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ARTICLE

Nano-composite Structured Environmental Barrier Coatings Prepared by Plasma Spray-Physical Vapor Deposition and Their Thermal Cycle Performance

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Abstract: Environmental barrier coatings (EBCs) consisting of a tri-layer structure (Si/mullite/Yb_2SiO_5) were prepared on SiC/SiC ceramic matrix composite (CMC). For decreasing the degradation of water-oxygen corrosion of SiC/SiC CMC, a novel EBCs fabrication method of plasma spray-physical vapor deposition (PS-PVD) was proposed in this work. Prior to EBCs preparation, agglomerated Yb_2SiO_5 powders was fabricated by spray dryer. After that, dense EBCs were fabricated by PS-PVD technique, where the Yb_2SiO_5 coating with laminar and columnar composited structure was achieved. And the deposition diagram of this special structure was presented. Besides, the thermal cycle performance of PS-PVD EBCs was tested from 1300 °C to room temperature in water. Results show that no apparent spallation appears after 30 cycles, indicating that the EBCs have a good thermal shock performance.

Key words: EBCs; PS-PVD; thermal cycle; Yb_2SiO_5 coating

Developing advanced aero-engine with high performance has received persistent attention for decades. High inlet temperature is an important factor in achieving high thrust-to-weight ratio and high thermal efficiency for turbine engines [1,2]. Turbine inlet temperature (TIT) of 1650 °C corresponds to a thrust–to-weight ratio of 8. For attaining the thrust-to-weight ratio of 10~12, TIT of 1850 °C is needed[3]. Ni-based superalloys are widely used as hot components in turbine engines. But their upper limit service temperature is ~1075 °C. Thus, the current superalloy cannot satisfy the requirement of advanced aero-engine[4-6]. Silicon carbide (SiC) fiber-reinforced SiC ceramic matrix composite (SiC/SiC CMC) has been envisioned as alternative next generation turbine engine hot-component material due to its low density, superior strength and oxidation resistance at high temperature[7]. But it will meet the rapid recession in a fast combustion environment (water-oxygen, glassy melts, etc), causing a degradation in its advanced performances[8].

Aforementioned problems can be alleviated by environment barrier coatings (EBCs) which can prevent SiC/SiC CMC from reacting with water-oxygen. Thus, EBCs are required for the implementation to avoid the loss of the protective SiO_2 thermally grown oxide through reactions with water vapor in the combustion gases[9,10]. Candidate materials for EBCs must be resistant to water-oxygen volatilization, and have a coefficient of thermal expansion that is well matched with the SiC/SiC CMC to enable their application as strain-tolerant[11]. Additionally, the EBCs should have a low recession rate and be thermochemically stable in turbine engine environments. It must completely protect surface from oxidize penetration, and

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remain adhered to the substrate during prolonged thermal cyclic exposure and thermal shock loading. A tri-layer coating containing a silicon bond coating, a mullite intermediate layer and an ytterbium monosilicate (Yb_2SiO_5) top coating has recently attracted significant interests[12,13]. The bond coating is intended to impede the transport of any oxygen or water vapor that penetrates the outer coating layers by generating a protective thermally grown oxide. The intermediate layer mullite serves as an oxidizing element diffusion barrier while avoiding potential solid-state reactions between thermally grown silica on bond coating and top coating. The top coating Yb_2SiO_5 serves as a low silica activity compound with a very low recession rate in water-oxygen environments.

The tri-layer EBCs were usually deposited using an air plasma spray (APS)[12,14-16]. But in this investigation, the plasma spay-physical vapor deposition (PS-PVD) was used to deposit the bond coating Si, intermediate coating mullite and top coating Yb_2SiO_5. PS-PVD is a novel coating process based on low pressure plasma spray. Unlike conventional techniques, deposition takes place from both liquid splat and vapor phase[17,18]. This offers new opportunities to obtain advanced microstructures, thus meeting the growing demands of EBCs. Due to its electrical current up to 3000 A, plasma gas flow up to 200 L/min, and input power level of 180 kW in PS-PVD, the plasma plume should be expanded to a length more than 2000 mm and 400 mm in diameter. Thus, with appropriate parameters, feedstock powder may be evaporated. And dense EBCs can be obtained. Low-porosity EBCs are important guarantee for avoiding infiltration of oxygen and vapor water into SiC/SiC CMC substrate.

1 Experiment

Before preparation of EBCs, the Yb_2SiO_5 powders were self-prepared through spray dryer equipment (Mobile Minor^{TM}). Then tri-layers EBCs (Si/mullite/Yb_2SiO_5) were produced by PS-PVD on SiC/SiC CMC substrate, where the EBCs system consisted of a ~50 μm thick Yb_2SiO_5 top coating and a ~50 μm thick mullite (commercial products from Xinte Ltd, Fig.1a) oxidation resistant layer, and both of them were sprayed on a substrate heated to 900 °C. And a ~50 μm thick silicon (commercial products from Xinte Ltd, Fig.1b) layer, sprayed on an heated substrate (1000 °C), was used to improve the bonding between the mullite coating and the SiC/SiC substrate. The preparation parameters of EBCs through PS-PVD are shown in Table 1.

Thermal cycle property is one of the important performances for EBCs. During the tests, the EBCs specimens were heated in an air furnace at an evaluated temperature of 1300 °C for 10 min and then directly water-quenched to room temperature for 5 min. The heating-up and subsequent cooling down is a thermal cycle. Following testing, the specimens were mounted and polished using standard metallographic techniques and examined using field-emission scanning electron microscope(FE-SEM). Besides, the samples were examined using transmission electron microscope (TEM, Titan Themis 200, FEI) assisted with FIB (focused ion beam, SMI3050MS2, SⅡ) to investigate the microstructure of EBCs.

2 Results and Discussion

2.1 Agglomerated Yb_2SiO_5 powder preparation

Agglomerated powders with a certain size distribution, good flow ability, etc are required in EBCs prepared by PS-PVD. Properties of the powders are determined by morphology and composition of powders. One of the most effective and convenient methods of producing agglomerated powders with narrow size distribution and controllable morphology and composition is spray drying. The spray drying process is usually described in three steps[19,20]: (1) droplet generation (spraying), (2) droplet-to-particle conversion by drying

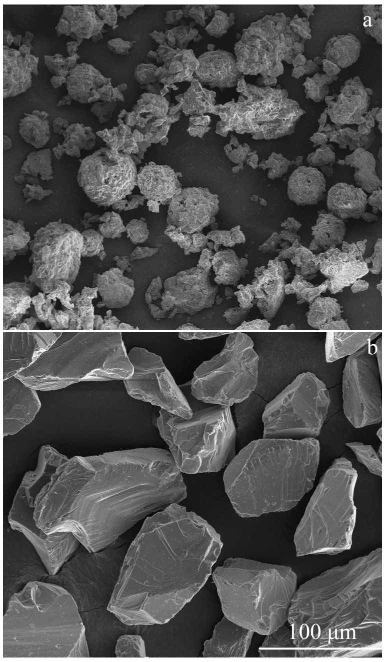

Fig.1 Micrographs of powders: (a) agglomerated and sintered mullite and (b) Si

Table 1 Parameters of EBCs (Si/mullite/Yb_2SiO_5) fabricated by PS-PVD

Layer	Current/ A	υ(Ar)/ L·min^{-1}	υ(He)/ L·min^{-1}	υ(H_2)/ L·min^{-1}	Feed rate/ g·min^{-1}	Stand-off distance/mm	Pre-heating temperature/°C	Chamber pressure/×10^2 Pa
Si	1650	110	-	6	9	350	1000	4.0
Mullite	2600	70	50	-	11	1000	900	1.5
Yb_2SiO_5	2600	100	20	-	13	1000	900	1.5

(solvent evaporation), and (3) particle collection (separation from drying gas). The diagram of spray dryer equipment (Mobile Minor^{TM}) is shown in Fig.2, including rotary nozzle, drying chamber, collection vessel and filter, etc. The mixed flow arrangement is used for coarse free-flowing powders and heat stable products. The atomized droplets were dried throughout their movement in the drying chamber and agglomerated powders were collected in the cyclone jar. Finer and lighter powders were separated with the air steam collected by filter.

In order to obtain dense Yb_2SiO_5 coating through PS-PVD, the original powders should be optimized to ensure that the particles can be melted sufficiently or evaporated. The original Yb_2SiO_5 powders were produced by solid-sate synthesis. And the XRD analysis of Yb_2SiO_5 powders is presented in Fig.3, indicating a high purity. The SEM image of synthesized Yb_2SiO_5 powders is shown in Fig.4a, where the size distribution of Yb_2SiO_5 powders ranges from 1 μm to 3 μm. Prior to spray drying, Yb_2SiO_5 slurry should be prepared. After that, the Yb_2SiO_5 slurry was spray dried and the prepared agglomerated Yb_2SiO_5 powders is shown in Fig.4b. The size distribution of agglomerated Yb_2SiO_5 powders is 10~45 μm.

2.2 EBCs preparation

In the EBCs materials, the Si and mullite powders are commercial products and the Yb_2SiO_5 powders were self-prepared. The EBCs (Si/mullite/Yb_2SiO_5) were fabricated by PS-PVD and the surface microstructures are shown in Fig.5. The SiC/SiC CMC was taken as substrate and its surface morphology is shown in Fig.5a. The substrate was interwoven with SiC fibers. Pores with different sizes are located in the substrate. Then, after EBCs deposition, the pores are filled with EBCs, as seen in Fig.5b. And surface microstructure of Yb_2SiO_5 coating is shown in Fig.5c, where no cracks and pores are observed.

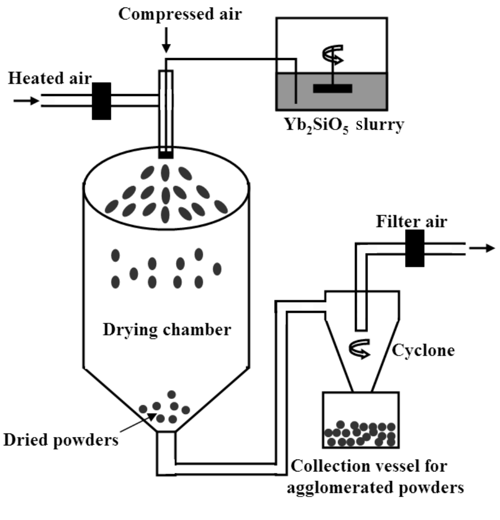

Fig.2 Diagram of spray dryer

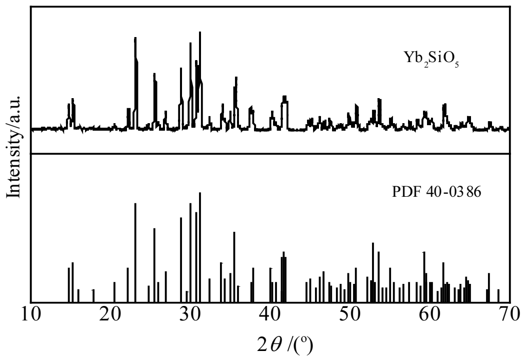

Fig.3 XRD patterns of solid-state synthesized Yb_2SiO_5

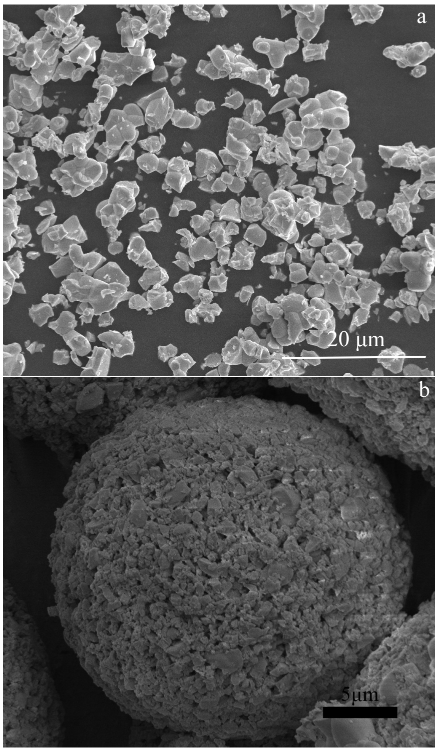

Fig.4 Micrographs of powders: (a) original solid-state synthesized powders and (b) agglomerated powders

The cross-sectional microstructures of EBCs are shown in Fig.6. Fig.6a indicates that no apparent pores and cracks are formed in the Si and Yb_2SiO_5 coating. On the contrary, lots of closed pores are generated in mullite coating. Melting point of Si material is about 1410 °C and its thermal conductivity is 150 W/(m·K). Due to high energy density and high velocity of plasma jet in O3CP plasma gun, the Si powders can be melted sufficiently. The molten Si splats will have a close packing when impacting the substrate. Thus, dense interface of Si and SiC/SiC substrate can be obtained, as indicated in Fig.6b. In contrast to mullite material, its melting point and thermal conductivity are ~1850 °C and ~150 W/(m·K), respectively. Moreover, the mullite powders are agglomerated and sintered. When the powders are injected into plasma gun, most of the large-sized powders cannot be fragmented into small-sized particles. The inner of large-sized powders cannot be melted

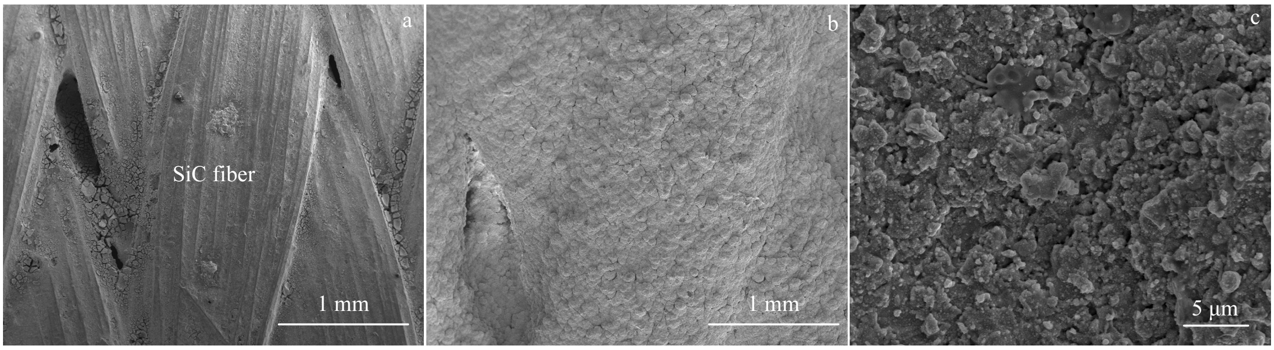

Fig.5 Surface morphologies: (a) SiC/SiC substrate, (b) substrate coated with EBCs, and (c) Yb_2SiO_5 coating

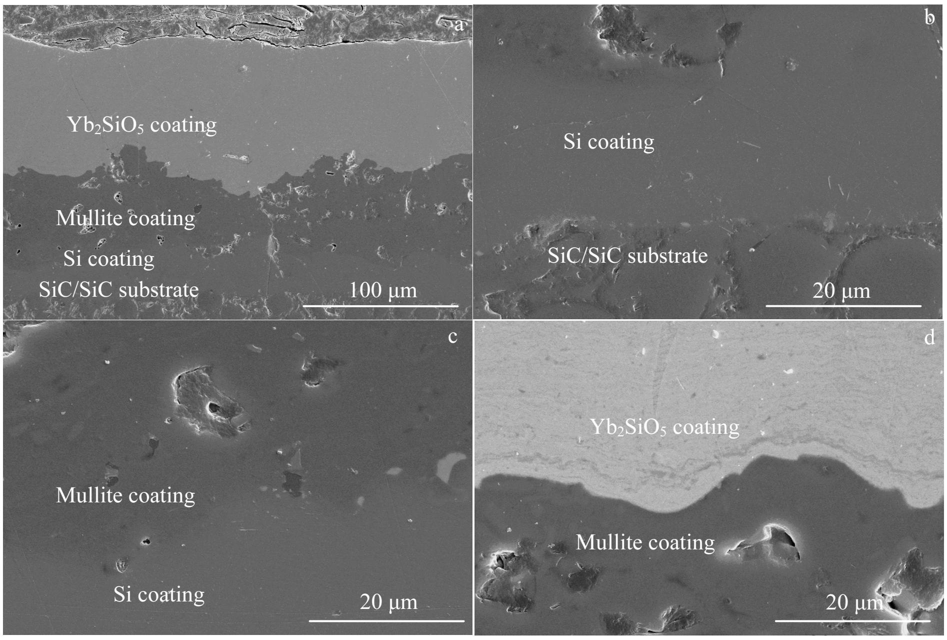

Fig.6 Cross-sectional microstructure of EBCs: (a) tri-layer coatings consisting of Si, mullite and Yb_2SiO_5, (b) interface of Si coating and SiC/SiC substrate, (c) interface of mullite and Si coating, and (d) interface of Yb_2SiO_5 and mullite coating

sufficiently, so that these molten droplets cannot be spread fully. Therefore, few closed pores are formed and the interface of mullite and Si coating is shown in Fig.6c. The size distribution of original powder in agglomerated Yb_2SiO_5 powder ranges from 1 μm to 3 μm. Besides, due to the absence of sintering process, the agglomerated Yb_2SiO_5 powders can be fragmented into small-sized particles quickly when injected into a plasma gun[21]. The small particles can be melted or even evaporated in the plasma jet despite the high melting point of ~1900 °C. Thus, dense Yb_2SiO_5 coating can be obtained and the dense interface between Yb_2SiO_5 and mullite coating is shown in Fig.6d.

The XRD analysis of mullite and ytterbium monosilicate in EBCs is shown in Fig.7. Fig.7a shows the XRD patterns of mullite powders and as-deposited mullite. The diffraction peak of mullite coating does not obviously broaden, indicating that the crystallinity of mullite crystals is high in the spraying process and no obvious metastable phase is formed through comparative analysis. Therefore, the high preheating temperature of PS-PVD substrate helps to avoid the amorphous coating, which is the disadvantage of traditional APS technology. The XRD patterns of Yb_2SiO_5 powders and as-deposited Yb_2SiO_5 are shown In Fig.7b. It was found that part of the diffraction peaks of the coating disappears, and the crystal growth is preferably oriented.

Due to high work power (net power 57 kW) and low operation pressure (150 Pa) of PS-PVD, the plasma plume can be expanded to a length more than 2000 mm. Thus, part of Yb_2SiO_5 powders can be evaporated. The Yb_2SiO_5 coating was characterized by transmission electron microscope (TEM), as shown in Fig.8. Fig.8a is the bright filed TEM image showing a laminar and columnar composited structure and its magni-

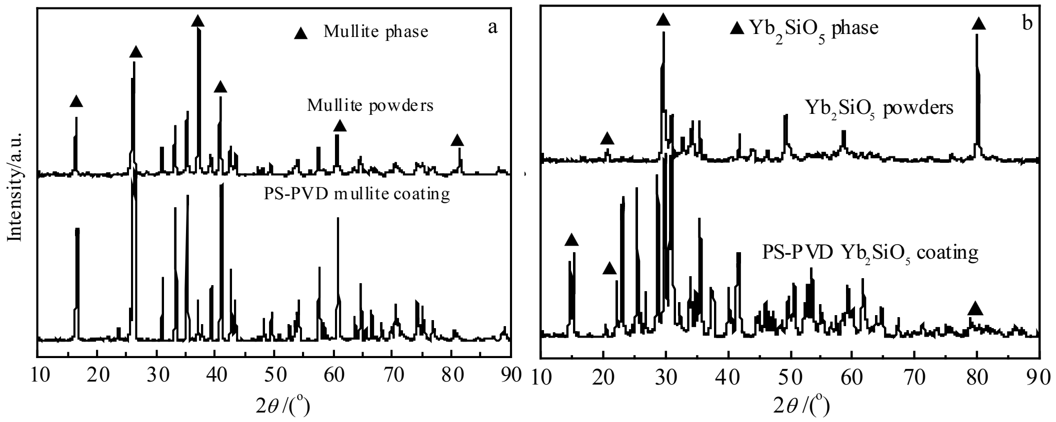

Fig.7 XRD patterns of mullite (a) and Yb_2SiO_5 (b)

fied image is presented in Fig.8b. The composition of laminar and columnar grains marked 1 and 2 zone in Fig.8b was analyzed by energy-dispersive spectroscope (EDS), as shown in Fig.8c and 8d, respectively, showing the presence of Yb, Si and O. The laminar grains are splats, which are caused by plastic deformation of molten powder impacting the substrate[22]. Between laminar grains, lots of columnar grains are formed, which results from condensation of evaporated Yb_2SiO_5[18, 23]. During the PS-PVD process, agglomerated powders will be fragmented into small primary particles ranging from 1~3 μm immediately after injection into plasma gun due to weak agglomeration of original particles. Through detailed comparison, it is notable that the size of nano-columnar grain is smaller than that of the primary particle. Thus, it can be inferred that these nano-columnar grains are formed by condensation of Yb_2SiO_5 vapor phase. However, not all the powders can be evaporated. The unevaporated particles with high velocity dragged by plasma jet will become splat grains in the coating due to plastic deformation.

The deposition process of Yb_2SiO_5 coating with laminar and columnar composited structure can be described, as shown in Fig.9. The agglomerated powders will be fragmented into

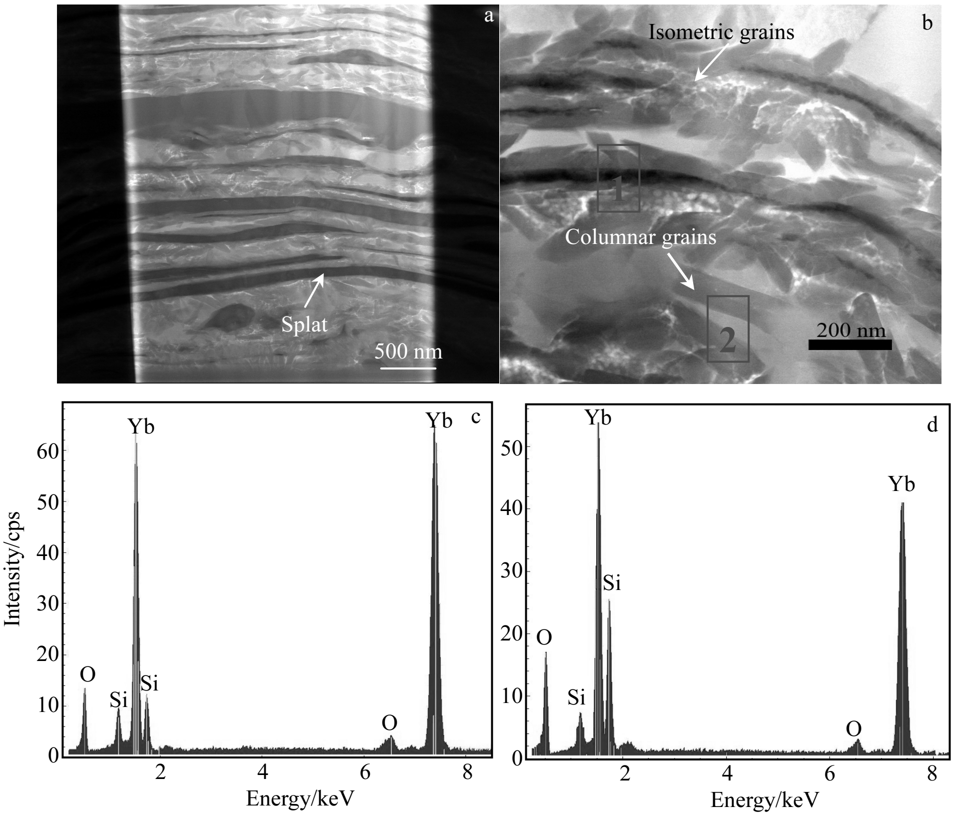

Fig.8 Bright field TEM images of Yb_2SiO_5 coating (a, b) and EDS spectra of grains marked 1 (c) and 2 zone (d) in Fig.8b

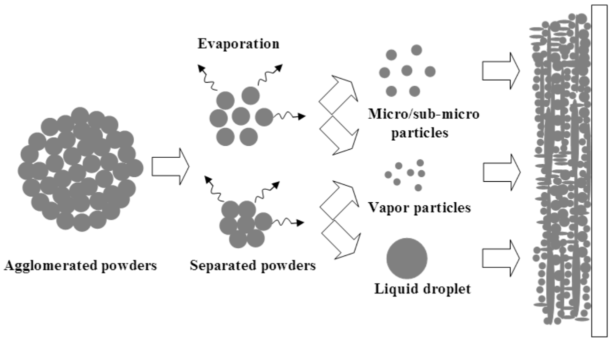

Fig.9 Diagram of deposition process of Yb_2SiO_5 coating prepared by PS-PVD

small particles due to weak bonding between original particles. Part of powders will be evaporated into vapor particles due to small diameter after interacting with high temperature plasma jet in O3CP plasma gun. With decreasing the temperature of plasma jet, the evaporated Yb_2SiO_5 will be condensed, generating nano-columnar and nano-isometric grains, as observed in Fig.7b, forming a columnar structure. Besides, the unevaporated powders will be transformed into molten micro or submicro droplets. When impacting on substrate, the molten droplets will change into splat, forming laminar structure because of great plastic deformation dragged by high velocity plasma jet.

2.3 Thermal cycle performance

Thermal cycle performance is a key for EBCs applied in turbine engine due to frequent take-off and landing during operation. The thermal cycle property of EBCs was characterized from 1300 °C to room temperature in water, as shown in Fig.10. Fig.10a~10k are images of in-situ observation of the same EBCs sample (Φ25.4 mm×6.0 mm) after different water-quenching thermal cycles. After 30 thermal cycles (Fig.10g), no apparent spallation is observed in EBCs sample. Until 35 thermal cycles (Fig.10h), a small area spallation at EBCs sample edge is observed. With increasing the thermal cycle, the spallation area tends to center gradually. But there is no apparent increase in the spallation area through comparison between 35 thermal cycles (Fig.10h) and 50 thermal cycles (Fig.10k). Additionally, based on above analysis, it can be concluded that there are different sized interspaces among

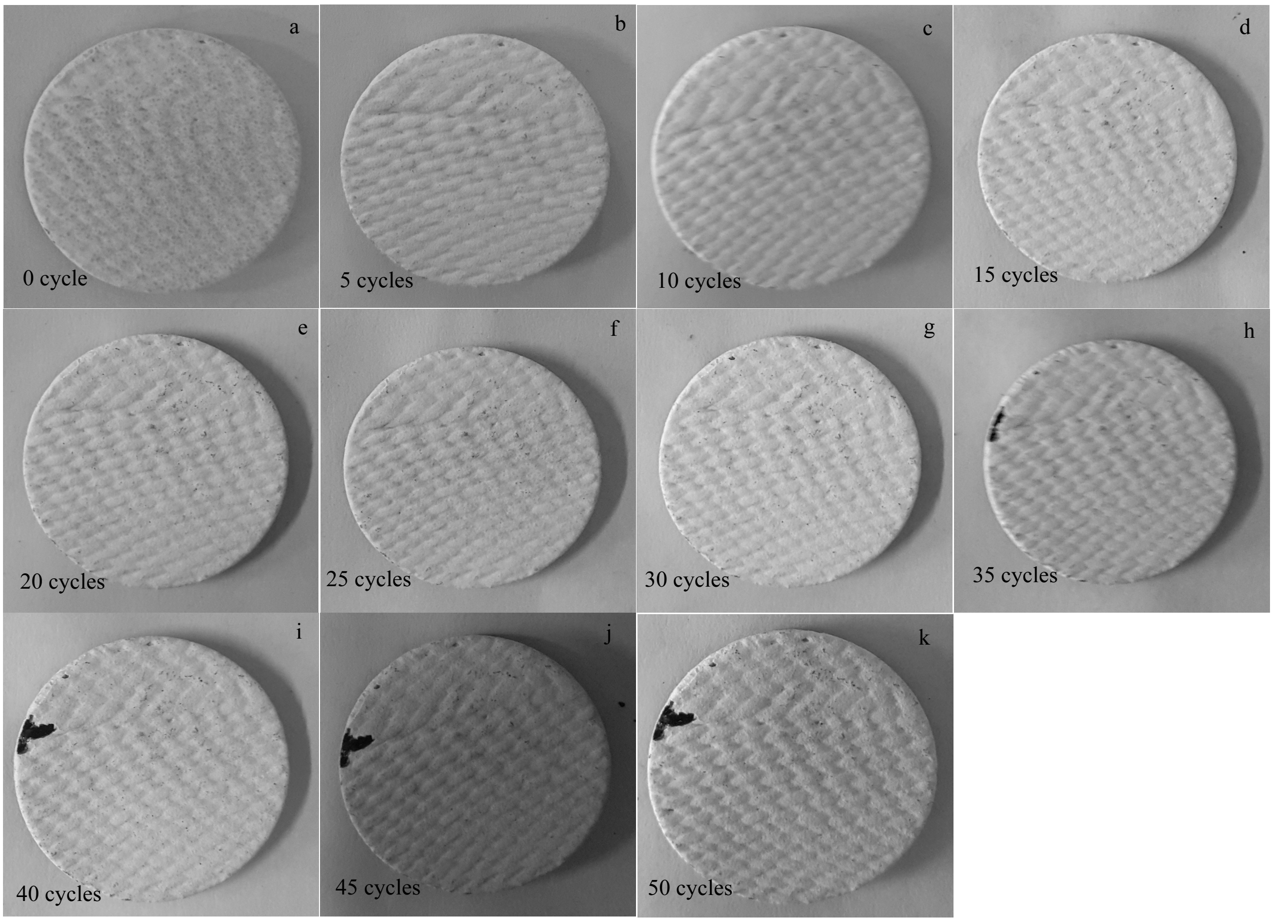

Fig.10 Images of the same EBCs sample after different water-quenching thermal cycles: (a) 0 cycle, (b) 5 cycles, (c) 10 cycles, (d) 15 cycles, (e) 20 cycles, (f) 25 cycles, (g) 30 cycles, (h) 35 cycles, (i) 40 cycles, (j) 45 cycles, and (k) 50 cycles

columnar grains, which can release the stress of Yb_2SiO_5 coating during thermal cycle. Thus the columnar structure contributes to better strain tolerance in thermal cycle and to avoid rapid spallation of EBCs[24]. In operation, apart from the thermal cycle, EBCs will also face oxygen-water corrosion and CAMS (calcium-magnesium aluminosilicate) corrosion. Due to laminar structure generated in the coating, the laminar splat will extend the diffusion path into SiC/SiC substrate as a diffusion barrier[4]. Therefore, laminar structure contributes to the improvement in corrosion performance.

The cross-sectional microstructure of EBCs after water-quenching for 50 times is presented in Fig.11. The bonding between coatings remains close because of the good thermal compatibility of Si/mullite/Yb_2SiO_5. Some unmelted particles are reduced, and transverse and through-wall cracks are generated in the coating due to the release of thermal stress, compared to Fig.6a after 50 thermal cycles of the sample.

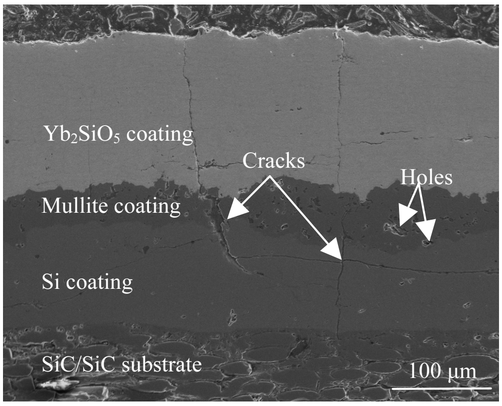

Fig.11 Cross-sectional microstructure of EBCs after 50 thermal cycles

3 Conclusions

1) No apparent cracks and pores in Si and Yb_2SiO_5 coatings form in EBCs system produced by PS-PVD. But a few closed pores are observed in mullite coating. Besides, dense interface among Si coating, mullite coating and Yb_2SiO_5 coating, and substrate can be obtained.

2) The Yb_2SiO_5 coating has a laminar and columnar composited structure. The laminar grains are generated by plastic deformation of un-evaporated powder when impacting on substrate. And the columnar grains are formed by condensation of Yb_2SiO_5 vapor phase.

3) EBCs have good resistance to thermal shock, as indicated by thermal cycle test of 30 times at 1300 °C. This is due to the laminar and columnar composited structure in Yb_2SiO_5 coating. The laminar structure contributes to a dense coating and the columnar structure is helpful to increase strain tolerance of EBCs in thermal cycle.

References

1 Clarke D R, Phillpot S R. *Materials Today*[J], 2005, 8(6): 22

2 Zhou X. *Journal of the European Ceramic Society*[J], 2018, 38(4): 1897

3 Josh Kimmel, Narendernath Miriyala, Jeffrey Price *et al. Journal of the European Ceramic Society*[J], 2002, 22(14): 2769

4 Xu Y, Hu X, Xu F *et al. Ceramics International*[J], 2017, 43(8): 5847

5 Padture N P. *Nature Materials*[J], 2016, 15(8): 804

6 Heveran C M, Xu J P, Sarin V K *et al. Surface & Coatings Technology*[J], 2013, 235(12): 354

7 Kakisawa H, Nishimura T. *Journal of the European Ceramic Society*[J], 2018, 38(2): 655

8 Tanaka M, Kitaoka S, Yoshida M *et al. Journal of the European Ceramic Society*[J], 2017, 37(13): 4155

9 Ramasamy S, Tewari S N, Kang N L *et al. Journal of the European Ceramic Society*[J], 2011, 31(6): 1123

10 Ramasamy S, Tewari S N, Kang N L *et al. Materials Science & Engineering A*[J], 2010, 527(21): 5492

11 Nasiri N A, Patra N, Jayaseelan D D *et al. Ceramics International*[J], 2017, 43(10): 7393

12 Richards B T, Sehr S, Franqueville F D *et al. Acta Materialia*[J], 2016, 103: 448

13 Richards B T, Wadley H N G. *Journal of the European Ceramic Society*[J], 2014, 34(12): 3069

14 Kang N L, Fox D S, Bansal N P. *Journal of the European Ceramic Society*[J], 2005, 25(10): 1705

15 Mesquita-Guimarães J, García E, Miranzo P *et al. Surface & Coatings Technology*[J], 2012, 209(38): 103

16 Cojocaru C V, Lévesque D, Moreau C *et al. Surface & Coatings Technology*[J], 2013, 216(2): 215

17 Mauer G, Jarligo M O, Rezanka S *et al. Surface & Coatings Technology*[J], 2015, 268: 52

18 Zhang X F. *Journal of the European Ceramic Society*[J], 2016, 36(3): 697

19 Stunda-Zujeva A, Irbe Z, Berzina-Cimdina L. *Ceramics International*[J], 2017, 43(15): 11 543

20 Yan J H, Xu J J, Din R U *et al. Ceramics International*[J], 2015, 41(9): 10 547

21 He W, Mauer G, Gindrat M *et al. Journal of Thermal Spray Technology*[J], 2017, 26(1-2): 83

22 Zhang X F. *Materials Science Forum*[J], 2015, 816: 219

23 Zhang X F. *Ceramics International*[J], 2018, 44(4): 3973

24 Guo S, Kagawa Y. *Ceramics International*[J], 2007, 33(3): 373

等离子喷涂-物理气相沉积制备纳米复合结构环境障涂层及其热循环性能

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摘 要：在 SiC/SiC 陶瓷基复合材料(CMC)上制备了具有 3 层结构（Si/Mullite/Yb_2SiO_5）的环境障涂层（EBCs）。提出了一种新的等离子喷涂-物理气相沉积（PS-PVD）方法制备 EBCs 以减少 SiC/SiC CMC 在水氧腐蚀下的降解。在制备 EBCs 之前，用喷雾干燥塔制备了团聚的 Yb_2SiO_5 粉末。然后通过 PS-PVD 技术制备了致密的 EBCs，得到了具有层状和柱状复合结构的 Yb_2SiO_5 涂层，并给出了这种特殊结构的沉积示意图。此外，测试了 PS-PVD 制备的 EBCs 在 1300 ℃ 到室温水中的热循环性能。在 30 次热循环实验后未出现明显的散裂现象，表明 EBCs 具有良好的抗热震性能。

关键词：环境障涂层；等离子喷涂-物理气相沉积；热循环；Yb_2SiO_5

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