linear	3	823406	76.48%	209550	69850	4795.91	<0.0001
R	1	279224	25.94%	73459	73459	5043.69	<0.0001
L	1	70444	6.54%	1679	1679	115.29	<0.0001
F	1	473737	44.00%	80127	80127	5501.52	<0.0001
Square	2	252709	23.47%	252709	126355	8675.53	<0.0001
R×R	1	96593	8.97%	114394	114394	7854.34	<0.0001
F×F	1	156117	14.50%	156117	156117	10718.99	<0.0001
Interaction	2	359	0.03%	359	179	12.31	0.005
R×L	1	273	0.03%	273	273	18.77	0.003
L×F	1	85	0.01%	85	85	5.85	0.046
Error	7	102	0.01%	102	15		
Lack of Fit	5	102	0.01%	102	20		
Pure Error	2	0	0.00%	0	0		
Total	14	1076576	100.00%				

R-Squared = 99.94 %, Adj R-Squared = 99.88 %, Pred R-Squared = 99.25 %.

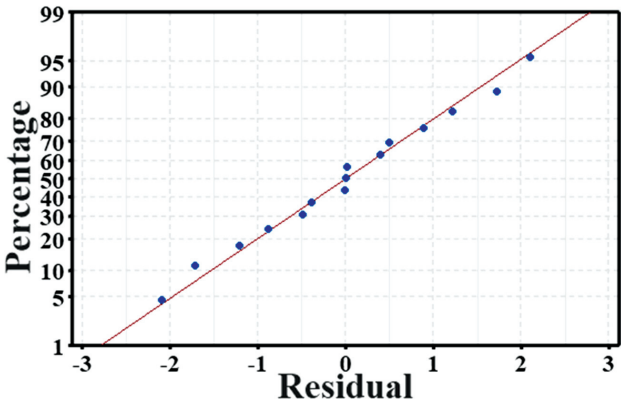


Figure 6: Graph of the residual normal distributions for particle oxide-layer thickness

demonstrates exceptional predictive precision with an R-Squared of 99.94 %. Furthermore, the minimal deviation (< 0.1) between the Adj R-Squared (99.88 %) and Pred R-Squared (99.25 %) confirms its robust capability for predicting oxide layer thickness.

Further validating this model, **Figure 6** presents the normal probability plot of the residuals. The data points align closely with a straight line and oscillate within permissible limits, confirming a normal distribution. This residual analysis perfectly corroborates the Analysis of Variance findings, substantiating the high validity and reliability of the response surface model.

3.2.2 The analysis of RSM results

Figure 7 visualizes the interactive effects of process parameters on oxide layer thickness via 3D response surfaces, where gradient steepness directly reflects a factor’s significance. Across all interactions, the parameters exhibit positive synergistic effects on oxidation. However, the distinctly steeper gradients along the reactant flow rate (*F*) axis compared to both the O/F ratio (*R*)

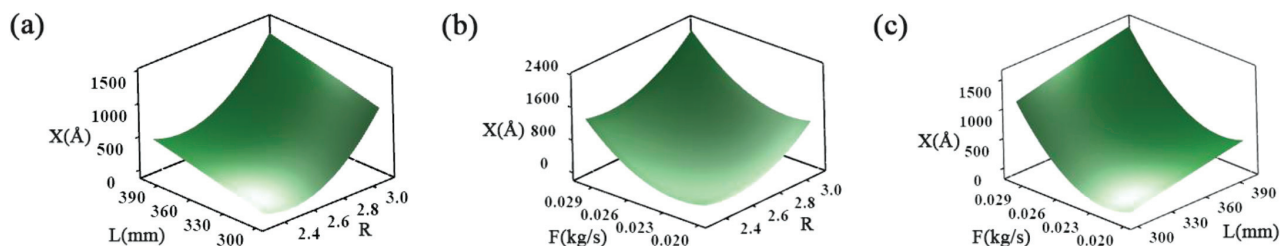


Figure 7: Response surface graphs for particle oxide layer thickness: a) effect of L and R , b) effect of F and R , c) effect of F and L

(**Figure 7b**) and spraying distance (L) (**Figure 7c**) highlight F as the most dominant driver, causing sharp, non-linear oxide growth when increased simultaneously. Similarly, the interaction between R and L (**Figure 7a**) demonstrates that R influences oxidation much more strongly than L , with maximum thickness occurring when both variables reach their peak values. Ultimately, these visual surface trends perfectly corroborate the Analysis of Variance results, conclusively validating the impact hierarchy: $F > R > L$.

3.3 Experimental validation

The mechanical and microstructural integrity of the optimized coating was comprehensively characterized. Cross-sectional Vickers microhardness (HVM-G 20ST; 300g load, 5s dwell) averaged 390 ± 5 HV across 15 valid indentations (**Table 3**), demonstrating exceptional

spatial consistency. Concurrently, pull-off tests (PosiTest AT) conducted strictly per the ASTM D4541-02 standard across five random locations yielded a robust adhesion strength of 48.08 ± 0.69 MPa.

Microstructurally, **Figure 8** compares the XRD patterns of the 316L feedstock powder and the as-sprayed coating. The coating's diffraction peaks perfectly align with those of the original powder, predominantly retaining the stable austenite (γ) phase. Although **Table 3** indicates an oxide content of 0.52 w/% for the optimal coating, no distinct oxide diffraction peaks are visible in the spectrum. This suggests that the formed oxide phases are likely present, but their trace concentration falls below the detection limit of conventional XRD. This confirms that the 316L stainless steel successfully preserved its fundamental structural integrity without undergoing detrimental phase transformations during the extreme thermodynamic conditions of the spraying process.

Figure 9 illustrates the cross-sectional microstructures of coatings deposited under various parameters. To rigorously evaluate these structures, quantitative porosity analysis (Image-Pro Plus 6.0; 20 random non-overlapping fields under strictly unified SEM conditions, including accelerating voltage, working distance, and magnification) and oxygen content measurements (LECO TC-436 analyzer) were conducted (**Table 3**). Notably, coatings synthesized under the Optimal Spraying Parameters (OSP; **Table 3**) feature a highly dense, uniform microstructure with a remarkably low porosity of 0.18 ± 0.06 %. Conversely, deviating from the OSP significantly increases the 316L coating porosity and degrades overall microstructural quality, primarily due to suboptimal in-flight particle velocities.

To validate the numerical simulations governing these crucial in-flight dynamics, real-time particle behavior was monitored via a Spray Watch system (**Ta-**

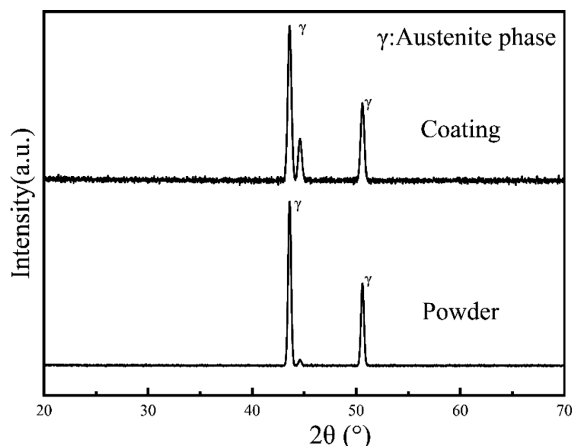


Figure 8: XRD patterns of the 316L stainless steel powder and the corresponding coating

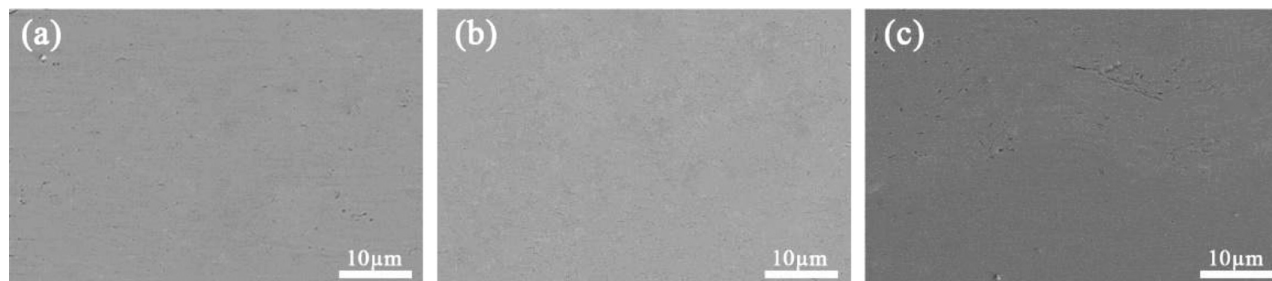


Figure 9: Cross-sectional microstructures of the as-sprayed 316L stainless steel coatings: a) low, b) optimal, and c) high spraying parameters

Table 3: Influence of Spray Parameters on 316L Coating Microstructure and Mechanics

Experiment	Spraying parameters				Oxide content	Coating porosity	Microhardness	Adhesion strength
	Reactant mass flow rate (kg·s ⁻¹)	O/F ratio	Particle mass flow rate (kg·s ⁻¹)	Spray distance (mm)	(w/%)		(HV)	(MPa)
Low	0.023	2.5	0.0005	325	0.09	0.79 ± 0.09 %	370±5	40.52 ± 0.30
Optimal	0.025	2.7	0.0005	350	0.52	0.18 ± 0.06 %	390±5	48.08 ± 0.69
High	0.028	3.0	0.0005	375	3.21	1.69 ± 0.05 %	320±5	33.20 ± 0.82

Table 4: Comparison between experimental results and CFD results

Experiment	Deposition Temperature (K)	Deposition Temperature (K)	Deposition Velocity (m/s)	Deposition Velocity (m/s)
	CFD Results	Experimental Results	CFD Results	Experimental Results
Low	1606.2	1607 ± 55	503.4	500 ± 25
Optimal	1687.5	1689 ± 55	577.9	580 ± 25
High	1579.8	1577 ± 55	479.7	483 ± 25

ble 4). Under OSP conditions, empirical diagnostics recorded an average particle temperature of 1689 ± 55 K and a velocity of 580 ± 25 m/s. This exceptional agreement between the experimental data and simulation predictions conclusively verifies the accuracy and reliability of the established computational model.

4 CONCLUSIONS

A HVOF spray gun model was established to identify optimal spraying parameters using CFD. The simulation was validated experimentally, attaining dense 316L stainless-steel coatings with a porosity of 0.18 % and an oxide content of 0.52 w/%.

Key findings include: "semi-molten"

1) Particle thermal and kinetic energy (velocity and temperature) exhibit a typical "increase-then-decrease" trend with O/F ratio and reactant flow rate, peaking at an O/F ratio of 2.7 and a flow rate of 0.025 kg/s. This indicates that excessive or insufficient parameter settings weaken the flow field's heating and acceleration capabilities. In contrast, spraying distance correlates negatively with particle velocity and temperature, decreasing gradually as distance increases. However, numerical results reveal a consistent influence of process parameters on oxidation behavior: increases in O/F ratio, reactant flow rate, and spraying distance all aggravate in-flight oxidation, leading to significant oxide layer thickening. The optimal process window (O/F = 2.7, 0.025 kg/s, 350 mm), derived from these laws, successfully maintains 30-μm particles in an ideal "semi-molten" critical state – precisely between the solidus and liquidus of 316L – while preserving high axial velocity, thereby effectively inhibiting excessive oxidation while ensuring coating density.

2) RSM was employed to quantitatively characterize the sensitivity of spraying parameters on particle behavior and oxidation characteristics. Analysis of Variance indicates that the reactant flow rate exerts the greatest influence on particle oxide layer thickness, followed by the

O/F ratio and spraying distance in descending order of significance. Moreover, the interactive effects among parameters exhibit non-negligible non-linear influences on the final particle state, implying that the adjustment of a single parameter is often constrained by other variables.

3) The optimum spray parameters, derived from simulation results and a multi-objective optimization strategy (maximizing velocity and minimizing oxide layer thickness under suitable melting temperature conditions), include an O/F ratio of 2.7, a reactant flow rate of 0.025 kg/s, and a spraying distance of 350 mm. Validation simulations demonstrate that using the OSP, dense 316L coatings with a porosity of merely 0.18% and an oxide content of 0.52 w/% were successfully produced.

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