Insights into the primitives and sequence of 7YSZ TBCs deposition mechanism

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**Article**

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Abstract

The deposition mechanism of 7YSZ (7 wt% Y₂O₃-ZrO₂) thermal barrier coatings (TBCs) prepared by plasma spray–physical vapor deposition (PS-PVD) and electron beam–physical vapor deposition (EB-PVD) were investigated in detail. The results show that the deposition mechanism of 7YSZ TBCs can be divided into two stages, including primitives and sequences. These coating primitives (grains) were deposited using atomic vapor. The PS-PVD primitives were short rod–shaped, while the EB-PVD primitives were needle-shaped. The PS-PVD coating primitives were ordered in the interior but disordered on the surface due to quenching under the influence of the plasma jet. However, the EB-PVD coating primitives were ordered from the interior to the surface. The feather-like columnar structure in PS-PVD was sequenced due to the vapor-liquid-solid mixed-phases deposition. In contrast, the needle-like columnar structure in EB-PVD was sequenced because of the single-vapor phase deposition.

Full Text

The performance improvement of aero-engines and gas turbines depends on the increase in gas temperature. Applying thermal barrier coatings (TBCs) can significantly reduce the temperature in high-temperature alloy blades, making the blades operate longer and at higher temperatures. Currently, 7YSZ (7 wt%Y₂O₃-ZrO₂) is the leading material for TBCs. Electron beam-physical vapor deposition (EB-PVD) columnar coatings are the most widely used TBCs. EB-PVD involves vaporizing the coating material using an electron gun. A columnar coating can be prepared under vacuum, in which the substrate temperature and cavity pressure affect the coating structure. The substrate temperature also directly affects the leap probability of atomic particles on the surface, thereby changing the density of the coating. Gao et al. investigated the deposition process of 7YSZ coatings by EB-PVD through kinetic Monte Carlo simulations and simulated the relationship between ZrO₂ particle diffusion energy and coating structure. The multilayer shadow effect is an important factor affecting the growth of EB-PVD coatings. It has been shown that the rotation of the workpiece and the incidence angle of the vapor phase affect cylindrical or conical coatings. EB-PVD coatings are formed from submicron columnar units. Another technique for preparing TBCs is plasma spray-physical vapor deposition (PS-PVD), which uses a high-power plasma gun to vaporize the coating material, forming a feathery columnar coating. In PS-PVD, the substrate temperature and cavity pressure also affect the coating structure. Unlike EB-PVD, non-line-of-sight deposition can be achieved by PS-PVD. Liu et al. elucidated the relationship between the shadowing effect at the microscopic level and non-line-of-sight deposition at the macroscopic level in PS-PVD. The deposition phase of PS-PVD varies with the radial and axial distances. PS-PVD is a type of vapor-solid-liquid mixed-phase deposition that forms a feather-like columnar coating. The vapor phase is delivered to the substrate as particles. The coating becomes dense because the liquid phase fills the intercolumnar gaps. PS-PVD coatings consist of individual nanoscale sub-columns. Deng et al. summarized a three-stage theory in PS-PVD columnar coating deposition. During the PS-PVD coating, the plasma gun oscillates up and down, resulting in a change.
in the orientation and size of the coating primitives \(^\text{21}\). Cheng et al. \(^\text{22}\) studied the relationship between a single column and the overall selective orientation of PS-PVD coatings. In the nucleation mode, PS-PVD primitives exhibit heterogeneous and homogeneous nucleation \(^\text{23}\). Homogeneous nucleation typically occurs in the substrate boundary layer \(^\text{24}\).

The PS-PVD deposition mechanism has been investigated for decades. However, few studies have been conducted on the formation and growth of primitives in feather-like columns. The deposition process is difficult to describe because of the instantaneity of coating formation. For example, the study of primitive growth in EB-PVD is still at the submicron level, and that of primitive growth in PS-PVD is limited to the size of a single sub-column. Also, the growth of atoms on substrates can be explored by computational simulations \(^\text{12,19,25}\). Therefore, in this study, the growth of 7YSZ TBCs was divided into primitive and sequence stages. The deposition mechanism of the 7YSZ TBCs is explained at the atomic scale.

A NiCoCrAlYTa bond coating was sprayed using PS-PVD. The surface of the coating was polished and sandblasted with silica powder to increase the surface roughness, thus improving the bonding strength of subsequent 7YSZ (the powders provided by Oerlikon Metco, M6700) coatings \(^\text{26}\). The PS-PVD substrate was a Nickel-based superalloy that is 25 mm in diameter and 6 mm in thickness. The NiCoCrAlYTa bond coating and the 7YSZ ceramic coating were deposited on a K417 substrate using EB-PVD (UE205). The substrate size in the EB-PVD and PS-PVD was the same. The microstructures of the coatings were observed using field-emission scanning electron microscopy (FE-SEM). The phase compositions were identified by X-ray diffraction (XRD) using Cu-K\(\alpha\) radiation (20–90°, 0.02°/step). Texture evolution was analyzed using electron backscattered diffraction (EBSD), and the microstructures of the coatings were investigated using transmission electron microscopy (TEM). In addition, a fast Fourier transform (FFT) was applied to high-resolution TEM (HRTEM) data to determine the crystal orientation \(^\text{27}\).

Fig. 1 shows the SEM images of PS-PVD and EB-PVD 7YSZ TBCs at different magnifications. Both TBCs exhibited columnar structure. PS-PVD coating exhibited a feather-like columnar structure with many sub-columns. The EB-PVD coating was composed of many needle-like columns. Figs. 1(a) and (e) show that the EB-PVD was denser and less porous than the PS-PVD coating. Some large particles between the PS-PVD coating columns were observed (Fig. 1(b)). These large particles were formed by the semi-melting or un-vaporized solid or liquid particles. In PS-PVD, some column growths were interrupted, and some new columns were regrown (Fig. 1(c)). This morphology of PS-PVD coating was caused by spray gun oscillation. Firstly, the plasma jet undergoes a reciprocating movement from the center to the edge. In addition, the radial distribution of the coating along the plasma jet is dominated by vapor deposition with a large proportion of vapor particles at the center. As the radial distance increases, liquid-solid-phase particles gradually dominate deposition. Thus, the large particles and new column re-growth in PS-PVD coating were caused by these two reasons. Figs. 1(f–g) show the EB-PVD coating growing in a relatively continuous manner from the bottom of the columns. Almost no particle inclusions were observed among the columns. Further, each column grew upward almost parallel with each other. It can be seen from Figs.
that the feather-like columnar PS-PVD coating had almost invisible boundaries and gaps between columns. However, the edges and gaps of the EB-PVD coating were clearly seen in each column.

The TEM electron diffraction patterns in Figs. 2(a–c) show that the PS-PVD coating primitives were single crystals. The single PS-PVD primitive had a unique crystal orientation, two of which were in the cubic phase and oriented in [01]. Based on the XRD patterns in Fig. 2(d), the ZrO$_2$ ceramic coatings of EB-PVD and PS-PVD were composed of cubic phases. The vaporization effect of the material was good, and the two types of coatings were mainly vapor-deposited. The primitives at the bottom of the coating were analyzed using EBSD (Figs. 2(e) and (f)) to investigate the growth orientation of PS-PVD. The EBSD results were the same as those of the XRD. The bottom was oriented in the same direction as the whole, growing in the {111} direction. Columnar growth was the favorable orientation of the vapor particles during deposition. As seen in Fig. 2(e), most of the primitives in PS-PVD were tetragonal phase, and a small amount was monoclinic phase. The monoclinic phase is formed by large particles of incompletely vaporized powder. Interrupted growth and regrowth columns lead to inconsistencies in individual primitives. In the ZrO$_2$ lattice, the periodic bond chain (PBC) theory provides {111}, {100}, {110}, and {113} planes of a family or form. No preferential trend was observed in these growth directions at the beginning of the deposition process. Sample rotation and spray gun oscillation affect the selection of growth planes, controlling the structure of the columnar coating. These factors lead to differences in the individual directions of the sub-columns and no significant directionality of the columns.

As shown in Fig. 3(a), the PS-PVD 7YSZ TBCs structure exhibited a feather-like columnar structure, in which staggered sub-columns tilt upward at a certain angle, resulting in increased porosity and spacing of the coating structure. Further, it can be seen from Fig. 3(b) that layered structures that were arranged periodically were present in the EB-PVD coating. These structures were caused by the rotational deposition of the substrate. Columnar primitives with a thickness of approximately 250 nm and a diameter of 10–30 nm can be observed in each layer. The line-of-sight deposition of EB-PVD resulted in a curved layer boundary of the columnar coating. As the substrate rotates, the deposition area rotates to approximately -90° and 90° from the vaporization source. The primitive growth direction allows for the vaporization source direction, and curved primitives are formed in each layer. This phenomenon was more pronounced near the substrate. As shown in Figs. 3(b) and 3(e), staggered, short rod-shaped (50–150 nm) PS-PVD primitives grew beside the main column. In contrast, high aspect ratio (20 nm × 150 nm) EB-PVD coating primitives grew vertically and had smaller dense intervals. Figs. 3(c) and (f) show the HRTEM images of the EB-PVD and PS-PVD primitives. The internal atomic arrangement of the PS-PVD primitives was ordered, while the surface atomic arrangement was disordered with large surface fluctuation. EB-PVD primitives were more ordered from the inside to the surface than PS-PVD primitives. Clearly, the primitives of PS-PVD were different from those of EB-PVD.

The growth of the 7YSZ coating primitive is shown in Fig. 4. Both the PS-PVD and EB-PVD primitives were deposited from the vapor particles of the 7YSZ TBCs. The different deposition environments of PS-PVD and EB-PVD led to the development of two different primitives. One of the differences between PS-PVD and EB-PVD is the plasma jet temperature, which can directly affect the coating deposition process. First,
the newly formed surface is extremely unstable. Vapor-phase particles must migrate and rearrange on the surface. Growth along a certain surface is a way of reaching a steady state. As seen in Fig. 3(c), the central particles of the PS-PVD primitives were ordered, whereas the surface particles were disordered. When the plasma jet was located in the deposition area, vapor-phase particles nucleated and grew rapidly. The temperature gradient and vapor-phase particle concentration were the highest along the axial direction, and the primitives mainly grew along the axial direction. The primitive sides also had particle deposition owing to nonlinear line properties, resulting in short rod-shaped primitives. At the same time, the energy was higher, and the surface particles diffused actively, thus, the central particles were ordered. When the plasma jet moved out of the deposition area, the temperature of the original deposition area dropped abruptly. The temperature was insufficient to provide the energy required for the diffusion of atomic particles on the surface so that the atoms could not be rearranged on the surface. The empty space caused by vapor particles and exfoliated particles accumulated through the microscopic shadow effect caused fluctuations in the primitive surface. The quenching and attenuation of the migration effect of atomic particles on the surface led to a disordered arrangement of particles on the primitive surface. In EB-PVD, the transport of coating material to the substrate is a diffusion process. Vapor-phase particles are deposited on the substrate at a relatively slow rate. During the deposition, the electron gun continuously heats the substrate. The EB-PVD deposits fewer vapor particles on the surface during each rotation. Surface atomic particles have high energy and strong diffusion ability on the surface. When surface atomic diffusion plays a dominant role, the vapor particles are more likely to move to preferential adsorption sites. The needle-column primitive surface is ordered. Therefore, the EB-PVD primitives were ordered from the inside to the surface atom particles.

The difference in the primitives influences the sequence. The disordered arrangement in the PS-PVD makes continuous growth difficult. In addition, the plasma gun oscillates up and down toward the substrate. The primitives were grown along a temperature gradient from the substrate. The axial temperature gradient was the largest, thus, columnar primitives generally tended to grow in the direction of the main axis. As the gun oscillates up and down, a certain temperature gradient in the radial direction is also present, causing the sub-columns to begin to split on the main column. The deposited particles of the PS-PVD jet consisted of a large amount of vapor phase and a small number of solids and liquids. In the vapor-solid-liquid mixed-phase deposition in PS-PVD, some solids and liquids appeared in the intercolumn gaps during the up-and-down oscillation of the gun. Some of these small columns stopped growing owing to the shadowing effect. Some solids and liquids grew into new columns, which interrupted the original growth pattern. The main effect of gun oscillation on the coating is the primitive growth interruption, which affects the continuity and stability of the coating. The PS-PVD coating structure can be regarded as a combination of feather-like interlaced columnar primitives (Fig. 3(a)). In contrast, the EB-PVD process vaporizes the material more fully, and the vapor phase is the main deposition phase. There is no plasma jet in the spraying chamber, and the coating process can be regarded as a diffusion process. The flatness of the surface enables continuous growth. Upon subsequent rotation to the deposition area, the vapor particles continue to grow epitaxially, forming a coherent needle-like structure (Fig. 3(d)).
In this work, the deposition mechanisms of 7YSZ TBCs prepared by EB-PVD and PS-PVD were investigated and summarized from the primitive and sequence perspectives. Several conclusions were drawn from this study:

1. The deposition mechanism of PS-PVD and EB-PVD 7YSZ TBCs consists of two stages: primitives and sequence. Coating deposition is a process in which primitives are formed from vapor-phase particles, and columnar structures are formed sequentially by the primitives.

2. The primitives in the PS-PVD coating exhibited a disordered surface arrangement. This arrangement is due to quenching because of the oscillating plasma jet. EB-PVD primitives were formed from the interior to the surface of the ordered vapor particles. High temperatures led to the diffusion of the surface of the vapor particles, forming a flat growth surface.

3. The state of the primitives and the coating process jointly determine the coating sequence. Feather-like coatings were formed by PS-PVD vapor-solid-liquid mixed deposition and gun oscillation. In contrast, EB-PVD achieved epitaxial growth, resulting in a needle-like–structured coating.

**Declarations**

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Investigation: RCH

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Visualization: RCH, XFZ

Supervision: XFZ

Project administration: JM, ML, YZZ, XFZ

Funding acquisition: XFZ
Data availability statements

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

References


**Figures**
Figure 1

SEM images of PS-PVD and EB-PVD coatings at different magnifications. (a-d) PS-PVD coating and (e-h) EB-PVD coating
Figure 2

PS-PVD and EB-PVD phase composition. (a) TEM image of the PS-PVD column structure. (b-c) Electron diffraction image of the area marked with red circles in (a). (d) XRD patterns of EB-PVD and PS-PVD coatings. (e) EBSD image of the root of the PS-PVD coating. (f) EBSD pole figure of PS–PVD coating cross-section.
Figure 3

TEM images of EB-PVD and PS-PVD coatings. (a) PS-PVD column structure at low magnification. (b) PS-PVD primitives at high magnification. (c) HRTEM of PS-PVD primitive surface. (d) EB-PVD column structure at low magnification. (e) EB-PVD primitives at high magnification. (f) HRTEM of EB-PVD primitive surface.
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