ARTICLE OPEN

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

Xiaofeng Zhang¹✉, Ziqian Deng^{1,2}, Hong Li^{1,2}, Jie Mao¹, Chunming Deng¹, Changguang Deng¹, Shaopeng Niu¹, Wenlong Chen¹, Jinbing Song¹, Jiafeng Fan¹, Min Liu¹ and Kesong Zhou¹

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.

npj Materials Degradation (2020)4:31; <https://doi.org/10.1038/s41529-020-00134-5>

INTRODUCTION

The development of aero-engine has benefited from the progress of thermal barrier coatings (TBCs)^{1–4}. Most research aimed at TBCs was started in the late 1940s and continued through the 1950s to the date^{5–7}. TBCs were first used in the injectors of X-15 rocket engines and in the combustion chamber of gas-turbine engines in the 1960s^{7,8}. Up to now, TBCs for hot components used in gas-turbine engines are still a hot research topic, even though the first paper testing turbine blades with TBCs was written in 1976 (refs. ^{9,10}). Due to the continuous modification and development of the airplane, the thrust-to-weight ratio continues to increase. Thus, the requirements for TBCs is constantly changing. In a TBCs system, the hot-component materials are constantly being developed, from casting alloys to directionally solidified alloys and single crystal alloys. Additionally, the methods for the preparation of TBCs are continuously updated, from atmospheric plasma spray (APS) to electron beam-physical vapor deposition (EB-PVD) and plasma spray-physical vapor deposition (PS-PVD). Meanwhile, the TBC structural designs are iterated repeatedly. The above-mentioned TBC system progress has been summarized in Fig. 1.

Now, the TBCs with different materials and various structure designs have been widely used for turbine blades protection in gas-turbine engines. Laminar-structured rare-earth-doped ZrO₂ (Y₂O₃/Ga₂O₃/La₂O₃/CeO₂/SmO₂/Dy₂O₃-ZrO₂) TBCs prepared by APS have been investigated since 1976 (refs. ^{3,9,10}). The thermal conductivity of APS TBCs is in the range of 1.0–2.25 W/mk (25–1000 °C)^{11–13}. A typical TBCs structure is shown in Fig. 2a. In the 1980s, the APS TBCs were unable to meet the necessary service conditions of moving turbine blades in some advanced gas-turbine engines due to high rotation velocities (>20,000 r/min) and frequent takeoffs and landings^{14,15}. Thus, EB-PVD TBCs were proposed to compensate the loss of thermal conductivity with good thermal cycle performance, compared to the APS TBCs^{16–18}. Columnar-structured TBCs (Fig. 2b) with better strain tolerance can

be prepared by EB-PVD due to its vapor deposition, in contrast to laminar-structured APS TBCs deposited with liquid/solid mixed states¹⁹. However, the disadvantage for EB-PVD TBCs is their high thermal conductivity (in the range of 1.6–2.3 W/mk), which needs to be lowered for their practical application²⁰. Meanwhile, PS-PVD was presented in the 2000s as a novel approach to achieve such goal^{21,22}, by developing feather-like columnar-structured TBCs (Fig. 2c), resulting from multiphase deposition (mainly vapor, some liquid and solid). The PS-PVD was developed based on low-pressure plasma spray by reducing the working pressure (~100 Pa) and improving the plasma power (~180 kW)²³. With a length and diameter of the plasma flame of up to 2500 and 400 mm, respectively, at low pressures (~150 Pa)²⁴, the TBCs materials can be evaporated²⁵. 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.

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^{26,27}. 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^{28–32}. 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^{23,30}. Even though the feedstock powders are injected in the inner plasma gun, part of powders fly along the outer edge of the plasma flame

¹National Engineering Laboratory for Modern Materials Surface Engineering Technology & The Key Lab of Guangdong for Modern Surface Engineering Technology, Institute of New Materials, Guangdong Academy of Science, 510650 Guangzhou, China. ²These authors contributed equally: Ziqian Deng, Hong Li. ✉email: zxf200808@126.com

Fig. 1 TBCs progress for gas-turbine engine. It includes Ni-based superalloys, thermal barrier coatings, and preparation methods (APS, EB-PVD, PS-PVD).

Fig. 2 Typical microstructure of 7YSZ TBCs deposited on turbine blades used in gas-turbine engines. Typical TBCs prepared by **a** APS, **b** EB-PVD, and **c** PS-PVD.

Fig. 3 Feather-like columnar 7YSZ coating by PS-PVD. **a** Top microstructure of 7YSZ coating showing columnar structure. **b** Magnified microstructure of **a** showing the feather-like structure. **c** Magnified microstructure of **b** showing nano-sized columns.

and cannot be effectively evaporated^{33,34}. In the 7YSZ coating, the columnar structure results from the vapor deposition and its feather-like structure arises from a shadowing effect^{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 structure³⁰. 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^{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–i). When particles impact the coating

Fig. 4 PS-PVD as-sprayed 7YSZ TBCs and failure phenomenon. **a–c** Microstructure of as-sprayed TBCs (**a** cross-section, **b** magnified image of top 7YSZ coating, **c** surface). **d–f** Microstructure after water-quenching testing (**d** cross-section, **e** surface, **f** magnified image). **g–i** Microstructure after particle erosion (**g** cross-section, **h** surface, **i** magnified image). **j–l** Microstructure after isothermal oxidation (**j** cross-section, **k** crack generation in the inner coating, **l** new surface after spallation).

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 Al₂O₃-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-Al₂O₃ 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 film of an oxide (Fig. 5j). This is assumed to be a-Al₂O₃ 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 Al₂O₃ 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).

Fig. 5 Preparation of Al_2O_3 -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 Al_2O_3 -modified 7YSZ TBCs. **e** Magnified image of top coating in **d**. **f** Surface microstructure of Al_2O_3 -modified TBCs. **g** Cross-sectional microstructure in **d** without polishing. **h** XRD patterns of as-sprayed and Al_2O_3 -modified PS-PVD 7YSZ coating. **i**, **j** Cross-section of **g** with FIB milling and TEM analysis. **k** Overlay HRTEM in **j**.

Fig. 6 Performance of Al_2O_3 -modified 7YSZ TBCs. **a** Five samples after water-quenching with 20, 40, 60, and 80 cycles, showing no apparent spallation. **b** Five samples after air-cooling with 4000, 9000, 13,000, and 16,000 cycles, indicating no apparent spallation. **c** Three samples after bend testing at 90° , indicating no spallation. **d** Three samples after isothermal oxidation for 25 and 100 h. **e** Five samples after simulated marine corrosion for 1200 h.

The Al_2O_3 -modified 7YSZ TBCs were evaluated as follows. Using the drawing method, the bond strength of Al_2O_3 -modified TBCs was calculated to be above 50 MPa, based on 10 samples. Additionally, the Al_2O_3 -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 Al_2O_3 -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 Al_2O_3 -modification process, an Al_2O_3 overlay was in situ synthesized on TBCs surface. This process will lead to porosity decrement. Moreover, the Al_2O_3 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 Al_2O_3 -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 $100 \times 25 \times 2$ 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 (Fig. 6c). Cylindrical samples of Al_2O_3 -modified TBCs were tested with isothermal oxidation at 1100°C for 25 and 100 h. The three samples tested showed that the average mass increase rate was $0.057588 \text{ g}/(\text{m}^2 \text{ h})$, based on 100 h, as seen in Fig. 6d. Marine corrosion resistance is another important factor for TBCs, because gas-turbine engines are often in service in marine environments. Five samples were tested with a combustion flame injected with NaCl solution (aviation kerosene and oxygen, at 900°C for 1200 h), seen in Fig. 6e. The experimental results show the mass variation rate is 0.0014, 0.0029, and -0.001 , -0.0016 , $-0.0013 \text{ g}/(\text{m}^2 \text{ h})$, correspondingly.

Traditional PS-PVD 7YSZ TBCs generally present low thermal conductivity due to their high porosity ($>15\%$). In the 7YSZ

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_2O_3 -modification process were proposed to improve the corrosion resistance of CMAS for PS-PVD 7YSZ coating. Because using above approach, a dense Al_2O_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_2O_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_2O_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_2O_3 overlay was formed on the surface of the Al_2O_3 -modified TBCs, which can act as an infiltration barrier, hindering the entrance of the molten CAMS 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_2O_3 -modified PS-PVD TBCs, an Al_2O_3 overlay was in situ synthesized on the surface, which will decrease the growing rate of TGO³⁶. 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_2O_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 ($>1.0 \text{ W/mK}$) 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_2O_3 -modified PS-PVD 7YSZ TBCs have the best overall performance.

Although the Al_2O_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_2O_3 -modified TBCs deposited on turbine blades should be characterized. Thus, a turbine blade with Al_2O_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_2O_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_2O_3 -modified TBCs have high potential for using in gas-turbine engines.

Fig. 7 As-sprayed and Al_2O_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_2O_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_2O_3 -modified PS-PVD 7YSZ TBCs.

Methods	APS	EB-PVD	Traditional PS-PVD	Al_2O_3 -modified PS-PVD
<i>Properties</i>				
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 ($\mu\text{m/min}$)	10–20	0.2–0.5	1–5	1–5

Fig. 8 Turbine blade with Al_2O_3 -modified TBCs after water-quenching testing (planform, front view, back view, lateral view). **a** Al_2O_3 -modified PS-PVD 7YSZ TBCs before water quenching. **b–d** The same turbine blade after 20, 60, and 80 cycles.

METHODS

Preparation of TBCs

The equipment used for these experiments consists of a PS-PVD multicoat system (Oerlikon Metco). The feedstock material consisted of NiCrAlY powders (Amdry 9624, Oerlikon Metco) and agglomerated 7YSZ powders (M6700, Oerlikon Metco). Disks made of DZ125 superalloy with different sizes were used as substrates. The substrates and turbine blades were coated with NiCrAlY bond coating and 7YSZ top coating, using the aforementioned PS-PVD. The preparation parameters of NiCrAlY coating (net power 46 kW, current 1650 A, Ar 110 slpm, H_2 6 slpm, feed rate 20 g/min, chamber pressure 40 mbar) and 7YSZ coating (net power 57 kW, current 2600 A, Ar 35 slpm, He 60 slpm, feed rate 18 g/min, chamber pressure 1.5 mbar) were optimized in previous investigation. Then, the feather-structured columnar 7YSZ coating was deposited on top of the bond coating. In order to improve its performance, the prepared TBCs were modified with an Al film on their surface by magnetron sputtering (J-1250, Jingzhou Industrial Coating, China). During deposition, Al target (99.99%) was used and the direct current, voltage, and pressure were set as 3 A, 150 V, and 5×10^{-3} Pa, respectively. Last, the Al-deposited TBCs samples were treated with vacuum heat treatment (608 °C for 1 h, 700 °C for 1 h, and 980 °C for 2 h), forming Al_2O_3 -modified 7YSZ TBCs.

Characterization of TBCs

The thermal cycling properties of PS-PVD 7YSZ TBCs were analyzed. For water-quenching testing, the specimens (sample size: $\Phi 30 \times 5$ mm) were heated at an evaluated temperature of 1050 °C in a furnace for 10 min followed by direct water-quenching at room temperature for 5 min. For air-cooling testing (sample size: $\Phi 30 \times 5$ mm), the same conditions were used as before, with a temperature of 1100 °C. The isothermal oxidation of the TBCs samples (sample size: $\Phi 15 \times 30$ mm) was carried out at 1100 °C for 100 h, and the performance was evaluated as a mass increase rate. The simulated marine corrosion of TBCs (sample size: $\Phi 7 \times 60$ mm) was conducted by combustion using aviation kerosene and oxygen (900 °C for 1200 h). The CMAS (5.6 wt% CaO, 2.7 wt% MgO, 10.9 wt% Al_2O_3 , 30.2 wt% SiO_2 , etc.) corrosion of TBCs (sample size: $\Phi 25.4 \times 5$ mm) was also analyzed. The experiment was designed as follows: CMAS powders mixed with alcohol were prepared as a suspension at a concentration of 5 mg/ml. The TBC samples were dipped into the suspension. After that, the samples were placed in a furnace kept at 1200 °C for 24 h, followed by air cooling. The bond strength of the TBCs (sample size: $\Phi 25.4 \times 5$ mm) was characterized using the drawing method. The particle erosion performance (sample size: $\Phi 25.4 \times 5$ mm) was tested according to GE standard (E50TF121). The surface roughness of the TBCs was tested optical profiler (Contour-GT, Bruker). The phase compositions of as-sprayed and Al_2O_3 -modified 7YSZ TBCs were identified by XRD (10–90°; SmartLab, Rigaku, Japan). The microstructure of Al_2O_3 -modified 7YSZ TBCs was characterized by field emission-scanning electron microscope (Nova-Nano430, FEI) and

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.

Received: 9 March 2020; Accepted: 11 September 2020;

Published online: 08 October 2020

REFERENCES

1. Miller, R. Thermal barrier coatings for aircraft engines: history and directions. *J. Therm. Spray Technol.* **6**, 35–42 (1997).
2. David, R. et al. Thermal barrier coating materials. *Mater. Today* **8**, 22–29 (2005).
3. Lakiza, S. et al. Thermal barrier coatings: current status, search, and analysis. *Powder Metall. Met. Ceram.* **57**, 82–113 (2018).
4. Vijay, K. et al. Progress update on failure mechanisms of advanced thermal barrier coatings: a review. *Prog. Org. Coat.* **90**, 54–82 (2016).
5. Dean, P. et al. High temperature materials for heavy duty diesel engines: Historical and future trends. *Prog. Mater. Sci.* **103**, 109–179 (2019).
6. Darolia, R. et al. Thermal barrier coatings technology: Critical review, progress update, remaining challenges and prospects. *Int. Mater. Rev.* **58**, 315–348 (2013).
7. Miller, R. *History of Thermal Barrier Coatings for Gas Turbine Engines: Emphasizing NASA's Role from 1942 to 1990*. NASA Technical Reports Server, <http://hdl.handle.net/2060/20090018047> (2009).
8. Torben, F. et al. A new metallic thermal barrier coating system for rocket engines: failure mechanisms and design guidelines. *J. Therm. Spray Technol.* **28**, 1402–1419 (2019).
9. Ajay, M. *Durability Challenges for Next Generation of Gas Turbine Engine Materials*. NASA Technical Reports Server, <http://hdl.handle.net/2060/20130010776> (2012).
10. Li, X. et al. Evolution of Rolls-Royce air-cooled turbine blades and feature analysis. *Procedia Eng.* **99**, 1482–1491 (2015).
11. Emine, B. et al. Ceramic top coats of plasma-sprayed thermal barrier coatings: materials, processes, and properties. *J. Therm. Spray Technol.* **26**, 992–1010 (2017).
12. Pierre, P. et al. Mechanical and thermo-physical properties of plasma-sprayed thermal barrier coatings: a literature survey. *Oxid. Met.* **88**, 133–143 (2017).
13. Benjamin, B. et al. Thermal insulation properties of YSZ coatings: suspension plasma spraying (SPS) versus electron beam physical vapor deposition (EB-PVD) and atmospheric plasma spraying (APS). *Surf. Coat. Technol.* **318**, 122–128 (2017).
14. Armelle, V. et al. The 2016 thermal spray roadmap. *J. Therm. Spray Technol.* **25**, 1376–1440 (2016).
15. Sudhangshu, B. *High Temperature Coatings*. Butterworth-Heinemann. 2nd edition, 199–299 (2018).
16. Zhu, D. et al. Thermal conductivity of EB-PVD thermal barrier coatings evaluated by a steady-state laser heat flux technique. *Surf. Coat. Technol.* **138**, 1–8 (2001).
17. Mineaki, M. et al. Thermal conductivity and thermal cycle life of La₂O₃ and HfO₂ doped ZrO₂-Y₂O₃ coatings produced by EB-PVD. *Surf. Coat. Technol.* **203**, 2835–2840 (2009).
18. Shen, Z. Rare earth oxides stabilized La₂Zr₂O₇ TBCs: EB-PVD, thermal conductivity and thermal cycling life. *Surf. Coat. Technol.* **357**, 427–432 (2019).
19. Flores, A. et al. Effect of morphology on thermal conductivity of EB-PVD PYSZ TBCs. *Surf. Coat. Technol.* **201**, 2611–2620 (2006).
20. Robert, V. et al. Overview on advanced thermal barrier coatings. *Surf. Coat. Technol.* **205**, 938–942 (2010).
21. Niessen, K. et al. Vapor phase deposition using plasma Spray-PVD™. *J. Therm. Spray Technol.* **19**, 502–509 (2010).
22. Li, J. et al. Twin-structured yttria-stabilized zirconia coatings deposited by plasma spray physical vapor deposition: microstructure and mechanical properties. *J. Am. Ceram. Soc.* **90**, 603–607 (2007).
23. Zhang, X. et al. Gas-deposition mechanisms of 7YSZ coating based on plasma spray-physical vapor deposition. *J. Eur. Ceram. Soc.* **36**, 697–703 (2016).
24. Zhang, X. et al. Toughness and elasticity behaviors in nano-structured 7 wt.% Y₂O₃-stabilized ZrO₂ coating. *Surf. Coat. Technol.* **276**, 316–319 (2015).
25. Liu, M. et al. Transport and deposition behaviors of vapor coating materials in plasma spray-physical vapor deposition. *Appl. Surf. Sci.* **486**, 80–92 (2019).
26. Gao, L. et al. Microstructure, thermal conductivity and thermal cycling behavior of thermal barrier coatings prepared by plasma spray physical vapor deposition. *Surf. Coat. Technol.* **276**, 424–430 (2015).
27. Rezanka, S. et al. Improved thermal cycling durability of thermal barrier coatings manufactured by PS-PVD. *J. Therm. Spray Technol.* **23**, 182–189 (2014).

28. Michael, P. et al. Process-structure-property relations for the erosion durability of plasma spray-physical vapor deposition (PS-PVD) thermal barrier coatings. *Surf. Coat. Technol.* **297**, 11–18 (2016).
29. Song, J. et al. Research of in situ modified PS-PVD thermal barrier coating against CMAS (CaO–MgO–Al₂O₃–SiO₂) corrosion. *Ceram. Int.* **42**, 3163–3169 (2016).
30. Zhang, X. et al. Mechanisms governing the thermal shock and tensile fracture of PS-PVD 7YSZ TBC. *Ceram. Int.* **44**, 3973–3980 (2018).
31. Cernuschi, F. et al. Solid particle erosion of thermal spray and physical vapour deposition thermal barrier coatings. *Wear* **271**, 2909–2918 (2011).
32. Konstantin, V. et al. Plasma spray-PVD: a new thermal spray process to deposit out of the vapor phase. *J. Therm. Spray Technol.* **20**, 736–743 (2011).
33. He, W. et al. Advanced crystallographic study of the columnar growth of YSZ coatings produced by PS-PVD. *J. Eur. Ceram. Soc.* **38**, 2449–2453 (2018).
34. He, W. et al. Investigation on growth mechanisms of columnar structured YSZ coatings in plasma spray-physical vapor deposition (PS-PVD). *J. Eur. Ceram. Soc.* **39**, 3129–3138 (2019).
35. Yang, J. et al. Thermal cycling behavior of quasi-columnar YSZ coatings deposited by PS-PVD. *J. Therm. Spray Technol.* **26**, 132–139 (2017).
36. Zhang, X. et al. In situ synthesis of α -alumina layer at top yttrium-stabilized zirconia thermal barrier coatings for oxygen barrier. *Ceram. Int.* **40**, 12703–12708 (2014).
37. Chang, F. et al. Microstructure and thermal shock resistance of the peg-nail structured TBCs treated by selective laser modification. *Appl. Surf. Sci.* **317**, 598–606 (2014).
38. Zhang, X. et al. Structural evolution of Al-modified PS-PVD 7YSZ TBCs in thermal cycling. *Ceram. Int.* **45**, 7560–7567 (2019).
39. Mumm, D. et al. Characterization of a cycle displacement instability for thermally grown oxide in a thermal barrier system. *Acta Mater.* **49**, 2329–2340 (2001).
40. Fedorova, E. et al. Microstructural and numerical analysis of fracture mechanisms in a thermal barrier coating system on Ni-based superalloys. *Procedia Struct. Int.* **13**, 741–745 (2018).
41. Xu, T. et al. A numerical assessment of the durability of thermal barrier coating systems that fail by ratcheting of the thermally grown oxide. *Acta Mater.* **51**, 3807–3820 (2003).

ACKNOWLEDGEMENTS

We would like to acknowledge the financial support from the National Natural Science Foundation of China (No. 51801034, No. 51771059), Guangdong Special Support Program (2019BT02C629), and Guangdong Academy of Sciences Program (No. 2020GDASYL-20200104030), Guangzhou Technical Research Program (No. 201906010015).

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

Supplementary information is available for this paper at <https://doi.org/10.1038/s41529-020-00134-5>.

Correspondence and requests for materials should be addressed to X.Z.

Reprints and permission information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2020