Al₂O₃-modified PS-PVD 7YSZ thermal barrier coatings for advanced gas-turbine engines

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Plasma spray-physical vapor deposition (PS-PVD), called the third-generation method for thermal barrier coatings (TBCs) fabrication, has great potential for their using in gas-turbine engines. Compared to atmospheric plasma spray (APS), called the first-generation TBCs, and electron beam-PVD (EB-PVD), called the second generation, PS-PVD has many interesting features, including non-line sight deposition, high deposition rate, and microstructural flexibility, among others. Such advantages make them a promising approach to prepare thermal barrier coatings for advanced gas-turbine engines. Using PS-PVD, feather-like columnar TBCs with good strain tolerance and low thermal conductivity can be fabricated. However, prior to their application in gas-turbine engines, some disadvantages, such as CMAS (CaO–MgO–Al₂O₃–SiO₂, etc.) corrosion and oxidation resistance, need to be addressed. In this work, a method to develop Al₂O₃-modified PS-PVD 7YSZ TBCs was proposed. The experimental results demonstrate that the Al₂O₃-modification process is an effective approach to address the aforementioned weaknesses of traditional PS-PVD 7YSZ TBCs.

RESULTS AND DISCUSSION

Performances of 7YSZ TBCs

Feather-like TBCs prepared by PS-PVD have attracted much attention worldwide (USA, Germany, Poland, China, etc.) due to its higher thermal cycle performance and lower thermal conductivity. Moreover, this technique has the advantages of presenting non-line sight coverage and high deposition rate, which are suitable for the TBCs preparation to protect turbine blades (single, double, multi-blades). However, prior to their application in gas-turbine engines, some challenges in the fabrication of PS-PVD TBCs need to be addressed, such as CMA corrosion and isothermal oxidation. During the PS-PVD, the 7YSZ coating is generally deposited not only in the vapor state but also in both liquid and solid states, to a less extent. Due to the higher concentration of vapor particles compared to EB-PVD (low concentration), feather-like structured 7YSZ coating can be generated by PS-PVD, as shown in Fig. 3a-c.
and cannot be effectively evaporated\textsuperscript{33,34}. In the 7YSZ coating, the columnar structure results from the vapor deposition and its feather-like structure arises from a shadowing effect\textsuperscript{34,35}. Meanwhile, non-evaporated particles, including slightly molten particles, will exist as spherical or flat particles in the columnar coating and influence the vapor atom nucleation, leading to a branch-like structure\textsuperscript{36}. Previous experimental results demonstrated that those non-evaporated particles are detrimental to the performance of the TBCs, because the interfaces between spherical grains, flat grains, and columnar grains present weak bond. Thus, such interface is the source of failure for TBCs\textsuperscript{26,30}.

The as-sprayed PS-PVD 7YSZ TBCs (DZ125/NiCrAlY/7YSZ) were characterized under typical testing conditions, as shown in Fig. 4. The cross-section and surface microstructure of as-sprayed 7YSZ TBCs are shown in Fig. 4a–c. After a water-quenching thermal cycle, coating spallation occurred at the interface between the flat grain and columnar grain (Fig. 4d–f). Particle erosion testing (GE standard: E50TF121) was carried out on the TBCs, and it was observed that the same phenomenon of 7YSZ coating spallation occurred at the weak interface between the splat grain and columnar grain (Fig. 4g–l). When particles impact the coating surface, stress and strain will form in the 7YSZ coating simultaneously, accompanied by crack generation. The 7YSZ-coated samples were isothermally oxidized in atmospheric furnace at 1000 °C. This leads to the formation of a layer of thermally grown oxides (TGOs) on the bond coating. The formation of the TGO layer leads to the generation of strain in the inner 7YSZ coating. Thus, cracks can be generated due to weak bonding between spherical and columnar grains in 7YSZ coating (Fig. 4j–l).

Performances of Al\textsubscript{2}O\textsubscript{3}-modified 7YSZ TBCs
Based on the deposition mechanism of PS-PVD, it is hard to avoid non-evaporated particles located in the 7YSZ columnar coating. To prevent this, a new approach was proposed, that is, an additional Al film with a thickness of 2–5 μm was deposited onto the PS-PVD 7YSZ TBCs (Fig. 5a, b). Afterwards, the Al film-covered TBCs were annealed in vacuum at 608 °C for 1 h, 700 °C for 1 h, and finally at 980 °C for 2 h (Fig. 5c). During the annealing, the film of Al, due to its low melting point (~667 °C), was melt. The molten Al was then penetrated along the vertical gap into the TBCs, driven under capillary force. This capillary force mainly depends on the geometric configuration of pore including radius and wall inclination in 7YSZ coating, as well as wetting property of molten Al on porous coating. After the annealing, the TBCs sample (Fig. 5d–g) was characterized by X-ray diffraction (XRD), which shows the formation of a-Al\textsubscript{2}O\textsubscript{3} phase (Fig. 5h). For further investigation of the microstructure and morphology of the oxide, the sample in the vicinity of the surface was cross-sectioned by focused ion beam (FIB) (Fig. 5i) for TEM investigation. It clearly indicates the formation of a 600-nm-thick transparent layer (–667 °C), which is assumed to be a-Al\textsubscript{2}O\textsubscript{3} phase, as confirmed by the corresponding high-resolution image (Fig. 5k). Above in situ reaction is feasible based on thermal kinetic analysis. Even though a dense Al\textsubscript{2}O\textsubscript{3} layer was formed on the surface of PS-PVD 7YSZ coating (compare Fig. 5e to Fig. 4b), it will likely not influence its stress tolerance since the gap between columns was not be filled (as seen in Fig. 5f, g).
The Al2O3-modified 7YSZ TBCs were evaluated as follows. Using the drawing method, the bond strength of Al2O3-modified TBCs was calculated to be above 50 MPa, based on 10 samples. Additionally, the Al2O3-modified TBCs were subjected to water-quenching (1100 °C for 10 min, followed by atmospheric water-cooling for 5 min), using five samples as shown in Fig. 6a (20, 40, 60, and 80 cycles). After 80 cycles, no apparent spallation occurred in the TBC samples, showing good thermal shock resistance and stable performance. Meanwhile, an air-cooling thermal cycle of the Al2O3-modified TBC samples was performed (1050 °C for 5 min, air-cooling for 5 min) with five samples (4000, 9000, 13,000, and 16,000 cycles). After 16,000 cycles, no apparent spallation was observed, as seen in Fig. 6b. During the thermal cycle, TGO grown stress will be generated at the rough interface of 7YSZ coating and bond coating. PS-PVD 7YSZ coating has high porosity and high oxygen diffusion rate. With Al2O3-modification process, an Al2O3 overlay was in situ synthesized on TBCs surface. This process will lead to porosity decrement. Moreover, the Al2O3 material has low oxygen diffusion rate, which can act as a barrier for oxygen diffusion. Thus, the TGO grown rate can be hindered. Finally, the Al2O3-modified PS-PVD 7YSZ TBCs show a good thermal shock performance.

Besides good thermal cycle performance, fracture toughness is an important property for TBCs. Three samples (with dimensions 100 × 25 × 2 mm) were characterized with a bend testing at 90°. Analysis of the two images, including front and lateral views, revealed only micro-cracks and no spallation. Three samples after bend testing at 90°, indicating no apparent spallation. Three samples after isothermal oxidation for 25 and 100 h. Five samples after simulated marine corrosion for 1200 h.

Fig. 5 Preparation of Al2O3-modified PS-PVD 7YSZ TBCs. a Diagram of PS-PVD facility for TBCs fabrication. b Diagram of magnetron sputtering for Al film. c Vacuum furnace for heating treatment. d Cross-sectional microstructure of Al2O3-modified 7YSZ TBCs. e Magnified image of top coating in d. f Surface microstructure of Al2O3-modified TBCs. g Cross-sectional microstructure in d without polishing. h XRD patterns of as-sprayed and Al2O3-modified PS-PVD 7YSZ coating. i, j Cross-section of g with FIB milling and TEM analysis. k Overlay HRTEM in j.
coating, it has many different-sized open vertical gaps between columns and various-sized open pores in each column. Those open gaps and pores will provide paths for molten CMAS infiltration at high temperature. Thus, Al$_2$O$_3$-modification process were proposed to improve the corrosion resistance of CMS for PS-PVD 7YSZ coating. Because using above approach, a dense Al$_2$O$_3$ layer was formed on surface of porous 7YSZ coating, which will act as a barrier to hinder the molten CMAS infiltration. A comparison of the CMAS corrosion between the as-sprayed TBCs and Al$_2$O$_3$-modified TBCs is presented in Fig. 7. The CMAS powders were sprinkled on the surface of TBCs (0.2 g/mm$^2$) for isothermal heating at 1200°C for 24 h (using ZrO$_2$ disk as a substrate). The experimental results show that a buckling phenomenon was observed in the as-sprayed 7YSZ TBCs after CMAS corrosion (Fig. 7a, b). Because the CMAS react with the 7YSZ coating, leading to spallation (Fig. 7c). However, the Al$_2$O$_3$-modified 7YSZ TBCs did not present the wavy crack between the 7YSZ coating and substrate (Fig. 7d, e). It can be hypothesized that a dense Al$_2$O$_3$ overlay was formed on the surface of the Al$_2$O$_3$-modified TBCs, which can act as an infiltration barrier, hindering the entrance of the molten CMAS into the porous coating (Fig. 7f). In China, the APS and EB-PVD 7YSZ TBCs have been widely utilized for the protection of hot components in gas-turbine engines. And the PS-PVD TBCs may soon be used for the protection of turbine blades. A comparison of the performance of APS, EB-PVD, and PS-PVD 7YSZ TBCs is summarized in Table 1, based on 8 years of research in the authors’ research group.$^{36-38}$ Due to their laminar structure, the air-cooling thermal cycle of APS TBCs is lower than 3000. Additionally, a columnar structure can release stress during a thermal cycle. Thus, the thermal cycle of EB-PVD and PS-PVD TBCs is more than 7000 and 8000, respectively. During the thermal cycle, stress will be generated at the interface of 7YSZ coating and bond coating, resulting from thermal mismatch between 7YSZ coating and bond coating, TGO grown stress, etc.$^{39-41}$ The rough interface including peak and valley will lead to stress concentration. However, the columnar structure has the ability to release the stress due to different-sized vertical gap among columns, avoiding crack generation. In the Al$_2$O$_3$-modified PS-PVD TBCs, an Al$_2$O$_3$ overlay was in situ synthesized on the surface, which will decrease the growing rate of TGO$^{46}$. This means that the interfacial stress of the ceramic/bond coating will increase at a low rate, presenting the greatest thermal cycle performance (>16,000). Similarly, the Al$_2$O$_3$-modified TBCs has the best water-quenching thermal cycle properties (>160), compared to the APS (>60), EB-PVD (>80), and traditional PS-PVD TBCs (>120). In its role as a protective coating for gas-turbine blades, thermal conductivity is an important property. Its laminar structure can hinder heat transmission effectively, thus APS 7YSZ TBCs (>1.0 W/mK) presented the best performance compared to the other TBCs. In addition, other characteristics including bond strength, surface roughness, coating uniformity, and deposition rate were analyzed and summarized in Table 1. Through the above comparison, it can be seen that the Al$_2$O$_3$-modified PS-PVD 7YSZ TBCs have the best overall performance.

Although the Al$_2$O$_3$-modified PS-PVD TBCs have good performance in typical simulation testing conditions. However, before practical application of TBCs in gas-turbine engines, the performance of Al$_2$O$_3$-modified TBCs deposited on turbine blades should be characterized. Thus, a turbine blade with Al$_2$O$_3$-modified 7YSZ TBCs was analyzed using a water-quenching testing (1100°C for 10 min, followed by atmospheric water cooling for 5 min). Water quenching is a simple and effective testing to evaluate the performance of TBCs. Figure 8a shows that the turbine blade used for testing consists of an irregular sample, with a high curvature surface and corners, which differs greatly from the regularly shaped samples used previously. The TBCs were deposited on the surface with different states (porosity, density, bond strength, etc.). The turbine blade with Al$_2$O$_3$-modified TBCs after 20, 60, and 80 cycles are shown in Fig. 8b–d. After 80 cycles, no spallation was observed in the turbine blade at the different directions (planform, front view, back view, lateral view), which suggests good thermal shock resistance. Thus, it can be confirmed that the Al$_2$O$_3$-modified TBCs have high potential for using in gas-turbine engines.

![Fig. 7 As-sprayed and Al$_2$O$_3$-modified PS-PVD 7YSZ TBCs after CMAS corrosion](image)

**Fig. 7** As-sprayed and Al$_2$O$_3$-modified PS-PVD 7YSZ TBCs after CMAS corrosion. **a-c** As-sprayed TBCs after CMAS corrosion (a as-sprayed TBCs showing buckling between 7YSZ coating and substrate, b cross-sectional microstructure without polishing, and c magnified image showing spallation). **d-f** Al$_2$O$_3$-modified TBCs after CMAS corrosion (d cross-sectional microstructure, e cross-sectional microstructure without polishing, and f magnified image showing no apparent spallation).

**Table 1.** Performance comparison among APS 7YSZ TBCs, EB-PVD 7YSZ TBCs, traditional PS-PVD 7YSZ TBCs, and Al$_2$O$_3$-modified PS-PVD 7YSZ TBCs.

| Methods                  | APS          | EB-PVD       | Traditional PS-PVD | Al$_2$O$_3$-modified PS-PVD |
|--------------------------|--------------|--------------|--------------------|----------------------------|
| Properties               |              |              |                    |                            |
| Air-cooling thermal cycle (1050°C) | <3000        | >7000        | >8000              | >16,000                    |
| Water-quenching thermal cycle (1100°C) | >60          | >80          | >120               | >160                       |
| Thermal conductivity (1100°C) (W/mK) | >1.0         | >1.6         | >1.1               | >1.1                       |
| Bond strength (MPa)      | <35          | >50          | >50                | >50                        |
| Surface roughness (µm)  | >10          | <5           | <5                 | <5                         |
| Coating uniformity      | Line sight deposition | Line sight deposition | Non-line sight deposition | Non-line sight deposition |
| Deposition rate (µm/min) | 10–20        | 0.2–0.5      | 1–5                | 1–5                        |
transmission electron microscopy (TEM; Titan Themis 200, FEI) assisted with FIB (450 S, FEI) milling.

DATA AVAILABILITY
Data that support the findings presented in this manuscript can be provided upon reasonable request by contacting the corresponding author.

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AUTHOR CONTRIBUTIONS
X.Z., Z.D., and H.L. conducted the experimental studies and analyzed the data. J.M., Chunming Deng, and Changguang Deng conducted the TEM experiments. S.N., W.C., and J.S. co-wrote the paper. J.F., M.L., and K.Z. contributed to the discussion of the results. Z.D. and H.L. are co-first authors for this work.

COMPETING INTERESTS
The authors declare no competing interests.

ADDITIONAL INFORMATION
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