Transport and deposition behaviors of vapor coating materials in plasma spray-physical vapor deposition

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ABSTRACT

The plasma spray-physical vapor deposition (PS-PVD) technology offers great potential to support the development of non-line-of-sight deposition. However, many researches indicated that the shadowing effect is a significant mechanism of PS-PVD for the coating growth and formation of the micro-structure. There seems to be an irreconcilable contradiction between the two theories. In this study, both the transport and deposition behavior of PS-PVD processes are researched from a macroscopic and microscopic perspective, respectively. The deposition processes of vapor coating materials are separated by the last collision position. The process before reaching the last collision position is defined as transport behavior, and the process after the last collision position is defined as deposition behavior. The results of simulation and experiment indicated that the flow behavior of plasma jet and the frequent collisions between plasma gas and vapor coating material provide opportunities for the vapor coating material to deposit in shadowed surfaces or non-line-of-sight positions. The shadowing effect under micro line-of-sight deposition is a major factor in the growth of columnar structures, and it accompanies the entire process of coating growth. This study divides the deposition process of vapor coating materials into the macro non-line-of-sight transport and micro line-of-sight deposition, illuminates the macro-non-line-of-sight transport behavior of vapor-phase materials, and sheds light upon the micro-line-of-sight deposition mechanism of the PS-PVD process.

1. Introduction

Plasma spray-physical vapor deposition (PS-PVD) is a novel method used to quickly prepare a coating [1]. In plasma spray-physical vapor deposition (PS-PVD) technology, the material powder is evaporated by the plasma spray (PS) method [2], and then transported and deposited by the physical vapor deposition (PVD) method [3]. The coatings prepared by PS-PVD can be used in many fields, such as in hydrogen production, biology and thermal barrier coatings (TBCs) [2,4,5]. Generally, mixed plasma gases such as helium/argon, helium/argon/hydrogen, or argon/hydrogen are used in PS-PVD to heat and evaporate the coating materials [6]. Meanwhile, an O3CP gun (Sulzer Metco), which allows a total gas flow of up to 200 slpm and a power level up to 180 kW, is used [7–9]. The coating material powders can be melted, even vaporized, in PS-PVD processes [10–12]. For example, by using lower powder feed rate and a finer powder such as Metco 6700 (YSZ, Suzlzer Metco), a higher amount of the powder can be vaporized [12].

The heated and evaporated coating materials are transported in the plasma jet. Due to the low chamber pressure of PS-PVD, the plasma jet range can be expanded to about 2 m long [7]. Thus, the coating materials arrive at the substrate after travelling a long distance. In our previous research, molten particles with a small diameter were completely evaporated in the free plasma jet [13]. In the event of vapor atom condensation in a free plasma jet, the gaseous material capacity of the jet at different axial positions was also previously studied. The results indicated that the condensation of vapor atoms in the free plasma jet can be avoided by applying suitable spraying parameters and using specific deposition positions [14], thereby achieving a very high vaporization degree, resulting in vapor deposition. Therefore, the main focus of many works investigating PS-PVD is to prepare a high-
temperature shock-resistant coating similar to the electron beam-physical vapor deposition (EB-PVD) coatings [1,15–17]. In addition, the plasma jet can be expanded to about 1–2 m long and 20–40 cm in diameter due to the high energy input [9] and the lower chamber pressure [18]. Therefore, a component with bigger size can be coated by the PS-PVD.

For conventional PS and PVD technologies [19], there are limitations as both technologies are line-of-sight processes. In there, even if rotated, only simple-geometry components can be coated. For complex geometries as well as multiple components, there are shadowed surface that cannot be avoided even with rotation [7,20]. Therefore, these methods will not deposit a coating at the shadowed surface. For example, in the case of EB-PVD, the material target is heated to evaporation by using high-energy electron beam bombardment [21–24], the stream of the gaseous material flies to the substrate in a nearly straight line due to the high vacuum [20,23,25]. In the process of deposition, the substrate needs to be rotated to change the incident angle of the deposition units, to yield a coating with a fine columnar structure [26]. When the stream of the vapor coating material is interrupted in this particular case by a second airfoil or by the complex geometries of the component, shadowed surfaces of components will not be coated. Therefore, only surfaces in the direct line-of-sight to the coating source (e.g., the plasma gun or targets) can be coated. Hence, it is difficult to coat components with complex geometries and shadowed surfaces by using conventional techniques.

Unlike the traditional PS and PVD technologies, PS-PVD is generally considered as a non-line-of-sight deposition process [27,28]. Many researches demonstrated that PS-PVD has the ability to coat surfaces which are in the non-line-of-sight of the coating source [7,27,28]. A simplified double vane model consisting of parallel platforms and solid airfoils was employed by Niessen et al. [7] to study non-line-of-sight deposition possibilities of the PS-PVD process. Results demonstrate that PS-PVD allows the complete coverage of parts having complex geometries and shadowed surfaces. Even platforms which are parallel to the plasma jet and more difficult to cover, have a coating. Therefore, the PS-PVD process has non-line-of-sight characteristics [7,10].

In contrast, Mauer et al. [29] and Zhang et al. [30] studied and described the deposition mechanism of PS-PVD. Their results indicated that shadowing mainly occurs during the roughening of the growing surface and with angular direction of the arriving particles, and it is intensified as the coating grows. That is, the shadowing effect is a significant mechanism of PS-PVD for the coating growth and formation of the micro-structure. There is a very obvious and serious contradiction between the non-line-of-sight behavior and shadowing effect: since the non-line-of-sight behavior can make the vapor coating materials bypass the barrier, it does not produce shadowing. Therefore, it is necessary to study the relationship between non-line-of-sight behavior and the deposition mechanism of PS-PVD further.

In this study, the transport and deposition behaviors of PS-PVD were researched. The last collision position before the deposition of vapor coating materials was defined as the demarcation point. The process of vapor coating materials before the demarcation point was considered as the transport process. The numerical simulation method was used to analyze the flow behavior of plasma jet around substrate, and the random collision behavior of vapor coating materials in the plasma jet was determined to explore the macro non-line-of-sight transport behavior of vapor coating materials. Experimental results indicated that the stream bypass substrate behavior of the plasma jet and the random collision of the vapor coating materials in the plasma jet are the reasons why PS-PVD has a macro non-line-of-sight behavior. The process of vapor coating materials, travelling from the demarcation point to the deposition position, was referred to as the deposition process. After last collision, the deposition directions of the vapor coating materials are random. The results of Monte Carlo simulation show that the shadowing effect under micro line-of-sight deposition is a major factor in the columnar structure growth, and is present throughout the process of coating growth. From the simulation and the experimental results, it can be seen that the coating has a feather-like hierarchical structure including primary, secondary, and tertiary structures. The results of the research on the coating columnar structure development show that the mean columnar spacing increases dramatically at first and then tends to stabilize due to the stoppage of growth and regeneration of the columnar structure. This study examines the macro non-line-of-sight transport behavior and micro line-of-sight deposition behavior of vapor coating materials. As part of the transport and deposition mechanism of vapor coating materials for PS-PVD, this study could provide theoretical support for the preparation of columnar coatings in complex component surface.

2. Evaluation method and experimental procedure

2.1. Transport behavior evaluation and experiment

As mentioned in the “Section 1”, the plasma jet expanded to about 1–2 m long and 20–40 cm in diameter under PS-PVD conditions. The vaporized coating material displays a long transport distance in the plasma jet before arriving to the substrate and forming the coating. Therefore, the transport process of the vapor coating material in the plasma jet will affect the deposition behavior. In our previous research [14], control conditions for the condensation of vapor coating materials in plasma jet were investigated. In the present study, it is assumed that the conditions satisfy the non-condensation of the vapor coating material, and only the transport behavior is considered.

The transport behavior of vapor coating material will be affected by the flow field during transported in the plasma jet. The original flow field structure will be destroyed when the substrate is placed in the plasma jet [24]. Meanwhile, the transport behavior of the vapor coating material will be changed. Therefore, the flow field of the plasma jet, where the substrate is placed, is studied first. Next, the transport behavior of the vapor coating material in the free plasma jet as well as around the substrate is analyzed. Finally, deposited coating structures at the position of the substrate surface parallel to the plasma as well as shadowed are investigated.

2.1.1. Numerical simulation of flow behavior

Since the coating material is transported in the plasma jet, the flow field characteristics of the plasma jet are investigated first. Because the operating pressure is reduced to 50–200 Pa, the plasma jet expands to about more than 1–2 m long and 20–40 cm in diameter. The plasma stream is able to flow around substrate which placed inside it. In this study, the flow behavior of plasma jet around the substrate is analyzed by using numerical simulation. The schematic diagram of the flow field geometry and boundary conditions is shown in Fig. 1. In this simulation, an argon and hydrogen mixed gas (Ar/H₂) was used, and the mixed gas data were calculated by using the NASA Chemical Equilibrium with Applications (NASA-CEAs) [31,32]. In addition, the
boundary conditions in the flow field are defined as follows.

1. Plasma inlet: pressure inlet boundary conditions.
2. Pressure-outlet: pressure outlet boundary conditions.
3. Symmetric axis: the flux of all quantities and the normal gradients of all flow variables are zero in a symmetric axis.
5. Substrate position: 1000 mm from the plasma inlet.

2.1.2. Transport behavior of vapor coating materials in plasma jet

One advantage of PS-PVD is that the coating is deposited by the vapor coating material [9]. Before deposition, the vapor coating material undergoes a long-distance transport within the plasma jet. In this process, vapor coating materials are collided randomly with other materials such as plasma gases and vapor coating materials itself. The collision model for vapor coating material transport in plasma jet is shown in Fig. 2(a). To study the random collision behavior of the vapor coating material in the plasma jet, the mean free path is introduced, as shown in Fig. 2(b).

In a large number of particle systems with irregular collisional motions, the mean free path is an important parameter for studying the characteristics of particle’ random collisions [33,34]. As shown in Fig. 2(b), we study a particle transporting in a path which the width is twice the diameter of the particle. In kinetic theory, the mean free path ($\lambda$) of a particle is the average distance that the particle travels between collisions with other moving particles. Thus, the following relationship applies [34,35]:

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 n}$$

(1)

where $d$ is the diameter of molecule, and $n$ is the molecular number density.

Under ideal gas law conditions, Eq. (1) can be changed to the following form:

$$\lambda = \frac{k_B T}{\sqrt{2} \pi d^2 p}$$

(2)

where $T$ is the temperature of the gas, $p$ is the pressure of the gas, and $k_B$ is the Boltzmann constant, $1.38 \times 10^{-23}$ J/K.

For a given gas particle, the mean free path is a function of temperature and pressure according to Eq. (2). In a PS-PVD process, the operating pressure range is approximately 50–200 Pa. Under such low pressure, the effective collision frequency and mean free path length in the plasma jet will be significantly altered [36]. The macroscopic and microscopic kinematic behavior of the vapor coating materials in PS-PVD can be studied according to the mean free path. In addition, the transport and deposition mechanism of PS-PVD can be studied, based on the macroscopic and microscopic behaviors of vapor coating materials.

The vapor coating material molecular and the plasma gas are both assumed to be spherical shape. The vapor coating material molecule collides with other particles after it travels approximately a mean free path distance at a certain velocity. The collision model is shown in Fig. 2(a). During the collision, it is assumed that: 1) The motion of all particles follows the classical Newton’s laws of motion; 2) The interaction between the particles only occurs during the collision, and the elastic collision is satisfied.

2.1.3. Experiment of transport behavior

In this part, there were two experiments designed to study the macro non-line-of-sight transport behavior of vapor coating material. Firstly, the sintered Al$_2$O$_3$ tubular with dimensions of $\Phi 16 \times 2$ mm (diameter × wall thickness) were employed as a substrate to study. The behavior of the vapor coating material at position 1 was investigated as shown in Fig. 3(a). Secondly, shielding was placed in front of the well sintered YSZ wafer (the dimensions of $\Phi 18 \times 2$ mm (diameter × thickness)). The behavior of the vapor coating material at position 2 was investigated as shown in Fig. 3(b). The macro non-line-of-sight transport behavior of vapor coating material was investigated by examining the coating structures from the substrate which were parallel to the plasma jet (Position 1) and behind the shielding (Position 2).

All samples were prepared based on 80 kW class plasma system. A commercial Fe plasma spray torch (80 kW class, GTV, Germany) was mounted on an ABB robot and placed in a 10 m$^3$ vacuum chamber. A multistage pump was used to maintain the chamber at very low pressure. Agglomerated 7YSZ powder (Metco 6700, Sulzer Metco) was used as the coating material. The detailed preparation parameters are listed in Table 1. The surface microstructures of the all coating samples were characterized by field-emission scanning electron microscopy (MIRA3 LMH, TESCAN Czech Republic).

2.2. Deposition behavior evaluation and experiment

2.2.1. Vapor ballistic deposition (VBD) model

Due to the random collision between the vapor coating material and the plasma gas, the vapor coating material will deposited to the substrate with different angles. There are two situations when the vapor coating materials reach and collide with the substrate. One situation is that the vapor coating material rebounds after colliding with the substrate with different angles. The detailed preparation parameters are listed in Table 1. The surface microstructures of the all coating samples were characterized by field-emission scanning electron microscopy (MIRA3 LMH, TESCAN Czech Republic).

<table>
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any angle, as shown in Fig. 4(a) and (b). Meanwhile, the simulation results only reflect the alternative collision frequency and mean free path length of vapor coating material in the plasma jet will be significantly altered [36]. Therefore, the macroscopic transport behavior of vapor coating materials in PS-PVD is studied.

The simulation results of the plasma jet flow around the tubular substrate are shown in Fig. 5(a1)–(c1). As a comparison, the velocity field of free plasma jet without substrate is shown in Fig. 5(d). Fig. 5(a2)–(c2) are variations of pressure, temperature, and velocity in the center of plasma jet with and without substrate. Initially, the plasma jet exhibits a typical under-expanded flow [38,39], and has successive alternating expansion and compression zones. However, the characteristics of the plasma jet are changed due to the substrate placed in the jet. It is obvious from the simulation results that pressure, temperature, and velocity of plasma jet are affected by the substrate. In the front of substrate, pressure, temperature, and velocity of plasma jet are all increased abruptly. The flow behavior tends to be stable after moving away the substrate at a certain distance.

As shown in Fig. 5(d), the plasma jet expands to about 2 m long and 20–40 cm in diameter. Due to the high velocity and the large dimensions of the plasma stream, the plasma gas is able to flow around the substrate. Fig. 5(e) shows the velocity flow vectors colored by velocity distributes around the sample. Owing to the substrate placed in the plasma jet, the jet flows to the sides at the front of the substrate, and

**Table 2**

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substrate or the coating (unit a in Fig. 4(a) and (b)), and the other is deposition (unit b in Fig. 4(a) and (b)). For rebounded vapor coating materials, there are two behaviors: one is re-deposition and the other is removal by the plasma gas. The rebounded vapor coating materials do not contribute to the deposition and only affect the deposition efficiency. For deposited vapor coating materials, diffusion occurs, and vapor coating materials move into an ideal lattice formation, especially at high temperatures.

In order to study the micro line-of-sight deposition behavior of vapor coating materials, the Monte Carlo method is used in the following simulations and only the deposition situation is considered. In addition, for simplicity, the problem is approached as one of deposition of atoms, rather than the more complex deposition of the various types of species occurring in the deposition environment of YSZ. Zhang et al. [30] has also studied the vapor coating deposition mechanism based on diffusion and nucleation, as diffusion occurs at higher substrate temperatures. However, in this simulation, a low substrate temperature during deposition is used; hence, diffusion is not considered. In this way, the simulation results only reflect the line-of-sight deposition behavior of vapor coating materials and eliminate the influence of diffusion. In fact, the actual structure of prepared coating should be denser than the simulation results due to the diffusion. This could also be confirmed by comparing the simulation results with the experimental results. Moreover, after the last collision, the vapor coating material is random in direction; thus, the vapor coating materials are deposited at any angle, as shown in Fig. 4(a) and (b). Meanwhile, the simulation units are considered as an ideal gas with consistent size.

Before the deposition begins, the substrate is planar as shown in Fig. 4(a). Each unit is dropped from a random position. Because the mean free path is the average distance travelled by a moving particle between successive collisions, it is assumed in this simulation that the initial position of unit is 0.5 × λ to 1.5 × λ, distanced from the deposited position. The units then follow linear trajectories in the direction of vapor incidence (such as α, β, α′, and β′, in Fig. 4(a) and (b) the direction varying between −90° and 90°) until they touch the surface of substrate or deposited unit [37]. As described in unit b in Fig. 4(a) and (b), all units are assumed to stick upon landing and immediately relax to a stable site. As soon as the unit is in contact with one of the surface units, it moves to the site in the lattice.

### 3. Macro non-line-of-sight transport of PS-PVD

#### 3.1. Flow behavior of plasma jet around the substrate

PS-PVD technology offers new prospects to develop a non-line-of-sight coating compared to the traditional coating preparation processes of PS and EB-PVD which are in line-of-sight behavior. In the PS-PVD process, the operating pressure range is approximately 50–200 Pa. Under these low pressures, the effective collision frequency and mean free path length of vapor coating material in the plasma jet will be significantly altered [36]. Therefore, the macroscopic transport behavior of vapor coating materials in PS-PVD is studied.

The simulation results of the plasma jet flow around the tubular substrate are shown in Fig. 5(a1)–(c1). As a comparison, the velocity field of free plasma jet without substrate is shown in Fig. 5(d). Fig. 5(a2)–(c2) are variations of pressure, temperature, and velocity in the center of plasma jet with and without substrate. Initially, the plasma jet exhibits a typical under-expanded flow [38,39], and has successive alternating expansion and compression zones. However, the characteristics of the plasma jet are changed due to the substrate placed in the jet. It is obvious from the simulation results that pressure, temperature, and velocity of plasma jet are all increased abruptly. The flow behavior tends to be stable after moving away the substrate at a certain distance.

As shown in Fig. 5(d), the plasma jet expands to about 2 m long and 20–40 cm in diameter. Due to the high velocity and the large dimensions of the plasma stream, the plasma gas is able to flow around the substrate. Fig. 5(e) shows the velocity flow vectors colored by velocity distributes around the sample. Owing to the substrate placed in the plasma jet, the jet flows to the sides at the front of the substrate, and
vortices are generated at the left and right rear of the substrate and flow back to the rear of substrate. As can be seen from the simulation results above, the plasma stream is flowing around the substrate. Since the vapor coating material is transported and randomly distributed in the plasma jet, the vapor coating material will flow around the sample with the plasma gas and deposit on the shadowed positions which are not in line of sight with the plasma gun.

3.2. Collision behavior of vapor coating material in plasma jet

Vapor coating materials are transported in the plasma jet. According to the above results, the plasma jet flow is a typical supersonic flow when there is no substrate [39]. However, when the substrate is placed in the plasma jet, the flow field changes and the plasma stream flows around the substrate. The transport behavior of the vapor coating material changes according to the variation of flow field. Therefore, the transport behavior of vapor coating material in plasma jet with and
without substrate is investigated in the present study. The simulation results are displayed in Fig. 6.

When the vapor coating material is transported in a free plasma jet without substrate, all simulated vapor coating materials and plasma gases are given an initial velocity in the jet hemisphere direction. The simulation results are shown in Fig. 6(a). From Fig. 6(a), it can be seen that the transport route of the vapor coating material is not a straight line from the start point to the end point. This means that in the plasma jet, the vapor coating material does not transport linearly, but its transmission route is often changed due to the constant collision. There were 92 collisions within a flight distance of 16 mm.

The transport path in free plasma jet (without substrate) indicates that the motion behavior of the vapor coating material is affected by the plasma gas. Therefore, the transport behavior is considerably affected by the plasma gas, which is due to the complex flow field around the substrate when the substrate is placed in the plasma jet. Fig. 6(b) shows the simulation results of the vapor coating material transport route in the substrate surrounding. When the vapor coating material is transported in a plasma jet with substrate, both vapor coating materials and plasma gases are given an initial velocity in a random direction. From the simulation results, the vapor coating material will constantly be collided with a large amount plasma gas molecule around the substrate. Therefore, the transport route of vapor coating material is varying frequently because it continuously collides with the plasma gas. The vapor coating material will bypass the shadow with the plasma gas and will have the opportunity to deposit at the shadowed surface under such frequent collisions.

3.3. Deposition behavior at different positions

The flow field of the plasma jet with substrate and the transport behavior of the vapor coating material in plasma jet have been studied. According to the above simulation results, the transport path twists and turns because the vapor coating material collides with the plasma gas multiple times, as shown in Fig. 7(a). The transport route is more complex in the surrounding of substrate. When the vapor coating material bypasses the barrier, more collisions causes more chance to reach the shadowed surface and deposit the coating, as shown in Fig. 7(b).

In the experiment, the surface coatings at the substrate with the surface parallel to the plasma jet axis (Position 1) as well as placed at the non-line-of-sight position (position 2) are both researched, as shown in the Fig. 3. Coating surface structures are shown in Fig. 8, where Fig. 8(a) and (b) are the coating structures obtained at position 1, and Fig. 8(c) and (d) are the coating structure obtained at position 2, respectively. According to the experimental results, the PS-PVD deposits at a position parallel to the plasma jet axis as well as in a non-line-of-sight position. These results indicate that the vapor coating material along the plasma gas successfully bypasses the obstruction and deposits into the non-line-of-sight position of the substrate. Both at the position 1 and 2, the droplets of coating materials cannot deposit on the surface because their flying direction is line-of-sight. At position 1, the coating presents an island microstructure, see in Fig. 8(a). The close examination revealed that the coating is deposited by vapor material, as shown in Fig. 8(b). The surface of the coating located at position 2 exhibited a cauliflower structure of typical PS-PVD structure. And this structure is loose than the coating structure at the position 1. The reason for having different coating structures for position 1 and 2 may be having a higher plasma temperature at position 1 (as shown in Fig. 9), thereby sintering the coating surface.

3.4. Macro non-line-of-sight transport behavior of PS-PVD

Using Eq. (2), the mean free path of vapor coating materials in PS-PVD was calculated (as shown in Table 3). In these calculations, the selected chamber pressure was 50–200 Pa and the plasma temperature was substituted with the gas temperature. According to our previous research, plasma temperature ranges from 3055 K to 4270 K in the entire plasma jet region [14]. Moreover, the excitation temperature and the heavy particle temperature calculated by Mauer et al. [11,41] ranged from 4500 K to 5500 K and from 3000 K to 4000 K, respectively. Therefore, a plasma temperature of 3000–5500 K was selected to be
used in this calculation. To compare the kinematic behavior of the vapor coating materials in EB-PVD, their mean free path was also calculated. The operating pressure of EB-PVD was approximately 0.005–0.15 Pa [20,23,25] and, for example, for ZrO₂, its boiling point (~4573 K) was chosen as the temperature of the vapor coating materials.

It can be seen from Table 3 that the mean free path of vapor coating materials in EB-PVD is much larger than that in PS-PVD. The mean free path of vapor coating materials in EB-PVD is on the scale of meters because the chamber pressure is about 10⁻³–10⁻¹ Pa. This implies that the vapor coating materials travel approximately straight, and cannot bypass the barrier, leading to the line-of-sight transport and deposition behavior of EB-PVD, and hence, it is difficult to coat complex geomorphic components or double vanes by using the EB-PVD technology. Therefore, in the case of complex geomorphic components or double blades, the shadowed regions cannot be covered by a line-of-sight coating process.

In the PS-PVD process, the mean free path of vapor coating materials is on the scale of millimeters. The coating material (such as YSZ) is injected inside the plasma gun, heated, evaporated, and transported in an expanding supersonic plasma stream. From Fig. 10, owing to the high velocity and the large dimensions of the plasma jet, the gas stream is able to flow around complex geometries and is “forced” to go through the shadowed areas. Since the vapor coating material is transported inside this stream and constantly collides with the plasma gas, once the plasma gas is in contact with the substrate surface, the vapor phase coating material may reach the surface due to the frequent collisions, thereby possibly forming a coating. Therefore, the entire surface of a double-guided vane can be coated, with a simultaneous coverage of both sides of the airfoils and the platforms during the same spray run.

Therefore, compared with EB-PVD, the transport behavior of vapor coating materials in PS-PVD process is affected by the frequently collisions. In the substrate surroundings, the vapor coating material will
collide more frequently than in the jet without substrate, as shown in Fig. 10. This results in a more opportunity for the vapor coating material to deposit in a non-line-of-sight surface.

The vapor coating materials transported in the plasma jet were able to be deposited on the shadowing surface of complex geometries for the reason that the plasma gas stream can flow around complex geometries, and is “forced” to go through the shadowing area, discussed by Niessen et al. [7]. When plasma gas collides with the barrier, it is refracted and reflected, and then collides with vapor coating materials. At the same time, vapor coating materials also collide with plasma gas that has not collided with the barrier. This series of collisions cause part of the vapor coating materials to bypass the barrier. Moreover, the vapor coating materials with different velocity directions exist in various locations of the plasma jet due to collisions of plasma gases with vapor coating materials from all directions. Therefore, in any position of complex geometry, there are depositions from all directions. The above series of processes leads to the macro non-line-of-sight transport behavior of PS-PVD.

For the larger sized materials that do not fully evaporated, such as particles and droplets, it is difficult to quickly change the directions of velocity under several collisions with plasma gas due to the initial inertia, and there is also no significant acceleration and deceleration [10,11]. Therefore, the behavior of incompletely vaporized materials in the PS-PVD is similar to that in the PS [42,43], which is a macro line-of-sight process.

4. Micro line-of-sight deposition of PS-PVD

Whether it is a line-of-sight surface or a shadowing surface, the vapor coating material need undergo multiple collisions during transport, then deposited at these positions. If the last collision position before the deposition of vapor coating materials is defined as the demarcation point, then the process of vapor coating materials before the demarcation point can considered as the transport process. The process of vapor coating materials, travelling from the demarcation point to the deposition position, can be referred to as the deposition process, as shown in Fig. 11. As a result, it is easy to classify the behavior of vapor coating materials in PS-PVD as the transport process before the last collision and the deposition process after the last collision. The above part analyzes the macro non-line-of-sight transport behavior of vapor coating materials in the PS-PVD from perspectives of the mean free path and the collision, as well the deposition process of vapor coating materials.

After the last collision position, the deposition direction of vapor coating materials is determined, and it will not undergo any collision before reaching the substrate. Therefore, the vapor coating materials, through a mean free path or less from the last collision position, will be deposit on the substrate from all directions. In this process, the flight process of vapor coating materials is a line-of-sight behavior. Therefore, the deposition process of the PS-PVD is micro line-of-sight deposition behavior.

4.1. Micro line-of-sight deposition behavior and shadowing

A surface-flat substrate was used as a simulation object. The coating growth behavior during the deposition of 8 million atoms was simulated. The simulation results of the coating structure development are shown in Fig. 12. Fig. 12(a) shows that the substrate surface fluctuates rapidly during the initial stage of deposition, and the smooth surface becomes roughened. An initial columnar structure emerges with continued deposition. Fig. 12(b)–(d) shows the coating formation process from the initial columnar structure to the final feather-like columnar structure. It can be seen that the initial columnar structure evolved and grew in the process of deposition, and finally formed a feather-like...
columnar structure. The experimental results also confirmed that the real coating had a similar structure.  

Fig. 13(a) shows the cross-section structure of the coating obtained in this experiment, and Fig. 13(b) shows the experimental results of Yoshida et al. [44]. It can be seen from Fig. 13 that the real coating has a feather-like columnar structure. Of course, there are still some differences between the real coating and the simulation results, mainly due to the fact that the effects of diffusion were not considered in the simulation. The actual structure of coating is denser than the simulation results due to the diffusion [29]. It is precisely for this reason that the simulation results more accurately reflect the line-of-sight deposition behavior of the vapor coating materials.

In conventional understanding, PS-PVD has non-line-of-sight deposition characteristics. However, the last movement of vapor coating materials deposition is line-of-sight behavior. Fig. 14 shows a schematic diagram of the atomic deposition process. Deposition unit \(a\) is deposited at the position of \(a_1\), when \(a\) reaches the substrate at a certain angle, as shown in Fig. 14. However, deposition unit \(b\) is blocked by the \(b_2\) position and cannot be deposited at the \(b_1\) position. This behavior results in a shadowing effect. In the initial stage of deposition, the shadowing

![Fig. 11. Division of transport and deposition process in PS-PVD.](image1)

![Fig. 12. Structure development of coating.](image2)
effect leads to a rapid fluctuation and roughening of the smooth substrate surface. The shadowing effect always exists in the subsequent deposition process, which leads to the formation of the final columnar structure of the coating. The same shadowing effect also occurs on the deposition unit c as shown in Fig. 14. It is the interplay between this roughness of the growth front and the vapor incidence pattern that exacerbates shadowing and produces inter-columnar porosity under conditions that would normally be expected to yield a dense film.

4.2. Hierarchical structure

The coating is not a single columnar structure from the simulation results in Fig. 12. Fig. 15 shows the detailed structure of the PS-PVD coating, revealing that the coating has a hierarchical structure.

The primary structure, with significant inter-columnar gaps, is the main structure of the coating, as shown in Fig. 15(a). The secondary structure can be observed in the primary structure. The gap between the secondary structures is significantly smaller than the gap between the primary structures. There is a smaller tertiary structure in the secondary structure, as shown in Fig. 15(b). There are smaller pores between tertiary structures. The primary, secondary, tertiary structures and pores form the fine feather-like columnar structure of coating.

As with the simulation results, a large number of experimental results show that the coating has a hierarchical structure. The coating structure in Fig. 13(a) is consistent with the primary structure of the simulation results, with inter-column voids between coating entities. Fig. 16(a) displays an enlargement of the coating structures shown in Fig. 13(a). It can be clearly seen that there is a secondary structure on the primary structure, as shown in the red ellipse of Fig. 16(a). Fig. 16(b) shows the bright field micrograph of the coating [30], and it reveals the presence of tertiary structures. Because the coating sample is still composed of stacked layers of atoms, additional microscopic structures in the coating cannot be observed by transmission electron microscopy (TEM). The simulation results solve this problem, and it can be seen that the tertiary structures are separated by micro-gaps and even nano-gaps.

4.3. Development of coating columnar structures

The above simulation results and experimental results reveal the micro line-of-sight deposition of the PS-PVD. Furthermore, the growth
In order to explore the development of the columnar structures, a series of simulations was performed. The columnar spacing of each simulation result is statistically averaged, and the average columnar spacing is obtained, as shown in Fig. 16. Fig. 17(a) shows a representation of the relationship between the mean columnar spacing of the coating and the coating thickness. In the simulation process, the length of one pixel is defined as unit 1. Then, the column spacing and coating thickness normalized with a pixel as the baseline. Therefore, when statistically analyzing the simulation results, one pixel is used as a baseline to achieve statistical standardization and unification between simulation results of different deposition thicknesses. In Fig. 17(a), the abscissa coordinates represent the thickness of the coating, and the vertical coordinates represent the columnar spacing. It can be seen from Fig. 17(a) that the change of mean columnar spacing tends to be stable with the increase of coating thickness, but the columnar spacing still increases. Compared with the experimental results (Fig. 17(b) and (c)), the growth tendency is consistent. In addition, a secondary structure can be easily found in the primary structure, see in the red ellipse of Fig. 17(c).

Due to the micro line-of-sight deposition behavior of vapor coating
materials, the initial columnar structures emerge under the shadowing effect even the substrate surface is flat. With continued deposition, some of columnar structures stop growing due to the shadowing effect, and other columnar structures continue to grow, as shown in Fig. 18. Meanwhile, some new columnar structures emerge, also due to the shadowing effect, as shown in Fig. 18. Moreover, the growth of the columnar structure might stop or continue at any time due to the shadowing effect.

In the initial stage of deposition, some of the columnar structures stop growing, and others are continuously growing, so that the average column spacing rapidly increases. As the deposition proceeds, the amount of columnar structures that stop growing and regenerate decreases. Thus, the amount of columnar structures changes slowly, and the mean columnar spacing changes gradually. At the later stage of deposition, the amount of columnar structures gradually stabilizes and the mean columnar spacing also becomes stable.

5. Conclusion

Compared to the conventional processes of PS and EB-PVD, which are in direct line-of-sight behavior, the PS-PVD technology offers novel potential to develop a non-line-of-sight coating. However, there seems to be an irreconcilable contradiction between non-line-of-sight behavior and shadow effect (one of the reasons for the formation of columnar structure). In this study, the deposition process of the vapor coating materials in PS-PVD is distinguished between transport behavior and deposition behavior by the last collision position.

Before the last collision, the vapor coating materials experience a macro non-line-of-sight transport process. The simulation results of plasma jet around the substrate show that the characteristics of the plasma jet vary greatly around the substrate, and that eddy currents are created behind the substrate. At the same time, the plasma gas can bypass the substrate and flow around it. Since plasma gas carries the vapor coating materials to flow together, the vapor coating materials can also flow around the substrate. In the substrate surrounding, the vapor coating material will collide more frequently than in the jet without substrate. This results in a more opportunity for the vapor coating material to deposit in a non-line-of-sight position. The experimental results indicated that the PS-PVD can deposit at a position parallel to the plasma jet axis as well as the non-line-of-sight position. The non-line-of-sight transport behavior of PS-PVD offers the possibility to deposit the coating in shadowed areas of complex geometries and multiple components.

After the last collision, the deposition process of the vapor coating materials is a micro line-of-sight behavior where the deposition direction is random. A Monte Carlo algorithm is used to simulate the deposition behavior of vapor coating materials on a substrate in two dimensions. The results of Monte Carlo simulation show that the shadowing effect under micro line-of-sight deposition is a major factor in the columnar structure growth, and is present throughout the process of coating growth. In order to only reflect the line-of-sight deposition behavior of vapor coating materials in PS-PVD, the diffusion is not considered. From the simulation and the experimental results, the coating has a feather-like hierarchical structure including primary, secondary, and tertiary structures. The actual structure of coating is denser than the simulation results due to the diffusion during in-deposition process. The results of the research on the coating columnar structure development show that the mean columnar spacing increases dramatically at first and then tends to stabilize due to the stoppage of growth and regeneration of the columnar structure.

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