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Assessment of the performance of Y₂SiO₅-YSZ/YSZ double-layered thermal barrier coatings

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Abstract:

Y₂SiO₅ is a promising material for the thermal barrier coatings due to its low thermal conductivity, high temperature stability and exceptional resistance for molten silicate attack. However, it suffers low fracture toughness and low coefficient of thermal expansion compared with yttria-stabilized zirconia (YSZ). In this study, a composite coating approach, i.e., incorporating YSZ into Y₂SiO₅ coating, was employed to overcome those limitations. The double-layered Y₂SiO₅-YSZ/YSZ coatings were fabricated using atomospheric plasma spraying and tested under thermal cycling at 1150 °C. The phase compositions, microstructure, mechanical properties and the failure behavior were evaluated. It was found that the amorphous phase during spraying would crystallize at high temperature accompanied by volume shrinkage,

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leading to cracks and spallation in the coating. With YSZ addition, the composite coatings exhibited a much longer lifetime than the single phase Y_2SiO_5 coating due to a lower volume shrinkage and enhanced toughness.

Keywords: Yttrium monosilicate; Thermal barrier coatings; Yttria-stabilized zirconia; Lifetime; Volume shrinkage

1. Introduction

Yttria-stabilized zirconia (7–8 wt. %, YSZ) is the state of art material for the thermal barrier coatings (TBCs) application due to its low thermal conductivity and exceptional mechanical properties [1-4]. As the engine temperature increases, the YSZ encounters the following issues: (i) tetragonal to monoclinic phase transformation (*t-m*) occurs at high temperature (e.g., $>1200^\circ\text{C}$) and lead to catastrophic failure of TBCs [5-6]; (ii) molten silicate attack becomes increasingly important which could degrade the strain tolerance of the coating and subsequently cause coating spallation [7]. To further increase the operating temperatures, new ceramic materials with low thermal conductivity, higher phase stability and resistance to molten silicate have attracted attention in recent years [4], such as rare-earth zirconate ($\text{Ln}_2\text{Zr}_2\text{O}_7$ -type, $\text{Ln}=\text{La}$, Sm and Gd) and rare-earth cerate ($\text{La}_2\text{Ce}_2\text{O}_7$) [8-9]. However, the emerging low thermal conductivity materials usually exhibit a lower fracture toughness ($\sim 1.2 \text{ MPa m}^{1/2}$) compared with the YSZ, which restricts their application in TBCs [8, 10].

It has been reported that, the yttrium monosilicate (Y_2SiO_5) exhibited a lower thermal conductivity ($\sim 1.2 \text{ W/(m K)}$), excellent thermal stability and good corrosion

resistance to molten silicates [11-12], which has been one of preferable materials for the environmental barrier coatings. When doped with Eu or Dy, Y_2SiO_5 can also be used as luminescence materials for sensing temperature at high temperature [13]. In this regard, Y_2SiO_5 might be a candidate top coat materials for the TBCs application. However, this material suffers a lower fracture toughness ($\sim 1.85 \text{ MPa m}^{1/2}$) and smaller coefficient of thermal expansion (CTE, $\sim 8 \times 10^{-6} \text{ K}^{-1}$) compared with YSZ [14]. Previous studies indicated that incorporation of secondary phase (e.g. YSZ) could improve both the toughness and the CTE. For example, Wang et al [10] incorporated YSZ into lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$), a $\sim 120 \%$ improvement in the toughness was achieved. In addition, nano-sized $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) was added into the $\text{La}_2\text{Zr}_2\text{O}_7$ and obtained a similar improvement for the fracture toughness [15]. Therefore, it is expected that the composite approach, i.e. incorporating YSZ into Y_2SiO_5 matrix might be a potential approach to enhance the fracture toughness and increase the CTE for TBCs application.

The objective of this study is to evaluate the feasibility of Y_2SiO_5 as a top coat material for TBCs application. To improve the fracture toughness and the CTE, the YSZ was added to form a Y_2SiO_5 -YSZ composite coating. To avoid the reaction between Y_2SiO_5 coating and the thermally grown oxide (TGO), the double layered system, i.e., a Y_2SiO_5 -YSZ upper layer and a YSZ buffer layer, was also employed with aim to increase the thermal cycling lifetime. Both of the above coatings were fabricated using atmospheric plasma spray and tested at $1150 \text{ }^\circ\text{C}$ in air. Then, the microstructure evolution, thermal and mechanical properties of the coatings were

evaluated. Finally, the failure mechanisms of the Y_2SiO_5 -YSZ/YSZ coatings were discussed.

2. Experimental procedure

2.1 Specimen preparation

The yttrium monosilicates (Y_2SiO_5) were synthesized by solid state reaction. The initial yttria (Y_2O_3 , 99.9 %) and silica (SiO_2 , 99.9 %) powders were calcined with 3 mol. % LiYO_2 additive at 1500 °C for 2 h, as detailed elsewhere [16]. The as-synthesized Y_2SiO_5 and Y_2SiO_5 -YSZ powders (the mass ratios are 1:1 and 1:4) was ball-milled in isopropanol for 36 h. The particle size of the as-milled powders was 0.5-1.0 μm .

To obtain good flowability and proper particle size for plasma spraying, the phase inversion assisted electrostatic spraying is used to fabricate uniform Y_2SiO_5 and Y_2SiO_5 -YSZ hollow microspheres, following procedure reported previously [17].

Table 1 The thermal spraying parameters for the fabrication of bond coat and top coats.

	Bond coat	Y_2SiO_5	Y_2SiO_5 -YSZ (1 : 1)	Y_2SiO_5 -YSZ (1 : 4)	YSZ
Current /A	380	420	420	420	420
Ar/H ₂ flow rate /slpm	90/16	100/11	110/15	110/18	110/19
Feed rate / g min ⁻¹	4.5	4.5	4.5	4.5	4.5
Sparying distance /mm	100	90	90	90	90
Substrate temperature / °C	~500	~500	~500	~500	~500
Coating thickness / μm	~170	~240	~280/~170	~280/~170	~280

The fabrication of the double-layered top coat was to increase Y_2SiO_5 toughness and reduce the thermal mismatch between top coat and bond coat. The bond coat was deposited by APS using the NiCoCrAlY powders (Amdry 365–2, Oerlikon Metco). Then, the top coats were deposited by APS using pure Y_2SiO_5 , Y_2SiO_5 -YSZ composite powders (the mass ratios are 1:1 and 1:4, respectively) and 7YSZ powders (Metco 204B NS, Oerlikon Metco). The parameters for the fabrication of bond coat and top coats are summarized in Table 1.

2.2 Thermal cycling test

The TBCs specimens ($15 \times 15 \times 4 \text{ mm}^3$) were tested by thermal cycling, which consisted of 10-min heat up to 1150°C , 23.5-h dwelling at 1150°C and followed by a 20-min air cooling. The failure of the TBCs was defined as the spallation area was $> 10\%$, which was examined using optical images plus image analysis (Image J). At least 10 specimens were used for each thermal cycling condition.

2.3 Characterization

2.3.1 Structure characterization

The phase compositions of the as-prepared powders and TBCs specimens were characterized using X-ray diffraction (XRD, Ultima IV, Rigaku) with the Cu Ka radiation ($\lambda = 0.15406 \text{ nm}$). In addition, the phase evolution of the coatings were also evaluated using Raman spectroscopy, which was performed using the Raman Microprobe (LabRAM HR, Horiba Jobin Yvon, France). A laser spot (Nd: YAG, 532 nm) with a diameter of about $3 \mu\text{m}$ was focused on the coating surface. The microstructures and cracks length of the specimens were characterized by field

emission scanning electron microscopy (FE-SEM, Inspect F50, FEI).

2.3.2 Thermal analysis

The linear thermal expansion coefficient was obtained using a high-temperature dilatometer (DIL 402 Expedis Select/Supreme, NETZSCH, Germany). The data were continuously recorded during heating at a rate of 2 °C/min. The specimens were cylindrical pieces with 6 mm in diameter and 10 mm in length. Differential scanning calorimeter (DSC) measurements were conducted on a free-standing coating using a thermo gravimetric analyzer (STA449F3, NETZSCH, Germany). The specimens were heated in air at a rate of 10 °C min⁻¹ up to 1200 °C.

In addition, the volume change of the Y₂SiO₅ coating after high temperature treatment was estimated by geometric change using a micrometer. Five free-standing Y₂SiO₅ coating specimens (20×10×0.45 mm³) were heated in air at a rate of 5 °C min⁻¹ up to 1150 °C for 2 h.

2.3.3 Young's modulus, hardness and fracture toughness tests

Young's modulus and hardness of the top coats were measured using a microindenter (Anton Paar, CPX MHT, Austria) with a diamond Vickers indenter tip. The Young's modulus and hardness were measured from the polished coating surface using unloading curves, following the Oliver and Pharr method [18]. A total of 10 indentations with 60 µm interval were performed with a load of 0.5 N and a dwelling time of 10 s. For fracture toughness measurements, indentations were performed at a constant load (2 N) on the polished surface of the top coats. The lengths of the radial cracks were measured from the center of indentation based on SEM images. A total of

10 indentations were conducted on each sample. The fracture toughness (K_{IC}) was evaluated according to Eq. (1) [10, 19]:

$$K_{IC} = \chi \left(\frac{E}{H} \right)^{1/2} \frac{P}{c^{3/2}} \quad (1)$$

where P is the applied load, N; χ is an empirical constant, H is the hardness, GPa; E is the Young's modulus, GPa and c represents the average crack length determined from the four radial cracks formed from indentations, m.

3 Results

3.1 Characterization of Y_2SiO_5 powders

Fig. 1 SEM images of the ball-milled Y_2SiO_5 powders (a) and the as-fabricated Y_2SiO_5 microspheres (b) by phase inversion assisted electrostatic spraying.

Fig. 2 XRD pattern of the ball-milled Y_2SiO_5 powders.

The ball-milled Y_2SiO_5 powders exhibited a particle size of $\sim 2 \mu\text{m}$ (Fig. 1a). To obtain good flowability and suitable particle size feeding stock for plasma spraying, Y_2SiO_5 microspheres with a particle size (40-80 μm) were fabricated by phase inversion assisted electrostatic spraying (Fig. 1b) [17]. The phase composition of Y_2SiO_5 microspheres exhibited a single monoclinic phase, as shown in Fig. 2.

Thermal expansion of Y_2SiO_5 was measured from the sintered bulk using a dilatometer. The bulk specimens were prepared at 1450 °C for 2 h using the ball-milled Y_2SiO_5 powders. It exhibited a linear expansion ($dL/L_0 = (L-L_0)/L_0$) as the temperature ranged from 400 °C to 1200 °C (Fig. 3). The linear thermal expansion coefficient was determined using the slope of the curve of thermal expansion vs. temperature, which is $7.91 \pm 0.32 \times 10^{-6} \text{ K}^{-1}$. This value was comparable to previous works ($\sim 8.4 \times 10^{-6} \text{ K}^{-1}$) [16, 20].

Fig. 3 Linear thermal expansion of polycrystalline Y_2SiO_5 bulk material sintered with LiYO_2 additive at 1450 °C for 2 h.

3.2 Microstructures of Y_2SiO_5 and Y_2SiO_5 -YSZ coatings

Fig. 4 Cross-sectional images of the single layer Y_2SiO_5 coatings (a) and after thermal treatment at 1150 °C for 2 h (b).

Fig. 4a shows cross-sectional images of the single layer Y_2SiO_5 coating in as-deposited condition. It exhibits a porous microstructure like conventional YSZ TBCs [21]. However, the top coat spalls from the bond coat completely after thermal treatment at 1150 °C for 2 h (Fig. 4b). Besides, the spalled coating presents fragment-like shape. This indicated that the coating has a significantly low toughness and CTE, which is responsible for the short lifetime of the coating. Thus, the composite and double-layered coatings will be fabricated to improve the lifetime of the coating.

Fig. 5 Surface XRD patterns (a) and Raman spectra (b) of as-prepared Y_2SiO_5 -YSZ/YSZ double-layered coatings.

To improve the fracture toughness and CTE of Y_2SiO_5 top coat, a

Y_2SiO_5 -YSZ/YSZ double-layered top coat was fabricated with different contents of YSZ addition into Y_2SiO_5 . Fig. 5a presented XRD patterns of the Y_2SiO_5 -YSZ top coats. With the composition changing from Y_2SiO_5 to YSZ, the top coats are composed of monoclinic Y_2SiO_5 , composited Y_2SiO_5 -YSZ and tetragonal YSZ phases, respectively, which were also confirmed by Raman spectra (Fig. 5b). No other phases or phase transformation can be detected [22, 23]. However, for the pure Y_2SiO_5 top coat, a small broad peak at 28° - 32° was observed in the as-sprayed coatings. It indicated that the amorphous Y_2SiO_5 was generated after plasma spraying. The presence of amorphous phase in the coating is detrimental to the lifetime of TBCs since it would be crystallized at high temperature, which could introduce cracks in the top coats due to the volume shrinkage during amorphous-crystalline phase transformation.

Fig. 6 Cross-sectional images of Y_2SiO_5 -YSZ/YSZ double-layered coating specimens: (a) Y_2SiO_5 /YSZ; (b) Y_2SiO_5 -YSZ (1:1)/YSZ; (c) Y_2SiO_5 -YSZ (1:4)/YSZ; (d) YSZ.

Fig. 6 demonstrates cross-sectional images of as-prepared Y_2SiO_5 -YSZ/YSZ

double-layered coating specimens with different YSZ addition. They consist of four layers, a Y_2SiO_5 -YSZ composite top layer (upper layer), a YSZ buffer layer (bottom layer), a NiCoCrAlY bond coat and a superalloy substrate. The thicknesses of the pure Y_2SiO_5 , Y_2SiO_5 -YSZ and pure YSZ are $\sim 240\text{ }\mu\text{m}$, $\sim 280\text{ }\mu\text{m}$ and $\sim 280\text{ }\mu\text{m}$ (Fig. 6), respectively. The thickness of YSZ buffer layer is about $170\text{ }\mu\text{m}$. The top layers have uniform and porous microstructure, which is attributed to partially melted YSZ or Y_2SiO_5 particles and splats structures in the APS-TBCs [24].

3.2 Thermal cycling test of Y_2SiO_5 -YSZ/YSZ double-layered APS-TBCs

Fig. 7 Cross-sectional images of Y_2SiO_5 -YSZ/YSZ double-layered coating specimens after thermal treatment at $1150\text{ }^\circ\text{C}$: (a) Y_2SiO_5 /YSZ for 2 h; (b) Y_2SiO_5 -YSZ (1:1)/YSZ for 24 h; (c) Y_2SiO_5 -YSZ (1:4)/YSZ for 24 h; (d) YSZ for 24 h.

Fig. 7 shows cross-sectional images of the Y_2SiO_5 -YSZ/YSZ double-layered coating specimens after thermal cycling at $1150\text{ }^\circ\text{C}$. Even with the YSZ buffer layer, the single phase Y_2SiO_5 top coat spalled completely after 2 h thermal treatment (Fig. 7a). The spallation can be attributed to the lower CTE of Y_2SiO_5 coating, which

introduced a large thermal mismatch stress by the substrate. Also the low fracture toughness of Y_2SiO_5 was responsible for the short lifetime. In contrast, the Y_2SiO_5 -YSZ (1:1)/YSZ coatings were still adherent after 24 h thermal treatment. Some vertical and horizontal cracks can be observed in Fig. 7b. The vertical cracks was generated by the tensile stress in the coating, resulted from the volume shrinkage induced by the amorphous crystallization transformation of Y_2SiO_5 . The horizontal cracks along the Y_2SiO_5 -YSZ/YSZ interface were caused by the propagation and interaction of vertical cracks [25]. Notably, the Y_2SiO_5 -YSZ (1:4)/YSZ coating specimens exhibited less vertical cracks after the same treatment (Fig. 7c) and no cracks was found in the pure YSZ TBCs (Fig. 7d).

Fig. 8 Cross-sectional images of Y_2SiO_5 -YSZ/YSZ double-layered coating specimens after thermal treatment at 1150 °C: (a1, a2 and a3) Y_2SiO_5 -YSZ (1:1)/YSZ; (b1, b2

and b3) Y_2SiO_5 -YSZ (1:4)/YSZ; (c1, c2 and c3) YSZ.

Fig. 8 shows cross-sectional images of Y_2SiO_5 -YSZ/YSZ double-layered coating specimens after thermal treatment at 1150 °C for different time. After 72 h thermal treatment, horizontal cracks propagated on the Y_2SiO_5 -YSZ/YSZ interface in the Y_2SiO_5 -YSZ (1:1)/YSZ coatings, some vertical cracks bridging with horizontal cracks (Fig. 8a1). Likely, only few vertical cracks were found in the Y_2SiO_5 -YSZ (1:4)/YSZ coatings (Fig. 8b1) and no apparent crack was observed for YSZ coating (Fig. 8c1). After 120 h, partial spallation of the top layer occurred in the Y_2SiO_5 -YSZ (1:1)/YSZ coatings (Fig. 8a2). For Y_2SiO_5 -YSZ (1:4)/YSZ coating after 120 h, no spallation was observed. Only some vertical cracks originated from the Y_2SiO_5 -YSZ top layer into the YSZ buffer layer (Fig. 8b2). For pure YSZ TBCs, the coating was intact and few vertical cracks was presented (Fig. 8c2).

However, after 168 h, the failure of Y_2SiO_5 -YSZ (1:1)/YSZ coating specimens occurred from the Y_2SiO_5 -YSZ/YSZ interface (Fig. 8a3). For the Y_2SiO_5 -YSZ (1:4)/YSZ coating specimens, the horizontal cracks along the YSZ/NiCoCrAlY interface started to form by deflect of vertical cracks (Fig. 8b3), which is similar to that of YSZ top coats (Fig. 8c3) [2, 26].

Fig. 9a shows XRD patterns of Y_2SiO_5 -YSZ/YSZ double-layered coatings after 2 h or 168 h thermal treatment at 1150 °C. The peak intensity of Y_2SiO_5 coating after 2 h thermal treatment is higher than that of as-sprayed Y_2SiO_5 coating and the broad peak disappeared due to the crystallization of amorphous Y_2SiO_5 . As the content of YSZ increased, the peaks intensities of YSZ increased gradually, which is in

agreement with Raman measurements (Fig. 9b).

Fig. 9 XRD patterns (a) and Raman spectra (b) of Y_2SiO_5 -YSZ/YSZ double-layered coatings after thermal treatment at 1150 °C: Y_2SiO_5 /YSZ for 2 h; Y_2SiO_5 -YSZ (1:1)/YSZ for 168 h; Y_2SiO_5 -YSZ (1:4)/YSZ for 168 h; YSZ for 168 h.

3.3 Volume shrinkage derived from phase transformation

Fig. 10 DSC curve for Y_2SiO_5 free-standing coating heated to 1200 °C at a rate of 10 °C/min in air.

To confirm the amorphous-crystalline transformation of Y_2SiO_5 coating specimens during thermal treatment, DSC analysis was performed on the free-standing Y_2SiO_5 coatings up to 1200 °C at a rate of 10 °C/min in air (Fig. 10). The sharp exothermic peak at 925 °C corresponded to the crystallization from

amorphous phase to X1-Y₂SiO₅ phase [16]. The exothermic peak at 1061 °C originated from X1-Y₂SiO₅ to high-temperature X2-Y₂SiO₅ phase transformation [27, 28]. Both of them can lead to the volume shrinkage of the top coats, resulting in a tensile stress in the Y₂SiO₅ coatings. The volume shrinkage of them before and after thermal treatment was estimated to be (2.92 ±0.12) % (marked as $\Delta V_{Y_2SiO_5}$ %).

$$\Delta f_{Y_2SiO_5} \% = \frac{I_{(310)}^{TE} - I_{(310)}^{GC}}{I_{(310)}^{GC}} \times 100 \% \quad (2)$$

$$\Delta f \% = (1 - \Delta W_{YSZ} \%) \times \Delta f_{Y_2SiO_5} \% \quad (3)$$

$$\Delta V \% = (1 - \Delta W_{YSZ} \%) \times \Delta V_{Y_2SiO_5} \% \quad (4)$$

The volume shrinkage upon amorphous crystallization and phase transformation affects the nucleation and propagation of cracks [29]. Therefore, understanding phase transformation and volume shrinkage is crucial for the lifetime. Based on XRD analysis, because the peak intensity of Y₂SiO₅ phase was proportional to the content in the coating, the Y₂SiO₅ phase change fraction can be estimated according to Eq. (2) [28, 30], where $\Delta f_{Y_2SiO_5} \%$ is the Y₂SiO₅ phase variation fraction; $I_{(310)}^{GC}$ and $I_{(310)}^{TE}$ are the (310)-peak intensity of Y₂SiO₅ (PDF NO. 22-0992) coating. The phase variation fraction and volume shrinkage in the Y₂SiO₅-YSZ top coats after thermal treatment were evaluated according to Eq. (3) and Eq. (4), respectively. Where $\Delta f \%$ is the Y₂SiO₅ phase variation fraction of Y₂SiO₅-YSZ top coats; $\Delta W_{YSZ} \%$ is the mass ratio of YSZ in the Y₂SiO₅-YSZ top coats; $\Delta V \%$ is the volume shrinkage fraction caused by Y₂SiO₅ amorphous-crystalline transformation; $\Delta V_{Y_2SiO_5} \%$ is the volume shrinkage fraction of as-sprayed Y₂SiO₅ caused by amorphous-crystalline transformation.

Fig. 11 presented the curves for volume shrinkage and Y₂SiO₅ phase variation

fraction in the Y_2SiO_5 -YSZ top coats after thermal treatment. According to XRD analyses (Fig. 5a and Fig. 9a), there is no t - m YSZ phase transformation in the top coats, the volume shrinkage derived from amorphous Y_2SiO_5 crystallization was mainly investigated in this work. The pure Y_2SiO_5 top coat exhibited a volume shrinkage of 2.92 ± 0.12 % and corresponding higher phase change fraction of 19.00 ± 0.76 % than other Y_2SiO_5 -YSZ composite coating specimens. As the content of YSZ increased, the volume shrinkage decreased.

Fig. 11 Plots for the volume shrinkage and Y_2SiO_5 phase variation fraction in the Y_2SiO_5 -YSZ top coats with different mass ratios of YSZ after thermal treatment.

3.5 Measurement of Young's modulus and hardness

Fig.12a presented the Young's modulus of the top coat measured using microindentation. For the as-sprayed Y_2SiO_5 -YSZ coating, the Young's modulus varied from 96.96 ± 7.03 GPa to 104.91 ± 7.04 GPa, close to the modulus of pure YSZ coating (102.42 ± 3.86). After 24 h thermal treatment, the Young's modulus of the Y_2SiO_5 -YSZ (1:1) coating specimens decreased sharply to 46.41 ± 3.42 GPa due to the

occurrence of the cracks. In contrast, it increased from 124.48 ± 21.18 GPa to 144.38 ± 13.90 GPa for Y_2SiO_5 -YSZ (1:4) and YSZ coatings. Similarly, the hardness decreased to 1.03 ± 0.27 GPa in the Y_2SiO_5 -YSZ (1:1) coating specimens, but increased from 6.85 ± 1.39 GPa to 7.56 ± 1.52 GPa in Y_2SiO_5 -YSZ (1:4) and YSZ coating specimens, respectively. Generally, the increase of the Young's modulus and the hardness can be attributed to the YSZ addition and the cracks in Y_2SiO_5 -YSZ (1:1) coating specimens (Fig. 7b) led to a lower Young's modulus and hardness [31]. In addition, the crystallization and sintering of the coating also increase the Young's modulus and hardness [34, 35].

Fig. 12 Young's modulus (a) and hardness (b) of the Y_2SiO_5 -YSZ top coats before and after 24 h thermal treatment.

3.6 Evolution of fracture toughness after thermal treatment

Fig. 13a shows fracture toughness of Y_2SiO_5 -YSZ top coats measured using Vickers indentation. For the as-sprayed coating, the fracture toughness slightly increased from 2.22 ± 0.18 MPa $\text{m}^{1/2}$ to 2.69 ± 0.19 MPa $\text{m}^{1/2}$ as the content of YSZ increases. After 24 h thermal treatment, the fracture toughness slightly decrease in all specimens, varying from 1.90 ± 0.22 MPa $\text{m}^{1/2}$ to 2.61 ± 0.16 MPa $\text{m}^{1/2}$. This

phenomenon was consistent with previous report [14, 32], which can be attributed to the sintering and the formation of the cracks. In summary, the toughness of the coating showed little improvement with YSZ addition. This indicated that the lifetime improvement by adding YSZ was mainly attributed to the increased CTE and less volume shrinkage.

Fig. 13 Fracture toughness of as-sprayed Y₂SiO₅-YSZ top coats before and after 24 h thermal treatment (a) and indentation morphology on polished surface of the Y₂SiO₅-YSZ top coat (b).

4 Discussion

Rare earth monosilicates such as Y₂SiO₅ have low thermal conductivity, high temperature stability and exceptional resistance to molten silicate attack [33]. Therefore, in this study, Y₂SiO₅ coating has been developed to fabricate as a top coating for TBCs, which can enhance the resistance to molten silicate attack of conventional YSZ TBCs. However, the single Y₂SiO₅ top coating spalled completely with 2 h thermal treatment. Because Y₂SiO₅ coating exhibited a lower fracture toughness (~1.85 MPa m^{1/2}) and smaller coefficient of thermal expansion (CTE, ~8×10⁻⁶ K⁻¹) compared with YSZ [14], leading to its complete spallation with

fragment-like shape. Here we have designed and fabricated double-layered Y_2SiO_5 -YSZ/YSZ to enhance the lifetime of Y_2SiO_5 coating. The double-layered coating lifetime improved remarkably from 2 h to 168 h at 1150 °C in the Y_2SiO_5 -YSZ (1:4) coating specimens. These results underline the need for systematic and rational comparison of volume shrinkage, toughness and CTE in Y_2SiO_5 -YSZ/YSZ specimens with adding different YSZ, which can identify the failure mechanism of them.

Fig. 14 Schematic illustration of the proposed failure model of the Y_2SiO_5 -YSZ/YSZ double-layered APS TBCs.

From the XRD analyses of Y_2SiO_5 -YSZ coating specimens, the broad peaks of Y_2SiO_5 changed into sharp peaks in all coating specimens after thermal treatment (Fig. 5a and Fig. 9a). It can be found that the as-sprayed Y_2SiO_5 and Y_2SiO_5 -YSZ top coat

can occur the amorphous-crystalline transformation under thermal treatment at 1150 °C, which causes the volume shrinkage confirmed by DSC and volume shrinkage estimation (Fig. 10 and Fig. 11). The rare earth monosilicates always had different polymorphs which can easily occur the phase transformation accompanied by the volume change during serving [33]. It is detrimental to the lifetime of the coating specimens. So, the proposed failure mechanisms of the Y_2SiO_5 -YSZ/YSZ double-layered APS TBCs after thermal treatment are illustrated in Fig. 14. The volume shrinkage in the coatings can trigger the cracking initiation and propagation [34], as shown in Fig. 14a and Fig. 14b. The vertical cracks deflection/branching resulted in horizontal cracking in the Y_2SiO_5 -YSZ/YSZ or YSZ/NiCoCrAlY interface (Fig. 14c1 and Fig. 14d1) [31, 35], finally leading to the coating delamination and spallation. As the content of YSZ increased in the Y_2SiO_5 -YSZ coatings, the amorphous-crystalline transformation gradually weakened with the volume shrinkage retarded. The amount of cracks reduced and the cracks exhibited from random to vertical direction, as observed in Fig. 8a1 and Fig. 8b1. Therefore, the volume shrinkage is the main factor for the failure of Y_2SiO_5 -YSZ/YSZ coating specimens. With adding YSZ as the bottom ceramic layer, the thermal mismatch between the Y_2SiO_5 -YSZ top coats and the bond coat was reduced, which can be beneficial for releasing their tensile stress during heating process and improving their strain tolerance [33]. The spallation from the Y_2SiO_5 -YSZ/YSZ interface can be restrained and the spallation model is similar to the failure behavior of conventional YSZ TBCs [35, 36] (Fig. 8b3 and Fig. 8c3), as shown in Fig. 14c2 and Fig. 14d2.

From the result of fracture toughness, it is apparent that the toughness of Y_2SiO_5 -YSZ top coats exhibited only a bit improvement with adding YSZ. The toughness of Y_2SiO_5 -YSZ coating specimens before and after 24 h thermal treatment had a little decline. However, the coating lifetime presented a large variation, i.e., the Y_2SiO_5 -YSZ (1:4) coating specimens could serve for 168 h and the pure YSZ coating specimens had much longer lifetime than other specimens.

5. Conclusions

In summary, Y_2SiO_5 and Y_2SiO_5 -YSZ/YSZ double-layered TBCs were developed and fabricated due to the unique properties of Y_2SiO_5 . With the incorporation of YSZ, the lifetime of the Y_2SiO_5 -YSZ/YSZ (1:4) coating specimens increased from 2 h to 168 h, the improvement of corresponding thermal cycling is more than 7-fold compared with the monolithic Y_2SiO_5 and Y_2SiO_5 /YSZ coating specimens after the same thermal treatment. The following conclusions can be drawn:

(1) The introduction of YSZ is an effective approach in suppressing the volume shrinkage caused by Y_2SiO_5 amorphous-crystalline transformation after thermal treatment. Additionally, the thermal mismatch between the Y_2SiO_5 -YSZ top coats and the bond coat was reduced using YSZ as buffer layer, significantly enhancing the lifetime of the Y_2SiO_5 -YSZ/YSZ coating specimens.

(2) With adding YSZ, the fracture toughness of Y_2SiO_5 -YSZ coating specimens before and after thermal treatment had a little decline. Thus, the change of fracture toughness is not a major reason for the failure of the Y_2SiO_5 -YSZ coating specimens.

(3) The failure of the Y_2SiO_5 -YSZ/YSZ coating is mainly attributed to the

Y₂SiO₅ amorphous-crystalline transformation accompanied by volume shrinkage of the Y₂SiO₅-YSZ upper layer. Consequently, the composite multilayered coating for rare-earth monosilicates is an effective way to improving the lifetime for TBCs.

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