



Foreign object damage behavior and failure mechanism of Al_2O_3 -modified TBCs prepared by PS-PVD

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Abstract: Particle erosion induced by foreign object damage (FOD) is an important factor that restricts the working life of thermal barrier coatings (TBCs). A dense $\alpha\text{-Al}_2\text{O}_3$ overlay was prepared by magnetron sputtering and vacuum treatment on the surface of 7YSZ TBCs sprayed by plasma spray-physical vapor deposition (PS-PVD) to improve the erosion resistance of the TBCs. The FOD behavior of the TBCs was systematically studied and the interface of $\alpha\text{-Al}_2\text{O}_3/\text{c-ZrO}_2$ was investigated by first principles calculations. The experimental results show that the erosion rates of the PS-PVD, atmospheric plasma spraying (APS), and electron beam-physical vapor deposition (EB-PVD) TBCs were 324, 248, and 139 $\mu\text{g/g}$, respectively, while the erosion rate of the Al_2O_3 -modified PS-PVD TBCs was reduced to 199 $\mu\text{g/g}$. In addition, the highest interface adhesive energy of 3.88 J/m^2 observed in the top configuration model of $\text{Al}_2\text{O}_3/\text{ZrO}_2\text{-O}$ is much higher than that of ZrO_2/Ni (2.011 J/m^2), which results in improved interface bonding performance.

Key words: thermal barrier coatings; plasma spray-physical vapor deposition; Al_2O_3 -modification; foreign object damage; first principles

1 Introduction

Thermal barrier coatings (TBCs) are critical thermal protection systems with excellent thermal insulation for aviation turbine engines which can improve the high-temperature durability of the alloy substrates and engine thermal efficiency [1–3]. At present, the most widely used ceramic coating

material is 7YSZ (zirconia stabilized with 7 wt.% yttrium), which is usually prepared as a coating by electron beam-physical vapor deposition (EB-PVD), atmospheric plasma spraying (APS), and plasma spray-physical vapor deposition (PS-PVD) [4–7]. Among the numerous microstructures that can exist in TBCs, the feather-like columnar structure fabricated using PS-PVD is the preferred microstructure because of its lower thermal conductivity

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and longer thermal cycle life [8–11]. However, the extensive application of TBCs with such structures in aero-engines is hindered by the fact that during engine operation, inertial forces may cause foreign debris and hard particles to depart from the air flow center, impinge the coating surface, and cause erosion induced by foreign object damage (FOD), which in turn results in coating peeling and failure [12–14]. Therefore, erosion resistance is a necessary property to prolong the service life of coatings, especially when these coatings are exposed to sand, dust, and volcanic ash environments [15].

A number of strategies such as laser glazing, composite dense structure coating, and process modification have been proposed to improve the erosion resistance of TBCs to date [16–19]. However, the loss of the original structure or the addition of an excessively thick dense overlay in these methods have adverse effects on the thermal conductivity and thermal cycle life of TBCs [20]. In contrast, Al₂O₃ modification is a reliable method. Previous research has shown that in-situ reactions in Al–ZrO₂ can produce a dense Al₂O₃ overlay that is effective against molten salt invasion [21–23]. However, the ability of Al₂O₃ modification to provide protection against particle erosion is unknown and the erosion characteristics and failure mechanisms of the TBCs produced using the APS, EB-PVD, and PSPVD have not been sufficiently studied systematically under the same erosion conditions.

In this study, a novel approach that in-situ Al₂O₃ modification by the formation of low-stress Al₂O₃ overlays on PS-PVD 7YSZ TBCs was presented to improve the erosion performance of TBCs over that of TBCs prepared by traditional methods is investigated. The interface state between the Al₂O₃ overlay and 7YSZ coating was studied through first-principles calculations and the erosion failure mechanisms of TBCs produced using APS, EB-PVD, PS-PVD, and Al₂O₃-modified PS-PVD were systematically investigated.

2 Experimental

2.1 Sample preparation

Stainless-steel 316 L disks with the dimensions of $d25.4\text{ mm} \times 5\text{ mm}$ were used as the substrate material. The APS and PS-PVD 7YSZ top coating powder was provided by H. C. Starck and Oerlikon Metco, and NiCrAlY metal powder (Oerlikon Metco) was used as the bond-coating feedstock material. The EB-PVD 7YSZ TBCs were provided by Shenyang Aircraft Industry (China). The preparation methods and material compositions of the TBCs are presented in Table 1. Prior to the deposition of the bond coating, the substrates were degreased and cleaned with petrol, acetone, and ethanol in sequence followed by grit blasting with alumina under 0.4 MPa. A bond coating with a thickness of approximately 100 μm and a top ceramic coating with a thickness of approximately 250 μm were then successively deposited on the substrate. Subsequently, Al₂O₃ modification was performed on the PS-PVD 7YSZ TBCs based on the Al–ZrO₂ in-situ reaction. First, an Al film with a thickness of 15 μm was deposited on the surface of the PS-PVD 7YSZ TBCs using direct current circular magnetron sputtering (J–1250, Jingzhou Industrial Coating, China). For the magnetron sputtering, an Al target (99.99%) was used and the direct current, voltage, and pressure were set to be 18 A, 500 V, and $5 \times 10^{-3}\text{ Pa}$, respectively. In the process of magnetron sputtering, Al ion has a large kinetic energy under the action of high bias, which can be quickly adsorbed on the surface of the coating and grow in the form of island. The Al film and YSZ have metallurgical bonding of atomic level rather than mechanical bonding, with good compactness, strong binding force and high deposition efficiency. Finally, vacuum heat treatment was continuously applied at 606 °C for 1.5 h, 808 °C for 1 h, and 980 °C for 1 h on the Al-deposited PS-PVD 7YSZ TBCs to form Al₂O₃-modified 7YSZ TBCs.

Table 1 Powder materials and coating preparation methods

Preparation method	Bond coating		Ceramic coating	
	Powder	Particle size/ μm	Powder	Particle size/ μm
APS	67Ni–22Cr–10Al–Y	22–45	93ZrO ₂ –7Y ₂ O ₃	15–45
PS-PVD	67Ni–22Cr–10Al–Y	22–45	93ZrO ₂ –7Y ₂ O ₃	1–30

2.2 Erosion tests

The erosion tests were performed on an erosion experimental setup that was self-modified from a sand-blasting machine. Compressed air (0.2 MPa) was used to supply power for spraying Al_2O_3 particles ($D_{50}=49\ \mu\text{m}$) on the surface of the TBC samples. A schematic of the erosion equipment is shown in Fig. 1. Prior to erosion, the Al_2O_3 particles were dried at $70\ ^\circ\text{C}$ for 5 h. The erosion parameters were formulated according to the GE E50TF121 standard and the erosion angle and distance were set to be 20° and 102 mm, respectively. 100 g Al_2O_3 particles was fed in a single erosion process. After feeding 600 g of Al_2O_3 particles, the coating erosion rate (E_w) was calculated as

$$E_w = \frac{m_2 - m_1}{m_0} \quad (1)$$

where m_1 is the original mass of sample, m_2 is the mass of sample after erosion, m_0 is the mass of Al_2O_3 particles used for erosion. The eroded mass loss of the coating was obtained using a precision electronic balance with a precision of 1×10^{-4} g.

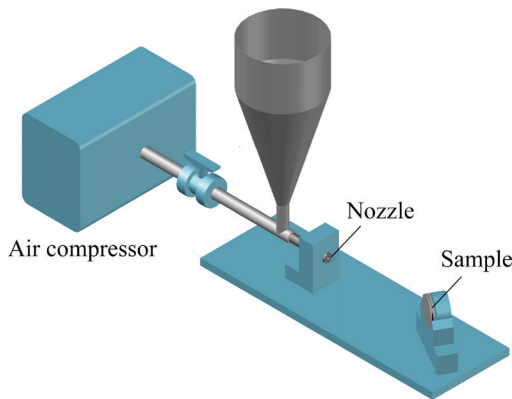


Fig. 1 Schematic of sand-blasting erosion tester

2.3 Characterization of TBCs

The microstructures of the specimens were characterized using field-emission scanning electron microscopy (FE-SEM, Nova–Nono430, FEI). Their phase transformation was characterized

through X-ray diffraction (XRD, D8–Advance, Bruker) with a step size of 0.02° ($\text{Cu K}\alpha$, incident angle of 3° , and 2θ range of 10° – 90°). Moreover, the phase structure of the PS-PVD 7YSZ TBCs with the Al_2O_3 overlay was studied using transmission electron microscopy (TEM, JEOL–2100F) with the assistance of a focused ion beam (FIB, 450S, FEI). The mechanical properties of the 7YSZ TBCs were evaluated using a nanoindentation technique at a load of 30 mN using a nano-indenter (NHT3, Anton Paar) with a Berkovich tip (tip radius $<150\ \text{nm}$). In addition, a scratch tester (RST3, Anton Paar) was used to evaluate the erosion resistance of the TBCs. This is a dead-loaded machine in which a separate scratch was made for each applied load. A constant load of 5 N was used to scratch the sample surface at a rate of 1 mm/s.

2.4 Computational method

The calculations in this study were focused on the modified interface. The α - Al_2O_3 primitive cell belongs to the trigonal crystal system and is a hexagonal close-packed crystal that contains 30 atoms comprising 18 O atoms and 12 Al atoms while c - ZrO_2 belongs to the cubic crystal system. The calculated lattice parameters are compared to the reference values in Table 2. All the calculations were performed using VASP [24], in which the exchange-correlation potentials were described using the generalized gradient approximation and Perdew–Burke–Ernzerhof functionals [25]. After preliminary calculations, the cut-off energy for the plane-wave expansion was set to be 540 eV and a Γ -centered k -point mesh of $5 \times 5 \times 1$ was adopted for the interface calculation. The convergence criteria for the total energy and forces were set as 10^{-7} eV/atom and 200 eV/ μm , respectively, and the atomic positions were relaxed using conjugate gradient methods. The surfaces and interfaces were modeled with periodic boundary conditions and a vacuum layer thickness of $15 \times 10^{-4}\ \mu\text{m}$ was chosen for the calculations with van der Waals force correction added to the calculations.

Table 2 Lattice parameters of α - Al_2O_3 and c - ZrO_2 (μm)

Cell	Lattice parameter	This work	Theoretical	Experimental
α - Al_2O_3	a	4.78×10^{-4}	4.81×10^{-4} [26]	4.76×10^{-4} [28]
	c	13.03×10^{-4}	13.12×10^{-4}	12.99×10^{-4}
c - ZrO_2	a	5.09×10^{-4}	5.07×10^{-4} [27]	5.086×10^{-4} [29]

3 Results and discussion

3.1 Microstructure characteristics of three types of 7YSZ TBCs

Figures 2(a–c) show cross-sectional morphologies of the APS, EB-PVD, and PS-PVD 7YSZ TBCs. The cross-section of the APS TBCs exhibited a spongy microstructure with numerous irregularly and randomly distributed pores (Fig. 2(a)). Figure 2(b) showed that the typical microstructure of the EB-PVD TBCs had a fine straight columnar structure with through-pores. This unique columnar structure of the EB-PVD TBCs had good strain tolerance, but the thermal insulation performance was degraded compared to that of the APS TBCs [30]. The PS-PVD TBCs exhibited a loose feather-like columnar microstructure that was in turn further composed of loose micro-nano secondary crystals, as shown in Fig. 2(c). The PS-PVD TBCs differed from the EB-PVD TBCs in that the columnar crystals and gap size were larger but there were more branches of feather-like columnar crystals at the top of the coating, which exerted a shielding effect on the pores.

The surface characteristics of three 7YSZ TBCs are shown in Figs. 2(a₁–c₁). It can be seen

that the surface of APS 7YSZ TBCs exhibited the typical characteristics of a liquid-deposited microstructure with many solidification cracks around the lamellar structure. It is worth noting that the surface of APS TBCs was rough ($R_a = 5.378 \mu\text{m}$) because of the presence of semi-molten or un-melted powder during the deposition process, as shown in Figs. 2(a₁, a₂). The EB-PVD 7YSZ TBCs shown in Figs. 2(b₁, b₂) exhibited a flat surface ($R_a = 1.449 \mu\text{m}$) with a compact combined polyhedron structure. In contrast, the PS-PVD 7YSZ TBCs had a loose surface microstructure and a cauliflower-like structure ($R_a = 6.692 \mu\text{m}$), as shown in Figs. 2(c₁, c₂).

3.2 Al₂O₃ modification of PS-PVD 7YSZ TBC

To improve the strength of the surface layer on the PS-PVD 7YSZ TBCs, a dense overlay was prepared via Al₂O₃ modification, as shown in Fig. 3. The XRD patterns in Fig. 4 show that the surface of the PS-PVD 7YSZ TBCs exhibited an increased number of α -Al₂O₃ characteristic peaks after Al₂O₃ modification. In addition, a small Al₃Zr peak was observed at $2\theta = 28^\circ$ in the XRD pattern of the Al₂O₃-modified coating. This result is consistent with the Al and ZrO₂ in-situ reaction:

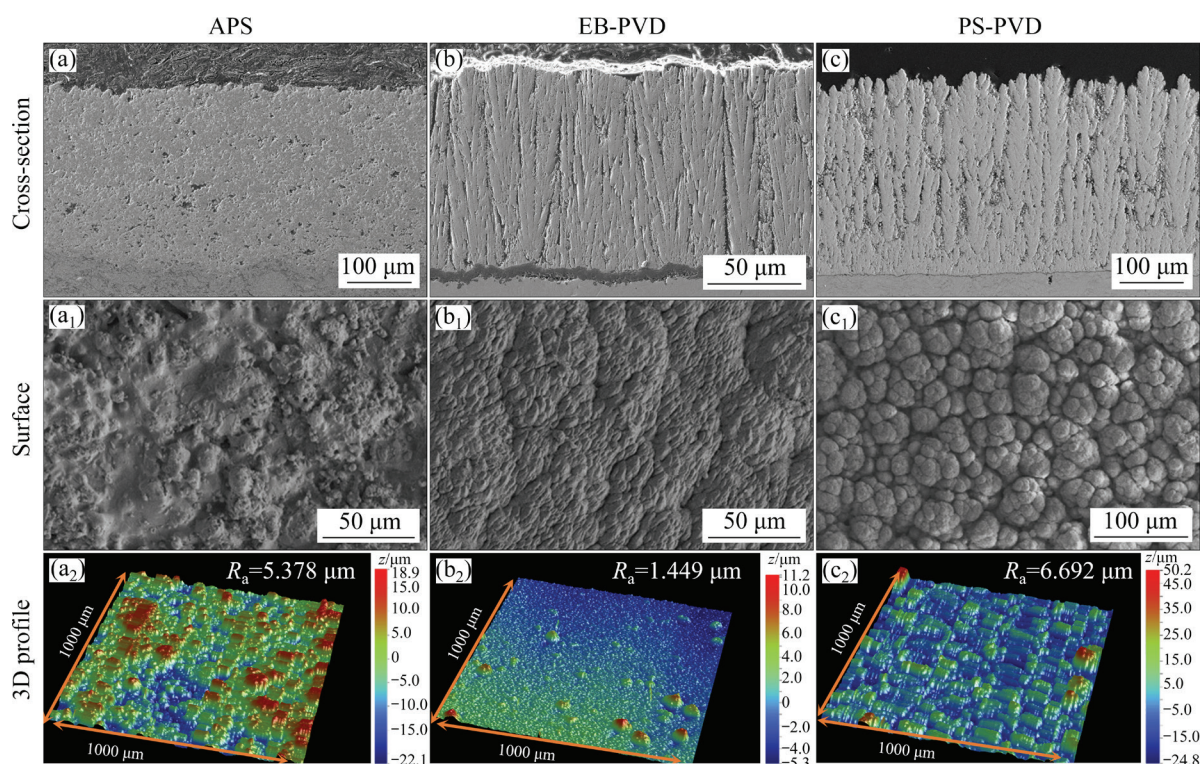


Fig. 2 SEM morphologies of 7YSZ TBCs

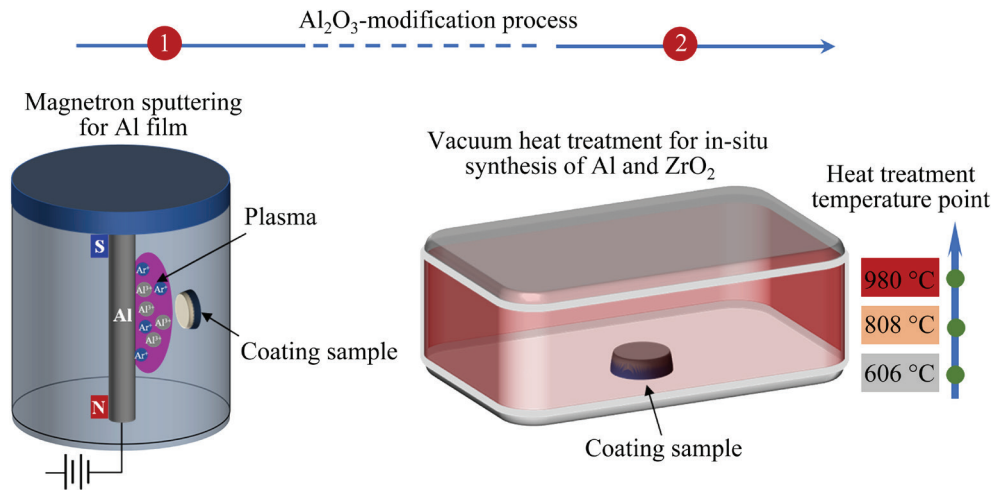


Fig. 3 Schematic of Al_2O_3 modification process

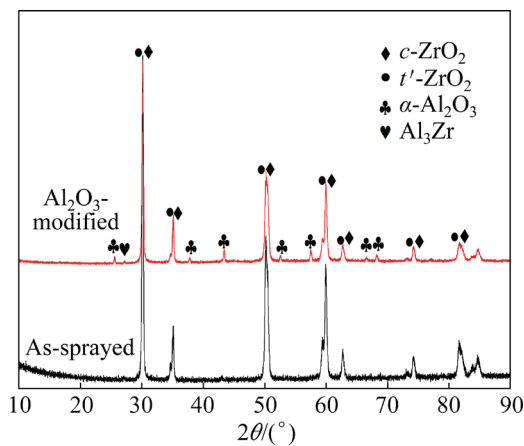


Fig. 4 XRD patterns of as-sprayed and Al_2O_3 -modified coatings

Figures 5(a, b) show the surface morphologies of the Al_2O_3 -modified PS-PVD 7YSZ TBC, which still retained a cauliflower-like microstructure. However, it can be seen that a denser covering was coated on the surface of the coating.

The cross-sectional microstructures of the Al_2O_3 -modified overlays are shown in Fig. 6. Figure 6(a) shows the cross-sectional backscatter morphology, which indicates a uniform and dense overlay with a thickness of approximately 5 μm . Figure 6(b) shows a combination image of the distributions of Al, Zr, O, and Y, which indicates that the overlay mainly contained O and Al. Meanwhile, the clear interface between Al and Zr indicates that the modified area was only in the shallow layer and had little effect on the feather-like columnar structure. The interface between the overlay and PS-PVD 7YSZ TBCs was characterized

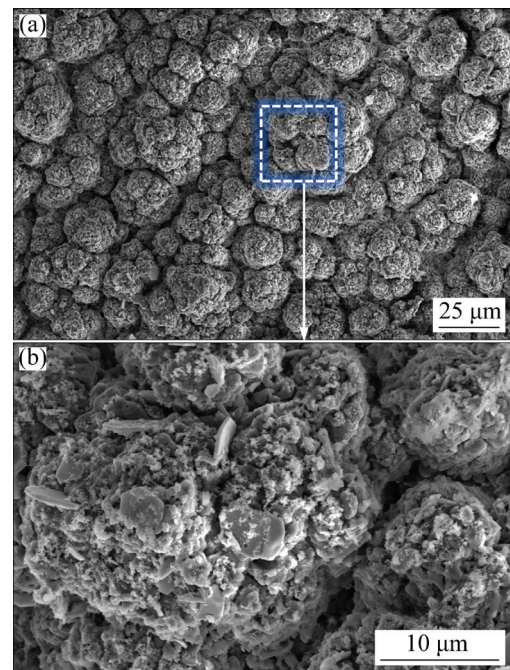


Fig. 5 Surface morphologies of Al_2O_3 -modified PS-PVD 7YSZ TBCs

using TEM. A high-quality and uniform continuous interface was observed in the bright-field image, as shown in Fig. 6(c). This interface was formed by the chemical reaction between the cover layer and 7YSZ coating described by Eq. (2). The high-quality interface is expected to improve the thermal shock resistance of the overlay without premature spalling. Figure 6(d) shows a high-resolution TEM image of the marked area in Fig. 6(c). Combined with the composition analysis of the overlay, it can be confirmed from the fast Fourier transform (FFT) image in Fig. 6(d) that the overlay was mainly composed of α - Al_2O_3 . It is worth noting that FFT

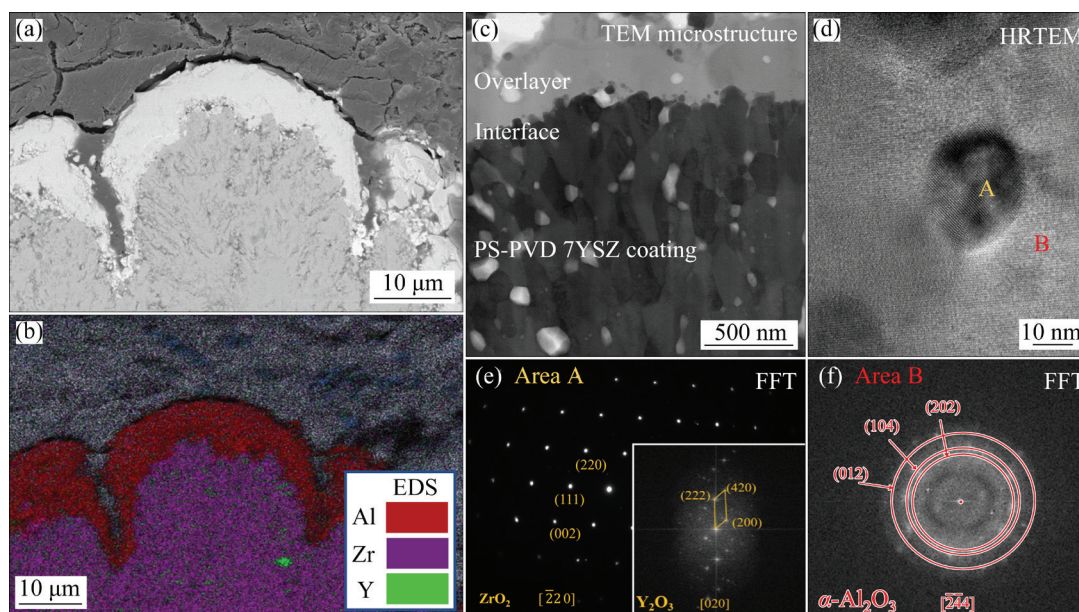


Fig. 6 Cross-sectional view of Al_2O_3 -modified PS-PVD 7YSZ TBCs: (a) Backscattered morphology; (b) EDS results for area in (a); (c) Bright-field image of interface between 7YSZ coating and overlay; (d–f) High-resolution view of marked area in (c) and FFT results for Areas A and B

image of Area B (Fig. 6(f)) indicates the presence of a small amount of Y_2O_3 near the interface due to the participation of ZrO_2 in the in-situ reaction Eq. (2) and Y_2O_3 precipitates from YSZ.

3.3 Modeling approach of $\alpha\text{-Al}_2\text{O}_3/c\text{-ZrO}_2$

To understand the binding at the modified interface, the obtained interface was modeled experimentally. Because $\alpha\text{-Al}_2\text{O}_3$ is the most stable phase and the other Al_2O_3 phases have more complex structures, only $\alpha\text{-Al}_2\text{O}_3$ was studied. ZrO_2 has three phases comprising the cubic, tetragonal, and monoclinic phases. The cubic phase of ZrO_2 is the high-temperature polymorph. By considering its interfacial cohesion and thermal resistance properties, $c\text{-ZrO}_2$ was chosen for the model. Because the $\alpha\text{-Al}_2\text{O}_3$ (012) and $c\text{-ZrO}_2$ (002) planes were observed in the experiment, $\alpha\text{-Al}_2\text{O}_3/c\text{-ZrO}_2$ interface bonding model was constructed.

The $\alpha\text{-Al}_2\text{O}_3$ (012) plane is a $4.78 \times 10^{-4} \mu\text{m} \times 5.15 \times 10^{-4} \mu\text{m}$ rectangle and the $c\text{-ZrO}_2$ (002) plane is a $3.60 \times 10^{-4} \mu\text{m} \times 3.60 \times 10^{-4} \mu\text{m}$ square. The $c\text{-ZrO}_2$ (002) plane was rotated by the lattice vector to form a $\sqrt{2} \times \sqrt{2} R 45^\circ c\text{-ZrO}_2$ (002) plane. The lattice mismatch is determined as [27]

$$\mu = 1 - \frac{2|\Omega|}{|A| + |B|} \quad (3)$$

where $|A|$ is the area of the $\alpha\text{-Al}_2\text{O}_3$ phase, $|B|$ is the area of the $c\text{-ZrO}_2$ phase, and Ω is the overlap area. The calculated lattice mismatch of $\alpha\text{-Al}_2\text{O}_3$ (012)/ $\sqrt{2} \times \sqrt{2} R 45^\circ c\text{-ZrO}_2$ (002) interface is 3.7%.

$|\text{O}-\text{Al}-\text{O}-\text{Al}-\text{O}|$ was selected as a period of $\alpha\text{-Al}_2\text{O}_3$ (012) and the Zr and O terminations were considered in the approximately $2.1 \times 10^{-4} \mu\text{m}$ thick $c\text{-ZrO}_2$ (002) layer with an atomic stacking order of $|\text{Zr}-\text{O}-\text{Zr}-\text{O}|$. The stackings considered at the combined interface are shown in Fig. 7. The All atom of $\alpha\text{-Al}_2\text{O}_3$ (012) is on top of the outermost Zr1 atom in the Zr termination of $c\text{-ZrO}_2$ (002) in the top model; the All atom of $\alpha\text{-Al}_2\text{O}_3$ (012) is on top of the second-outer O_2 atom in the Zr termination of $c\text{-ZrO}_2$ (002) in the hcp model; the All atom of $\alpha\text{-Al}_2\text{O}_3$ (012) is on top of the third-layer Zr3 atom of the Zr termination of $c\text{-ZrO}_2$ (002) in the top model. Similarly, the top, fcc, and hcp combinations are considered for the interface between $\alpha\text{-Al}_2\text{O}_3$ (012) and the $c\text{-ZrO}_2$ (002) O termination.

3.4 Erosion behavior of 7YSZ TBCs

Four TBCs comprising the APS, EB-PVD, PS-PVD, and Al_2O_3 -modified PS-PVD 7YSZ TBCs were subjected to erosion testing. Figure 8(a) shows the optical photographs of the TBC evolution

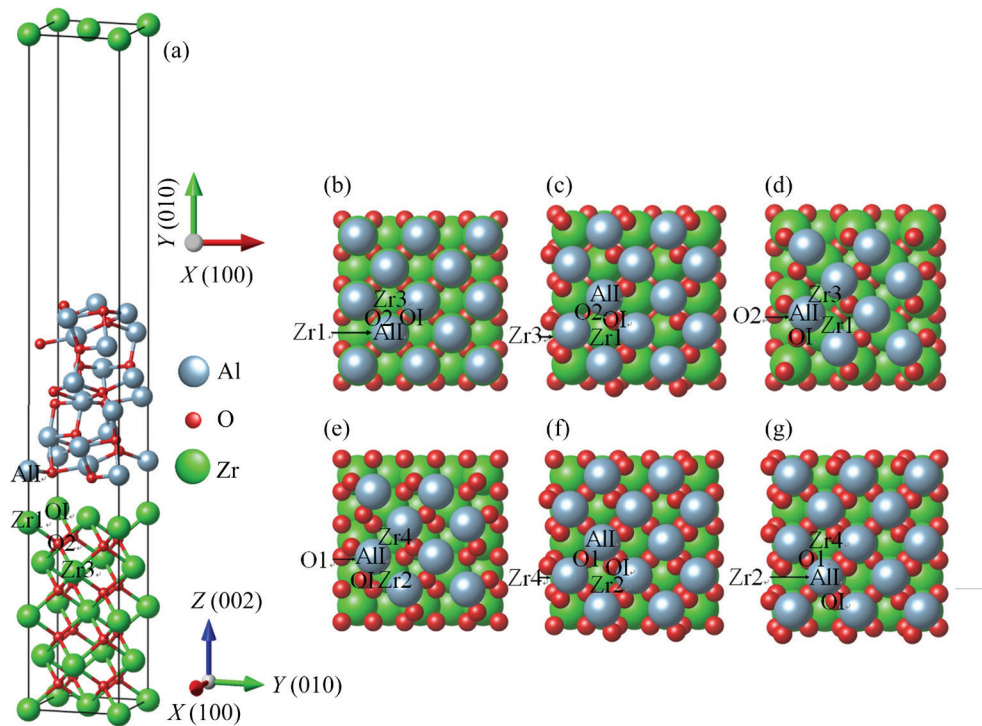


Fig. 7 $\text{Al}_2\text{O}_3/\text{ZrO}_2\text{-Zr}$ top configuration model (a); Top views of top (b, e), fcc (c, f), and hcp (d, g) models of $\text{Al}_2\text{O}_3/\text{ZrO}_2\text{-Zr}$ (b-d) and $\text{Al}_2\text{O}_3/\text{ZrO}_2\text{-O}$ (e-g) configuration (The plots were generated using VESTA [31])

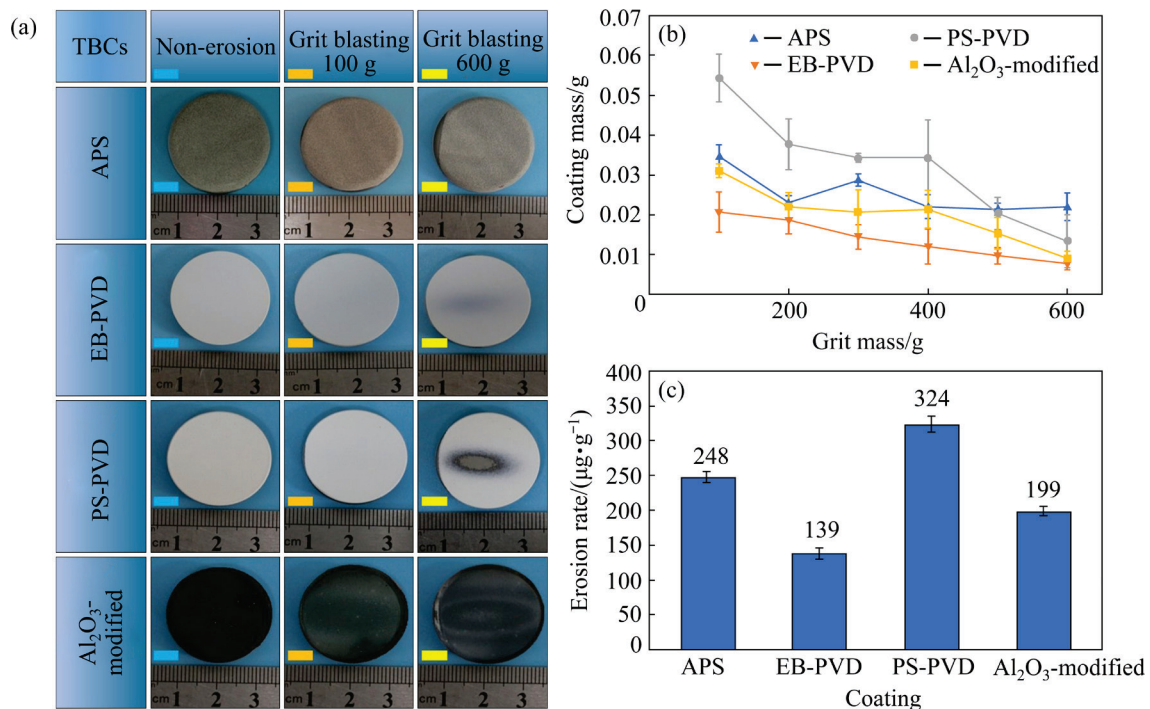


Fig. 8 Erosion test results for four types of TBCs: (a) Optical photographs of 7YSZ TBCs evolution after erosion; (b) Mass loss changes of 7YSZ TBCs; (c) Erosion rate based on erosion with 600 g corundum

during the erosion test. It can be seen that the tested surfaces of the APS and EB-PVD TBCs exhibited thinning in the erosion zone that has undergone erosion with 600 g corundum, but both coatings

remained intact. Similarly, the PS-PVD ceramic top coating in the erosion zone was eroded, which resulted in the exposure of the metal coating after erosion by 600 g corundum. Instead of a completely

damaged ceramic coating, a certain thickness of the coating was retained in the erosion zone of the Al_2O_3 -modified PS-PVD 7YSZ TBCs. These results provide preliminary evidence for the improved erosion resistance of the Al_2O_3 -modified TBCs compared to that of the as-sprayed TBCs.

The mass losses of the four coatings during the erosion tests are shown in Fig. 8(b). It can be seen that the PS-PVD TBCs had the largest mass loss at the beginning because of its loose feather-like structure, which led to fracturing of the feather columnar crystals at the early stage of erosion and a significant change in mass. The initial erosion mass loss of the modified coating was low because of the overlay protection and good interface bonding. The mass loss decreased with the passage of erosion time because of the compact bonding of the coating near the bond coat.

The erosion rates of the four tested TBCs after erosion with 600 g corundum are summarized in

Fig. 8(c). The erosion rates of the APS, EB-PVD, and PS-PVD 7YSZ TBCs were 248, 139, and 324 $\mu\text{g/g}$, respectively. The EB-PVD TBCs had the lowest erosion rate followed by the APS TBCs, while the PS-PVD TBCs had the highest erosion rate, which was more than two times that of the EB-PVD TBCs. Therefore, the PS-PVD TBCs had poor erosion performance. Notably, the Al_2O_3 -modified PS-PVD 7YSZ TBCs exhibited significantly improved erosion performance with a decreased erosion rate of 199 $\mu\text{g/g}$.

The surface morphologies of the four 7YSZ TBCs after erosion are shown in Fig. 9. Figure 9(a) shows the degradation of the APS TBCs surface, in which fracturing of the lamellar structure on the surface was the main damage behavior. Similarly, the large number of erosion grooves and compaction areas on the surface of the EB-PVD TBCs indicate that the cutting mode was its main damage behavior, as shown in Fig. 9(b).

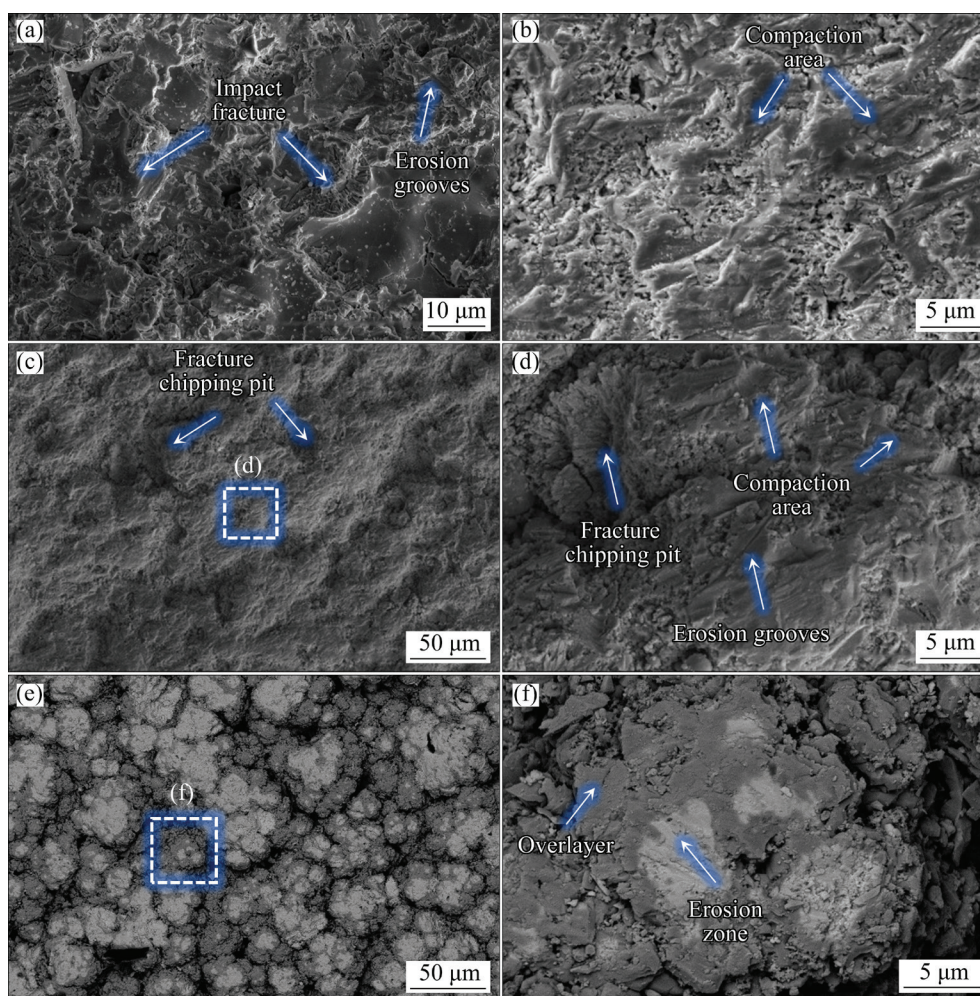


Fig. 9 Surface morphologies of 7YSZ TBCs after erosion: (a) APS TBCs; (b) EB-PVD TBCs; (c, d) PS-PVD TBCs; (e, f) Al_2O_3 -modified TBCs

Figures 9(c, d) show the degraded surfaces of the PS-PVD TBCs, which also exhibited erosion grooves and compaction area formation. However, unlike the EB-PVD TBCs, there was a large number of fracture spalling pits on the PS-PVD TBCs formed by the fracture of the columnar crystals or cauliflower-like structures after continuous impact. This indicates that the erosion damage mode of the PS-PVD 7YSZ TBCs was a mixed cutting and columnar crystal fracture mode. The overlay on the Al_2O_3 -modified PS-PVD TBCs blocked the erosive particles from directly damaging the feather-like structure before it was worn away, as shown in Figs. 9(e, f).

The APS and EB-PVD TBCs exhibited a thickness variation across the cross-sectional areas after erosion in which small impact fatigue cracks were observed on the APS coatings, as shown in Figs. 10(a, b). Figures 10(c, d) show the cross-sectional images of the edge and erosion zones of

the PS-PVD TBCs. Significant fracture morphology could be observed on the top of the feather-like columnar crystals after erosion. Moreover, transverse cracks were formed on the feather-like columnar crystals inside the coating. These cracks were similar to the columnar crystal fractures that were already present before the erosion. Correspondingly, only a few feather-like columnar crystal fracture areas were observed on the top of the Al_2O_3 -modified PS-PVD TBCs, and no obvious transverse cracks were found inside the coating, as shown in Figs. 10(e, f). In other words, the proportion of columnar crystal fracture mode that occurred during the erosion of the Al_2O_3 -modified PS-PVD TBCs decreased.

3.5 Mechanical properties of TBCs after erosion

The erosion degradation of TBC performance is irreversible. From the above experimental results, it is found that the coatings experienced the two

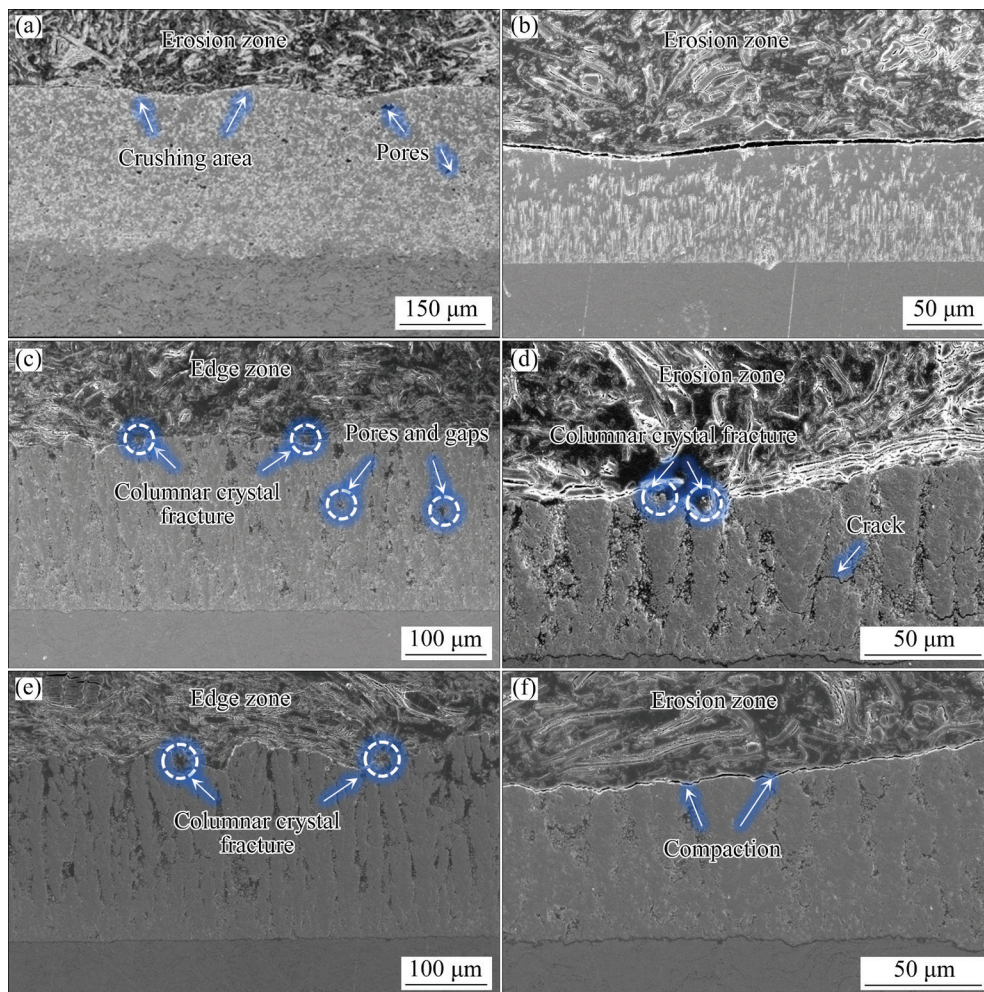


Fig. 10 Cross-sectional morphologies of 7YSZ TBCs after erosion: (a) APS TBCs; (b) EB-PVD TBCs; (c, d) PS-PVD TBCs; (e, f) Al_2O_3 -modified TBCs

failure modes of cutting and columnar crystal fracture during the erosion process. The particle-cutting effect is a common form of erosional damage. In general, the erosion rate of a target material is closely related to its hardness. The relationship between the hardness and erosion rate is usually given by the following relation of JANOS et al [32]

$$v = 10^{10} a H_t^{-b} \quad (4)$$

where v is the erosion rate, H_t is the Vickers microhardness of the target material, and a and b are constants (>0). Therefore, the higher the microhardness of the target material, the lower the erosion rate is.

To determine the hardness of the TBCs, nanoindentation tests were performed on the lamellar and columnar (APS, EB-PVD, and PS-PVD) structures, and the results are shown in Fig. 11. Figures 11(a–c) show the displacement–load curves under a maximum load of 20 mN, and Fig. 11(d) shows the hardness and indentation depth

values at the cross-section of the coating. The hardness of the liquid-deposited APS TBCs reached HV 1271 with an indentation depth of 163 nm, while the hardness values of the PS-PVD and EB-PVD TBCs deposited by vapor deposition were HV 699 and HV 669, respectively. The indentation depth of the PS-PVD is significantly larger than that of the EB-PVD TBCs. The actual erosion rates of the three coatings are inconsistent with Eq. (4) because the fracture of the target structure is also an extremely important factor in erosion damage. Therefore, the strength of the target structure should also be discussed.

From the cross-sectional view of the coating in Fig. 2, it can be seen that the feather-like columnar crystals of the PS-PVD TBCs were approximately 16 μm wide and had large intercolumn gaps. Therefore, only several or single feather-like columnar crystals could be formed on the target surface when it was impacted by a single particle ($D_{50}=49 \mu\text{m}$). However, the feather-like columnar crystals were also composed of loose secondary

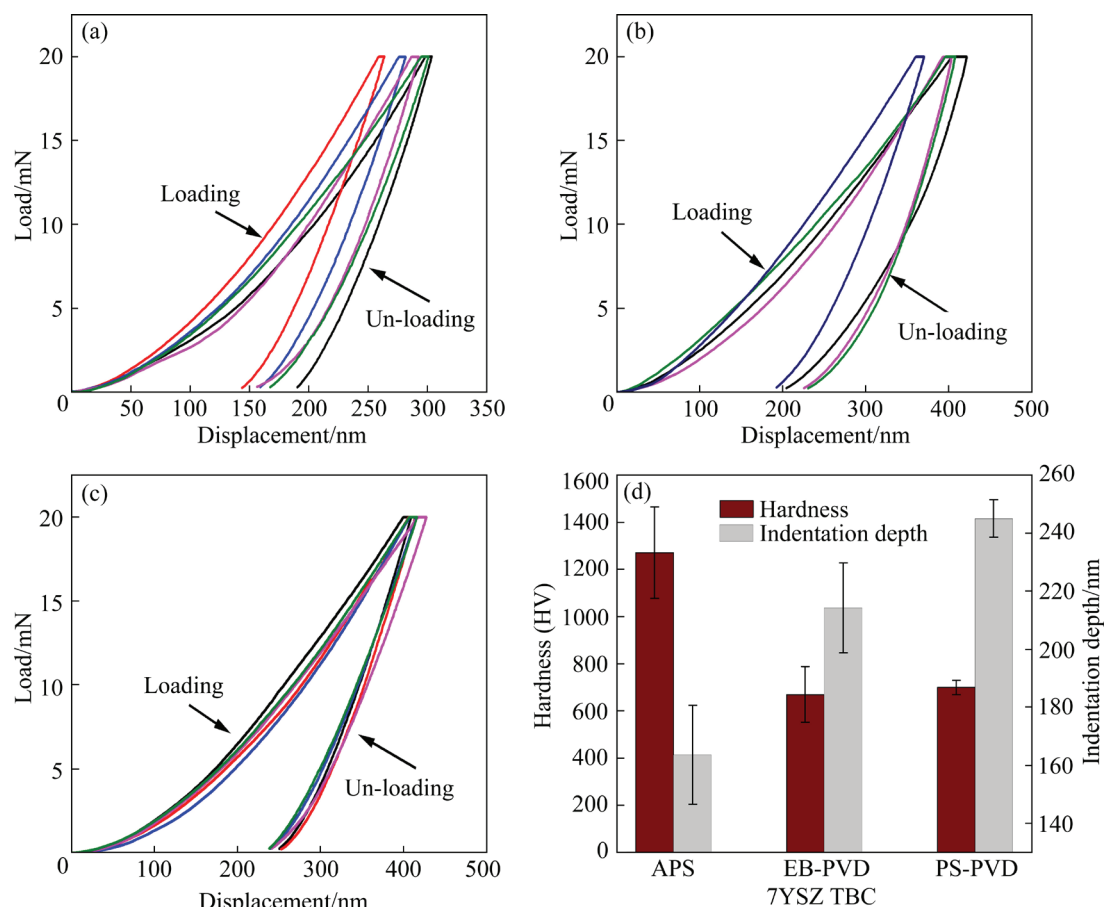


Fig. 11 Evaluation of 7YSZ TBCs by nanoindentation: (a) Displacement–load curves of APS TBCs; (b) Displacement–load curves of EB-PVD TBCs; (c) Displacement–load curves of PS-PVD TBCs; (d) Coating hardness and indentation depth

crystals, which resulted in poor impact strength of the target structure. Therefore, numerous columnar crystal fractures occurred in the morphologies shown in Fig. 10. Moreover, the fracture chipping pit exposed additional loose target surface, which aggravated the erosion of coating. Consequently, the PS-PVD 7YSZ TBCs with the feather-like columnar structures exhibited the worst erosion performance. Although the target structure of the EB-PVD 7YSZ TBCs had low hardness, the coating comprised tightly bonded fine straight columnar crystals and no significant columnar crystal structure fracture was found. Therefore, the target structure of the EB-PVD TBCs can be regarded as a monolithic block with a small area in resisting particle erosion. During the erosion process, the EB-PVD TBCs were mainly thinned by cutting. After the initial period of erosion, the loose structure of the coating surface was compacted and the erosion rate gradually decreased. In fact, Fig. 10 shows that the EB-PVD TBCs experienced more thinning than the other two coatings, indicating that the effect of cutting on the EB-PVD TBCs were greater than that on the APS coating. However, the numerous semi-molten and un-melted powder particles deposited on the surface of the APS TBCs produced island structures that were vulnerable to particle impact, which increased the erosion rate of the APS TBCs. In addition, the erosion target of the APS TBCs had many pores and cracks between the

lamellar structures, which negatively impacted the erosion resistance performance. Therefore, under the combined damage of cutting and fracture of the target structure, the coating erosion rate of the EB-PVD TBCs was smaller than that of the APS TBCs, which was in turn smaller than that of the PS-PVD TBCs.

To characterize the effect of the Al_2O_3 modification on the surface strength of the PS-PVD TBCs, a scratch test was performed on the surfaces of the as-sprayed and Al_2O_3 -modified TBCs and the results are shown in Fig. 12. The cauliflower-like structure on the surface of the as-sprayed PS-PVD TBCs was destroyed by the compression of the scribe to form a scratch. The scratch surface exhibited a compacted morphology with cracks perpendicular to the scratch direction, as shown in Figs. 12(a, b). The Al_2O_3 -modified PS-PVD 7YSZ TBCs exhibited less damage under the compression of the scribe and only a small area of the overlay was scratched, as shown in Figs. 12(c, d). This indicates that the coating surface was effectively strengthened by the Al_2O_3 modification overlay. In fact, $\alpha\text{-Al}_2\text{O}_3$ has an extremely high hardness of 9 on the Mohs hardness scale. The overlay composed of dense $\alpha\text{-Al}_2\text{O}_3$ therefore had a strong protective layer that protected the coating from cutting damage by erosive particles and strengthened the top of the feather-like columnar crystals against fracture. It is worth noting that the overlay was too

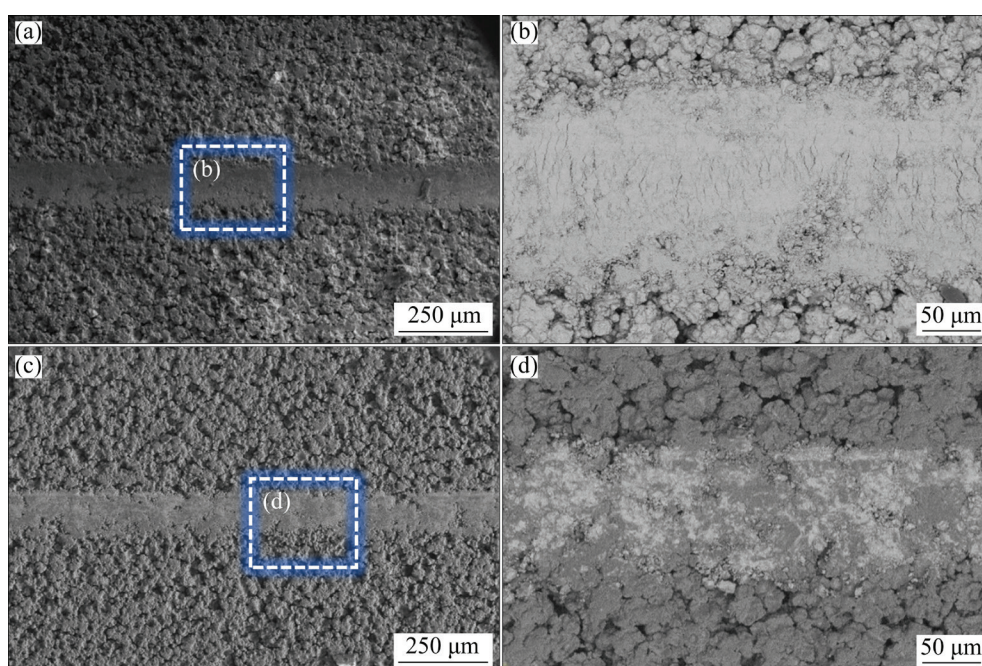


Fig. 12 Surface scratch morphologies of PS-PVD 7YSZ TBCs: (a, b) As-sprayed TBCs; (c, d) Al_2O_3 -modified TBCs

thin to prevent particles from affecting the columnar crystals in the core zone of the coating. Consequently, columnar crystal fracture under particle impact in the Al_2O_3 -modified PS-PVD TBCs was still the main factor for its high erosion rate.

The erosion failure mechanisms of the APS, EB-PVD, PS-PVD, and Al_2O_3 -modified PS-PVD 7YSZ TBCs are schematically shown in Fig. 13. The main erosion damage mode of the APS TBCs was the fracture of the islands on the surface and the lamellar structures and the particles had a weak cutting effect on the coating. The EB-PVD 7YSZ TBCs had a uniform and dense microstructure in which the main erosion damage mode was cutting by the particles. The PS-PVD 7YSZ TBCs had a loose microstructure and low hardness, which resulted in both cutting damage and columnar crystal fracture damage in the erosion process. Moreover, the cutting rate in the PS-PVD TBCs was intensified by the exposure of a new loose surface after columnar crystal fracture. Therefore, PS-PVD 7YSZ TBCs exhibited the highest erosion rate. Correspondingly, Al_2O_3 -modified PS-PVD 7YSZ TBCs provided a strong protective overlay that weakened the damage due to both the cutting and columnar crystal fracture damage modes and significantly improved the erosion resistance.

3.6 Interface adhesive energy of $\alpha\text{-Al}_2\text{O}_3/\text{c-ZrO}_2$

To gain a deeper understanding of the reasons for the improved erosion resistance of the Al_2O_3 -modified PS-PVD TBCs, the interface adhesive energy of the Al_2O_3 -modified PS-PVD TBCs was calculated from first principles. The interface adhesive energy [33] is the energy required per unit area to reversibly divide an interface into two free surfaces and reflects how tightly the interface is integrated and its mechanical properties. A larger interface adhesive energy implies a closer interface combination. The interfacial adhesive energy (W_{ad}) is given by

$$W_{\text{ad}} = \frac{1}{A} (E_1 + E_2 - E_0) \quad (5)$$

where A is the interface area, E_0 is the total energy of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ interface slab, E_1 is the energy of the Al_2O_3 slab models combined at the interface, and E_2 is the energy of the ZrO_2 slab models combined at the interface. Parameter consistency was maintained during the calculation to eliminate the error.

As given in Table 3, the highest interface adhesive energy of 3.60 J/m^2 for the $\text{Al}_2\text{O}_3/\text{ZrO}_2\text{-Zr}$ termination occurred for the hcp configuration. The interface adhesive energy of the fcc configuration is similar to that of the hcp configuration. The interface adhesive energy of 3.88 J/m^2 for the

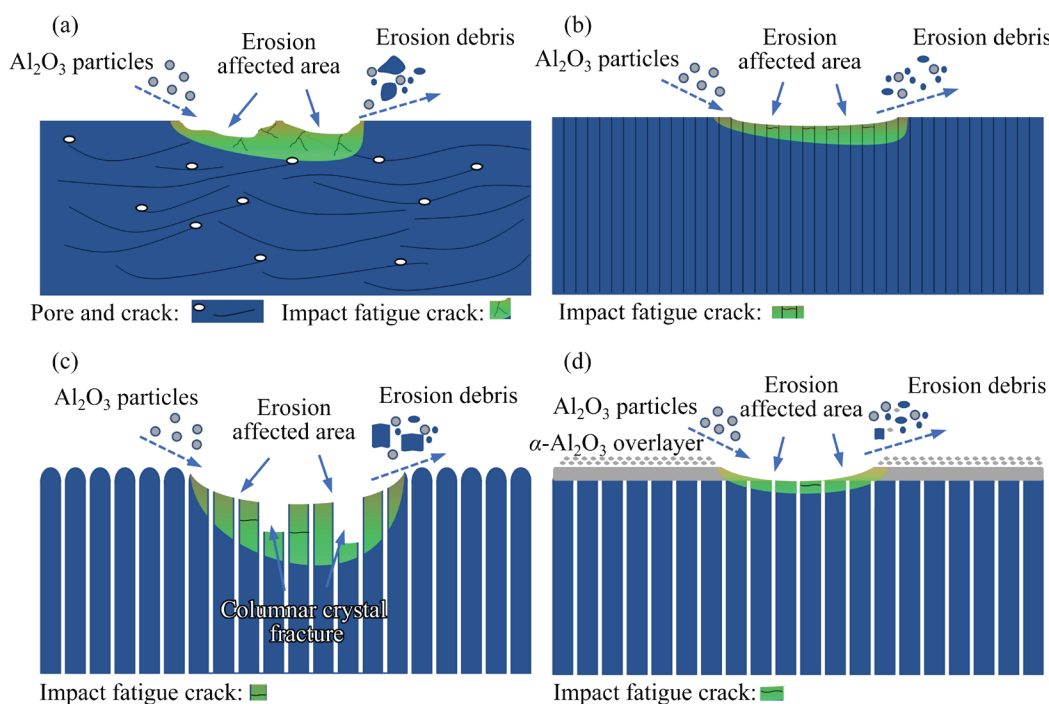


Fig. 13 Schematic diagrams of 7YSZ TBCs erosion mechanisms: (a) APS TBCs; (b) EB-PVD TBCs; (c) PS-PVD TBCs; (d) Al_2O_3 -modified TBCs

Table 3 Interface adhesive energy, interface distance, interface bond, and bond length of α -Al₂O₃ (012)/ $\sqrt{2} \times \sqrt{2} R 45^\circ$ *c*-ZrO₂ (002) with different terminations and stackings

Termination	Stacking site	Adhesive energy/(J·m ⁻²)	Interface distance/ μ m	Bond	Bond length/ μ m
Al ₂ O ₃ /ZrO ₂ -Zr	top	3.55	1.91×10^{-4}	O—Zr	2.12×10^{-4}
	fcc	3.59	1.92×10^{-4}	O—Zr	2.12×10^{-4}
	hcp	3.60	1.89×10^{-4}	O—Zr	2.12×10^{-4}
Al ₂ O ₃ /ZrO ₂ -O	top	3.88	1.79×10^{-4}	Al—O	1.80×10^{-4}
	fcc	3.55	1.96×10^{-4}	Al—O	1.82×10^{-4}
	hcp	3.75	2.14×10^{-4}	Al—O	1.79×10^{-4}

Al₂O₃/ZrO₂-O termination occurred for top configuration. This value is similar to 3.54 J/m² in Ref. [34] and larger than 1.208 J/m² in Ref. [35]. The higher interface adhesive energy of Al₂O₃/ZrO₂ than that of ZrO₂/Ni (2.011 J/m²) [36] indicates that the Al₂O₃/ZrO₂ interface is tightly bound. The interface adhesive energy of the top configuration of Al₂O₃/ZrO₂-O is the highest, indicating that the interface is bound most closely with this configuration. The shortest bond length of 1.80×10^{-4} μ m occurs between the Al atom in Al₂O₃ and the O atom in ZrO₂, indicating that the Al metal atom is bonded strongly to the O atom.

4 Conclusions

(1) The erosion damage modes of the APS, EB-PVD, and PS-PVD 7YSZ TBCs were fracture of the lamellar structure, cutting, and a mixed cutting and columnar crystal fracture mode, respectively.

(2) The EB-PVD TBCs, which had a flat surface and dense structure, exhibited the lowest erosion rate of 139 μ g/g. In contrast, the APS and PS-PVD TBCs exhibited the high erosion rates of 248 and 324 μ g/g due to the fracture of the surface or internal structure, respectively. The Al₂O₃ overlay effectively improved the surface strength and weakened the cutting and impact of the erosion particles, and reduced the erosion rate of the Al₂O₃-modified PS-PVD TBCs to 199 μ g/g.

(3) Six interface binding models with different termination ends and stackings were constructed. By calculating the interface binding energy, the interface with the best binding strength was determined to be the one with an Al—O bond at the top configuration interface of the Al₂O₃/ZrO₂-O termination, which was the most stable. These

computational results indicate that the Al₂O₃ overlay cannot be easily peeled off from the ZrO₂ substrate.

CRediT authorship contribution statement

Zi-fan WANG: Conceptualization, Methodology, Data acquisition, Data analysis, Writing – Original draft, Writing – Review & editing; **Jia-feng FAN:** Data analysis, Experimental support, Writing – Original draft; **Kai-wen KANG:** Software, Investigation, Writing – Original draft; **Jian WU:** Data analysis, Experimental support; **Min LIU:** Supervision; **Ke-song ZHOU:** Supervision; **Qian ZHANG:** Discussion, Supervision; **Zhi-bo ZHANG:** Discussion, Supervision; **Xiao-qiang LI:** Discussion, Supervision; **Xiao-feng ZHANG:** Resources, Methodology, Discussion, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Al_2O_3 改性等离子喷涂–物理气相沉积热障涂层的 异物损伤行为及失效机理

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摘要: 由外来异物损伤引起的颗粒冲蚀是制约热障涂层使用寿命的重要因素。为了提高等离子喷涂–物理气相沉积(PS-PVD)热障涂层的耐冲蚀性能, 采用磁控溅射和真空热处理在 PS-PVD 喷涂的 7YSZ 热障涂层表面制备一层致密的 $\alpha\text{-Al}_2\text{O}_3$ 。系统研究热障涂层的异物损伤行为, 并采用第一性原理计算对 $\alpha\text{-Al}_2\text{O}_3/c\text{-ZrO}_2$ 界面进行研究。结果表明, PS-PVD、大气等离子喷涂(APS)和电子束–物理气相沉积(EB-PVD)热障涂层的冲蚀质量损失率分别为 324、248 和 139 $\mu\text{g/g}$, 而 Al_2O_3 改性的 PS-PVD 热障涂层的冲蚀质量损失率降至 199 $\mu\text{g/g}$ 。此外, 在 $\text{Al}_2\text{O}_3/\text{ZrO}_2\text{-O}$ 的顶部构型模型中观察到的界面结合能最高(3.88 J/m^2), 远高于 ZrO_2/Ni (2.011 J/m^2), 使界面结合性能得以提高。

关键词: 热障涂层; 等离子喷涂–物理气相沉积; Al_2O_3 改性; 外来异物损伤; 第一性原理

(Edited by Bing YANG)