

Article

Performance Evolution of $\text{Gd}_2\text{O}_3\text{-Yb}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-ZrO}_2$ (GYYZO) Thermal Barrier Coatings After Thermal Cycling

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Abstract

Ions of Gd^{3+} and Yb^{3+} have radii similar to those of Zr^{4+} , enabling them to form limited solid solutions in the ZrO_2 lattice through substitution. After solid solution formation, oxygen vacancy defects and complex defect aggregates are generated, which are crucial for stabilizing the high-temperature phase structure and reducing thermal conductivity. Therefore, in this study, 8 wt% Y_2O_3 and 5 wt% Yb_2O_3 were doped with 5 wt%, 10 wt%, and 15 wt% Gd_2O_3 , respectively, to stabilize zirconia powders. GYYZO thermal barrier coatings (TBCs) were fabricated via atmospheric plasma spraying (APS). Subsequently, the GYYZO coatings with different Gd_2O_3 addition amounts were subjected to continuous thermal shock cycling at 1100 °C for 10, 30, 60, 90, and 150 cycles. The results indicate that the incorporation of Gd_2O_3 , Yb_2O_3 , and Y_2O_3 leads to the formation of stable tetragonal ZrO_2 phase in the GYYZO coatings. Although increasing the Gd_2O_3 addition amount reduces the thermal conductivity of the coatings, excessive Gd_2O_3 addition causes coating spallation. The GYYZO coating with 10 wt% Gd_2O_3 exhibits the lowest thermal conductivity of 0.59 W/(m·K). Additionally, the GYYZO coating with 10 wt% Gd_2O_3 can withstand thermal cycling for 150 cycles, while the one with 5 wt% Gd_2O_3 can endure 90 of thermal cycles. In contrast, the 8YSZ coating cracks and spalls after 60 thermal cycles. These findings demonstrate that doping ZrO_2 with Gd_2O_3 , Yb_2O_3 , and Y_2O_3 can enhance the thermal cycling resistance of the coatings and effectively reduce their thermal conductivity, but excessive Gd_2O_3 addition will decrease the coating adhesion strength.

Keywords: limited solid solution; atmospheric plasma spraying (APS); GYYZO thermal barrier coating; thermal cycling; thermal conductivity



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1. Introduction

Thermal barrier coatings (TBCs), as a critical component of high-temperature structural materials, play a significant role in enhancing the thermal efficiency and service life of high-temperature equipment such as aero-engines. Directionally solidified Ni-based superalloys are widely used in aircraft turbine engines, especially for the fabrication of large-scale and complicated blades. In recent years, with the continuous improvement of performance requirements for aero-engines, higher demands have been put forward for the high-temperature phase stability, mechanical properties, and thermophysical properties of TBCs [1–5]. Commonly used TBCs typically have a double-layer structure with a thickness of approximately 300–500 µm, consisting of a heat-insulating ceramic layer with a high melting point and low thermal conductivity, and an oxidation-resistant metallic bond

coat [6–9]. TBCs isolate high-temperature working media from contact with the metal substrate; their excellent thermal insulation performance reduces the surface temperature of components, weakens heat exchange, and thus provides effective protection for the substrate [10]. As an advanced coating preparation method, atmospheric plasma spraying (APS) has been widely applied in the field of TBCs in recent years [11,12]. TBCs prepared by APS exhibit a typical lamellar structure, with poor compatibility with the substrate. Some coatings may have penetrating cracks, while others may have cracks parallel to the coating surface. Such cracks parallel to the surface are prone to cause coating failure by cracking, which is extremely detrimental to thermal shock resistance. However, these issues can be addressed by adding a bond coat between the substrate and the ceramic layer to improve compatibility, and by incorporating higher porosity with uniformly distributed small pores, which can shorten the effective crack length and thus prevent the formation of penetrating and parallel cracks [13–17].

ZrO₂ TBCs undergo reversible transformation between the monoclinic (m) and tetragonal (t) phases at different temperatures. This phase change causes volume variation in the coating, leading to cracking, spalling, and subsequent failure. Therefore, it is particularly important to obtain stable ZrO₂ coatings [18]. Studies have suggested that modifying the composition of TBC materials can achieve coating systems with low thermal conductivity and high-temperature resistance. Co-doping trivalent or pentavalent rare-earth oxides into zirconia ceramic materials can alter the structure of TBC systems and stabilize the zirconia thermal barrier coating in the tetragonal (t) phase [19]. The ionic radii of Gd³⁺ and Yb³⁺ are close to that of Zr⁴⁺, enabling them to form limited solid solutions in the ZrO₂ lattice through substitution. After solid solution, oxygen vacancy defects and complex defect aggregates are generated, which are crucial for stabilizing the high-temperature phase structure and reducing thermal conductivity [20]. Guo et al. investigated the thermal shock performance of nanostructured (Gd_{0.9}Yb_{0.1})₂Zr₂O₇/YSZ thermal barrier coatings (TBCs) [21]. Their results revealed that the coatings exhibited excellent high-temperature phase structural stability during flame thermal shock tests at 1350–1400 °C, with a thermal shock lifetime significantly longer than that of single-layer YSZ coatings. Sun et al. focused on Yb₃Al₅O₁₂ as a potential TBC material and explored its feasibility for TBC applications. They found that Yb₃Al₅O₁₂ coatings demonstrated superior thermal stability and a low oxidation weight gain rate; particularly in the Yb₃Al₅O₁₂/YSZ double ceramic layer structure design, thermal stress was effectively alleviated, and the high-temperature oxidation resistance of the coatings was enhanced [22]. He et al. fabricated (Gd_{0.9}Yb_{0.1})₂Zr₂O₇/Y₂O₃-stabilized ZrO₂ (GYbZ/8YSZ) TBCs on Inconel 600 substrates using the atmospheric plasma spraying (APS) process [23]. The coatings were subjected to 100 thermal cycles at 1100 °C, and the evolution of their composition, microstructure, and mechanical properties was systematically analyzed. The results indicated that the coatings maintained structural stability at high temperatures, with the elastic modulus and hardness reaching maximum values of 182.01 GPa and 9.13 GPa, respectively. High-temperature in situ indentation tests further confirmed that the high-temperature surface hardness of the coatings remained essentially stable. Gao et al. proposed a multi-doping approach to stabilize ZrO₂ for obtaining TBC materials with better comprehensive performance [24]. They doped Yb₂O₃ and Gd₂O₃ into 8YSZ powders as TBC materials, and the results showed that adding Gd₂O₃ and Yb₂O₃ to YSZ not only effectively reduced thermal conductivity but also improved mechanical properties, thereby further enhancing the performance of TBCs. Zhang et al. prepared Yb₂O₃-Gd₂O₃ co-doped SrZrO₃ ceramic powders via solid-phase deposition, and fabricated Sr_{0.8}(Zr_{0.9}Yb_{0.05}Gd_{0.05})O_{2.75}, Sr(Zr_{0.9}Yb_{0.05}Gd_{0.05})O_{2.95}, and pure SrZrO₃ TBCs [25]. The results demonstrated that SZYG/YGZO ceramics exhibited no phase transition in the temperature range of 600–1400 °C, with a thermal expansion coefficient

of $10.9 \times 10^{-6}/\text{K}$. Compared with SZO ceramics, the fracture toughness of SZYG/YGZO ceramics increased by more than 30%.

In summary, the incorporation of rare-earth oxides can further improve the performance of TBCs. Therefore, in this study, quaternary nano- Gd_2O_3 - Yb_2O_3 - Y_2O_3 - ZrO_2 (GYYZO) powders were prepared by doping 5 wt% Yb_2O_3 and 5 wt%, 10 wt%, and 15 wt% Gd_2O_3 into nano-8YSZ powders. GYYZO TBCs were fabricated using APS and subjected to continuous thermal cycling at 1100 °C for 10, 30, 60, 90, and 150 times. The microstructure, thermal conductivity, and other properties of the GYYZO TBCs were characterized, and the effects of Gd_2O_3 , Yb_2O_3 , and Y_2O_3 doping on the performance evolution of GYYZO coatings under thermal cycling were investigated. This work provides a basis for the material and structural optimization of TBCs and their stability research, as well as experimental support for the eventual application of TBCs in gas turbines. The results indicate that the incorporation of Gd_2O_3 , Yb_2O_3 , and Y_2O_3 leads to the formation of stable tetragonal ZrO_2 phase in the GYYZO coatings. Doping ZrO_2 with Gd_2O_3 , Yb_2O_3 , and Y_2O_3 can enhance the thermal cycling resistance of the coatings and effectively reduce their thermal conductivity.

2. Materials and Methods

2.1. Powder and Coating Deposition

The raw powder used was 8YSZ (Metco 204 NS, Oerlikon, Schaumburg, IL, USA). The purity of the 8YSZ was 99.99%. The manufacturer provided the D90 of the 8YSZ powder as 30 μm . For Gd_2O_3 and Yb_2O_3 powders, the manufacturer specified a D90 of 5 μm (Shandong Desheng New Materials Co., Ltd., Jining, China). The purity of the powders was 99.99%. To the 8YSZ powder, 5 wt% Yb_2O_3 was added in proportion, followed by the addition of 5 wt%, 10 wt%, and 15 wt% Gd_2O_3 powder, respectively. The powders were ball-milled using a ball mill to prepare GYYZO powders with different Gd_2O_3 contents, denoted by 5GYZZO (5 wt% Gd_2O_3), 10GYZZO (10 wt% Gd_2O_3), and 15GYZZO (15 wt% Gd_2O_3). The experimental equipment used was an XH-XOM12L cold-air ball mill. The specific process parameters are listed in Table 1. Figure 1 presents the morphologies of the ball-milled powders, where Figure 1a shows the surface morphology of the 8YSZ powder, Figure 1b corresponds to the 5GYZZO powder, Figure 1c corresponds to the 10GYZZO powder, and Figure 1d corresponds to the 15GYZZO powder. It can be observed from Figure 1 that the average particle size of the 8YSZ powder is 30 μm , while that of the Gd_2O_3 and Yb_2O_3 powders is 3 μm . The 8YSZ powder exhibits a spherical morphology, whereas Gd_2O_3 and Yb_2O_3 powders show irregular morphologies. After ball-milling and mixing, due to their irregular shapes, the small-sized Gd_2O_3 and Yb_2O_3 powders can better adhere to the large-sized 8YSZ powders to form mixed powders.

Table 1. Ball milling process parameters.

Item	Experimental Parameters
Raw materials	The powders of 5GYZZO, 10GYZZO, 15GYZZO Zirconia balls, with diameters of 10 mm, 20 mm, and 40 mm, each accounting for 1/3 Anhydrous ethanol 1:2:2 (Powder/ball/solvent) 260 r/min 8 h
Milling balls	
Solvent	
Powder/ball/solvent Ratio	
Milling rotational speed	
Milling time	8 h

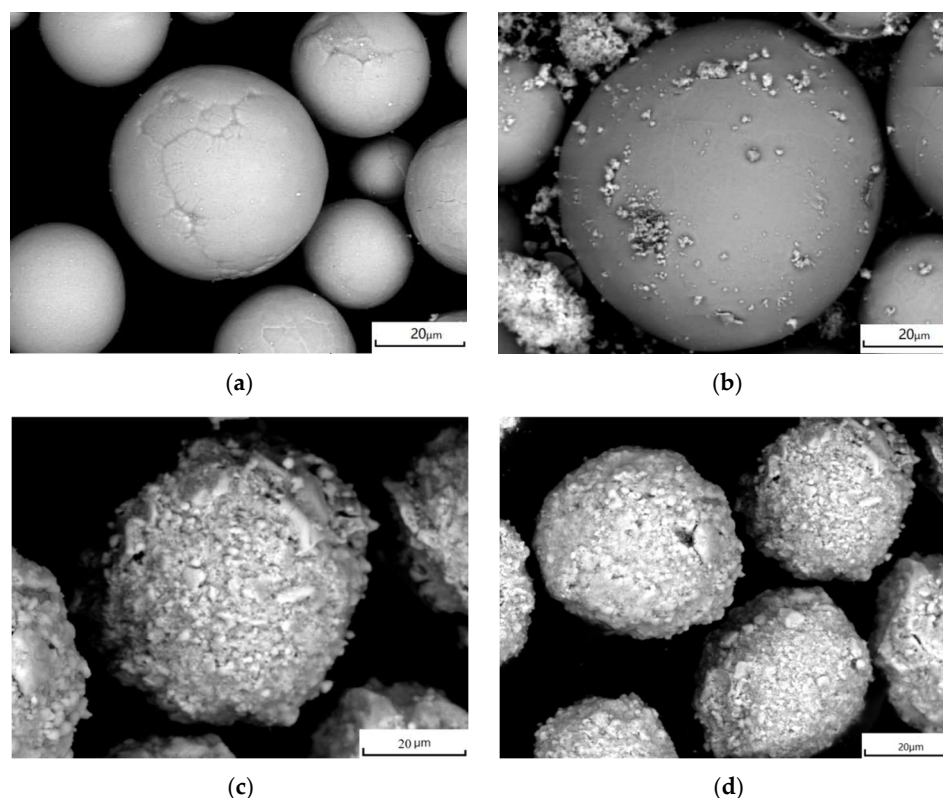


Figure 1. Surface morphology of powders [24]: (a) 8YSZ; (b) 5GYYZO; (c) 10GYYZO; (d) 15GYYZO.

2.2. Preparation of GYYZO Thermal Barrier Coatings

GYYZO coatings were prepared by atmospheric plasma spraying (APS) of the ball-milled powders onto nickel-based 718 alloy plates (AVIC Zhongmai Flagship Store, Shanghai, China). Meanwhile, spherical 8YSZ powders were used to fabricate thermal barrier coatings as reference samples. The experimental equipment employed was the ZB-80 (Beijing Zhengbang Co., Ltd., Beijing, China). The specific process parameters are listed in Table 2.

Table 2. Process parameters for plasma-sprayed thermal barrier coatings.

Coating	Experimental Parameters	
Bond Coat	Arc Voltage (V)	67
	Arc Current (A)	540
	H ₂ Pressure (MPa) and Flow Rate (SLPM)	0.2 and 2.7
	Ar Pressure (MPa) and Flow Rate (SLPM)	0.9 and 38.1
	Powder Feed Rate (rad/min)	3.5
	The standoff distance (mm)	150
	The substrate preheat temperature (°C)	100
Top Coat	The traverse speed (mm/s)	50
	Arc Voltage (V)	72
	Arc Current (A)	630
	H ₂ Pressure (MPa) and Flow Rate (SLPM)	0.3 and 3.4
	Ar Pressure (MPa) and Flow Rate (SLPM)	0.9 and 36.5
	Powder Feed Rate (rad/min)	3.7
	The standoff distance (mm)	150
	The substrate preheat temperature (°C)	100
	The traverse speed (mm/s)	200

2.3. Thermal Cycling of TBCs

The prepared coating is subjected to thermal cycling in a furnace. The specific thermal cycling parameters are shown in Table 3. It is heated to 1100 °C at a rate of 5 °C per minute. After holding at this temperature for 24 h, it is cooled down to room temperature at a rate of 3 °C per minute. Each holding period lasts for 24 h. This process is repeated for the cycle.

Table 3. Thermal cycling parameters.

Item	Experimental Parameters
Heating rate	5 °C/min
Holding temperature	1100 °C
Holding time	24 h
Cooling rate	3 °C/min
Number of cycles	10, 30, 60, 90 and 150 times

2.4. Performance Testing and Microstructure Observation

Scanning electron microscopy (SEM; VEGA II-XMU, TESCAN, Brno, Czech Republic) was used to characterize the original powders' morphology and the coatings' microstructure. Cross-sectional microstructures of the feedstocks were characterized after they were set in resins and polished. X-ray diffraction (XRD-6000, Shimadzu, Kyoto, Japan) was used to analyze the phases of the powder and the coating with Cu K α radiation in a steps of 0.02° from 20° to 80° at a scanning speed of 2°/min.

Thermal conductivity was measured using a laser flash apparatus (LFA, DLF-1200Lukens Drive, New Castle, TA, USA). The operating principle of this method is as follows: a short laser pulse is used to heat the sample, and an infrared detector is applied to measure the relationship between the temperature change on the back surface of the sample and time, thereby obtaining the thermal diffusivity of the sample. The thermal conductivity is then calculated via a formula based on the sample thickness. For this apparatus, the sample diameter is 12.7 mm, and the thickness is generally 1–6 mm. During the test, nitrogen (N₂) is filled for protection, and a graphite layer is sprayed on the sample surface. This graphite layer facilitates the sample's absorption of laser energy and prevents the laser beam from directly penetrating the sample at high temperatures. The thermal conductivity is calculated using the formula (1):

$$K = DC_p\rho \quad (1)$$

In the formula, K is the thermal conductivity (W·m^{−1}·K^{−1}); D is the thermal diffusivity (m²·s^{−1}); C_p is the specific heat (J·kg^{−1}·K^{−1}); and ρ is the room temperature density of the sample (kg·m^{−3}) (The Archimedes drainage method is used to measure the density).

3. Results

3.1. Microstructure of Coatings Before and After Thermal Cycling

Figure 2 shows the cross-sectional morphologies of the TBCs fabricated in this study, where Figure 2a–d correspond to 8YSZ, 5GYYZO, 10GYYZO, and 15GYYZO coatings, respectively. It can be observed from the figures that the 8YSZ, 5GYYZO, and 10GYYZO TBCs exhibit good bonding between the ceramic layer and bond coat, as well as between the bond coat and substrate. The thickness of the ceramic layer in these three coatings all reaches 200 μ m. In contrast, the ceramic layer of the 15GYYZO coating is extremely thin, with a thickness of only approximately 20 μ m, and contains numerous irregular cracks. This phenomenon can be attributed to the spraying process: large 8YSZ particles wrapped by Gd₂O₃ melted first, and the molten 8YSZ then coated and protected the Gd₂O₃. However,

the addition of a large amount of Gd_2O_3 resulted in a significant portion of the powder remaining unmelted during spraying, retaining its granular form and thus leading to poor coating adhesion. Under such conditions, the lamellar stacked coating structure tended to spall.

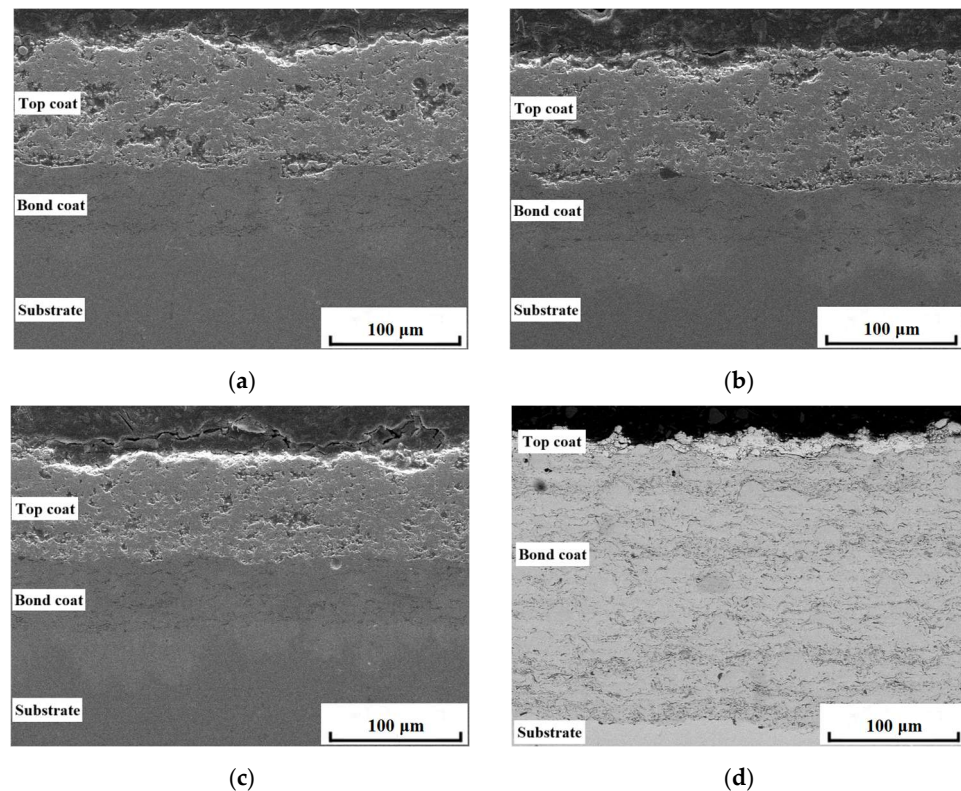


Figure 2. Cross-sectional morphology of TBCs: (a) 8YSZ; (b) 5GYYZO; (c) 10GYYZO; (d) 15GYYZO.

The cross-sectional morphology data of the coatings were analyzed using computer image processing technology, and their porosities were measured to be 6.44%, 10.52%, 15.36%, and 43.55%, respectively. Due to the spallation of the 15GYYZO coating, a well-bonded TBC was not formed; therefore, this coating was excluded from the subsequent test result analysis.

Figure 3 shows the cross-sectional morphologies of the 8YSZ TBC after thermal cycling at 1100°C for different durations. Specifically, (a) to (f) correspond to the states without cycling, and after 10, 30, 60, 90, 150 cycles, respectively. It can be observed from the figures that after the 8YSZ TBC was cycled at 1100°C , some nanoscale small pores deposited at the coating boundaries gradually disappeared, while some micron-sized pores that were close to each other cracked and connected to form larger pores. This phenomenon occurs because the diffusion path between 8YSZ particles is too long, and small particles can easily pass through micron-sized pores, and especially macropores of several tens of microns. Thus, micron-sized pores and macropores of several tens of microns do not easily disappear. Moreover, with the extension of cycled time, when the duration reaches 30 cycles, the macropores in the coating gradually connect with each other. When the cycled time reaches 60 cycles, the micron-sized macropores in the coating are completely connected, forming large cracks. At this point, the coating undergoes spallation failure. It can be observed from the cross-sectional morphology images that after the coating failed due to thermal cycling, spallation occurred, resulting in an overall decrease in the coating thickness. After 30 days of thermal cycling, the thickness of the 8YSZ coating decreased from $200\text{ }\mu\text{m}$ to $150\text{ }\mu\text{m}$. It

drops to 100 μm after 90 days of thermal cycling, and only 50 μm remains after 150 days of thermal cycling.

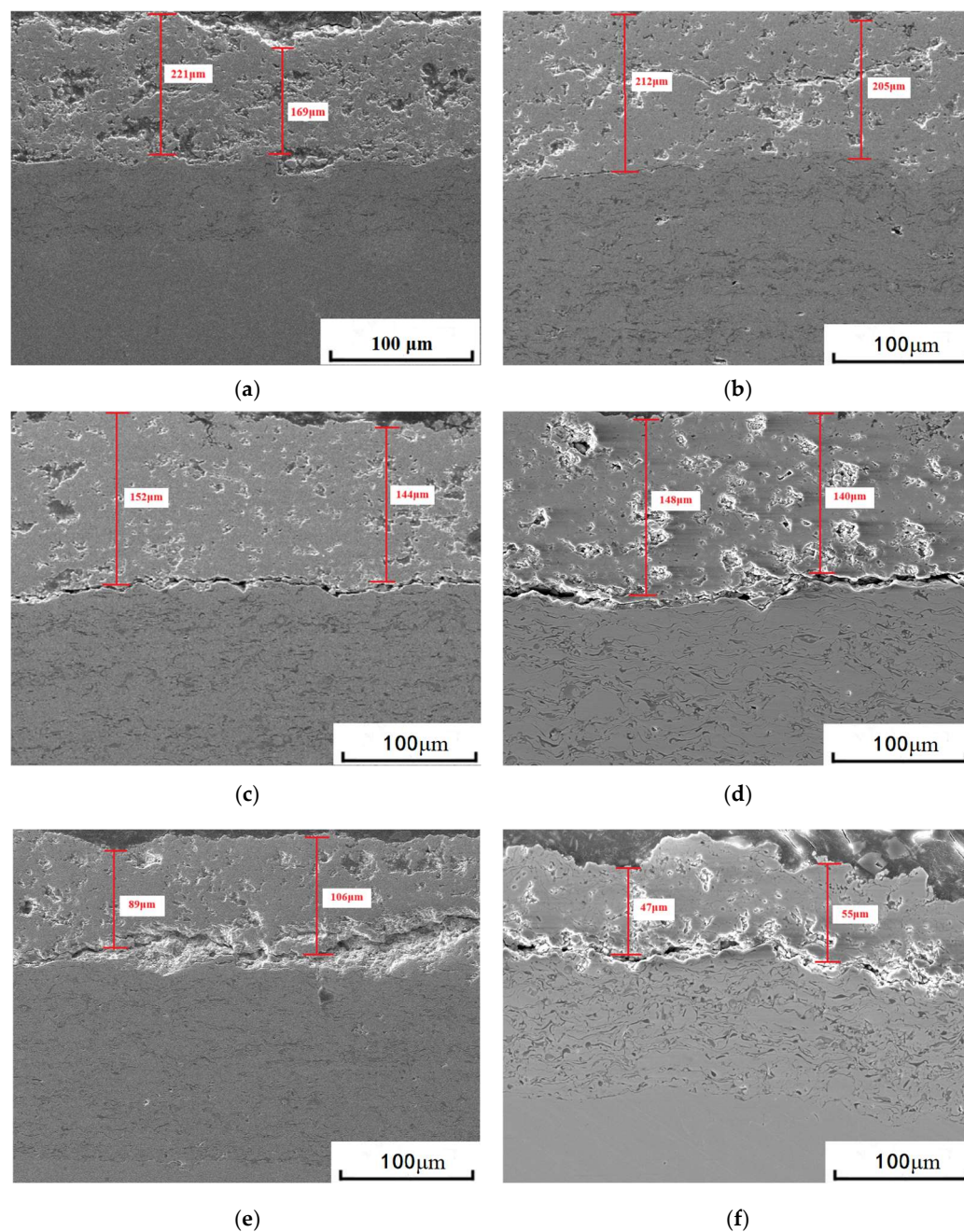


Figure 3. Cross-sectional morphologies of 8YSZ TBCs before and after service: (a) without cycling; (b) 10 cycles; (c) 30 cycles; (d) 60 cycles; (e) 90 cycles; (f) 150 cycles.

Figure 4 presents the cross-sectional morphologies of the 5GYYZO TBC after thermal cycling at 1100 $^{\circ}\text{C}$ for different durations. Specifically, (a) to (f) correspond to the states without cycling, and after 10, 30, 60, 90, 150 times of cycling, respectively. It can be observed from the figures that after the 5GYYZO TBC was cycled at 1100 $^{\circ}\text{C}$, the evolution mechanism of pores was similar to that of 8YSZ. Some nanoscale small pores deposited at the coating boundaries gradually disappeared, while some micron-sized pores in adjacent locations cracked and connected to form larger pores. The key difference lies in the timing of failure. For the 5GYYZO TBC, the micron-sized macropores in the coating did not completely connect to form large cracks until the cycling time reached 90 cycles. It was at this point

that the coating exhibited spallation failure. After 30 days of thermal cycling, the thickness of the 5GYYZO coating decreased from 200 μm to 170 μm . It dropped to 130 μm after 90 days of thermal cycling, and only 50 μm remained after 150 days of thermal cycling.

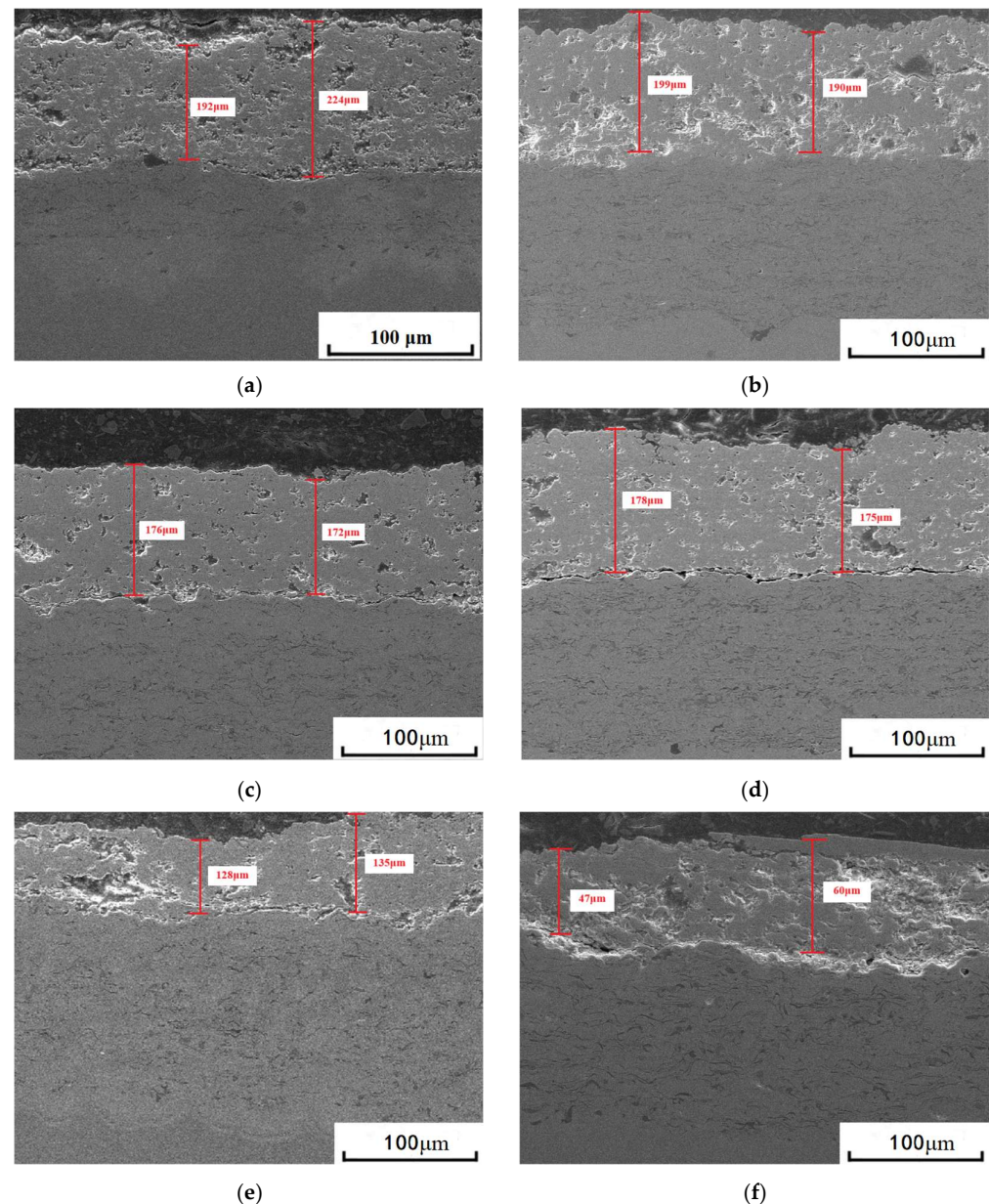


Figure 4. Cross-sectional morphologies of 5GYYZO TBCs before and after Service: (a) without cycling; (b) 10 cycles; (c) 30 cycles; (d) 60 cycles; (e) 90 cycles; (f) 150 cycles.

Figure 5 shows the cross-sectional morphologies of the 10GYYZO TBC after thermal cycling at 1100 $^{\circ}\text{C}$ for different durations. Specifically, (a) to (f) correspond to the states without cycling, and after 10, 30, 60, 90, 150 cycles, respectively. It can be observed from the figures that after the 10GYYZO TBC was cycled at 1100 $^{\circ}\text{C}$, the evolution mechanism of pores was consistent with that of 8YSZ and 5GYYZO. However, the distinct difference is that the 10GYYZO TBC exhibited a longer cycling life. Large cracks were not formed until the cycling time reached 150 cycles, which ultimately led to the spallation failure of the coating. Unlike the previous two coatings, the thickness of the 10GYYZO coating did not show a significant decrease after 90 days of thermal cycling and remained at around

200 μm . It was not until 150 days of thermal cycling that the coating thickness dropped to 50 μm .

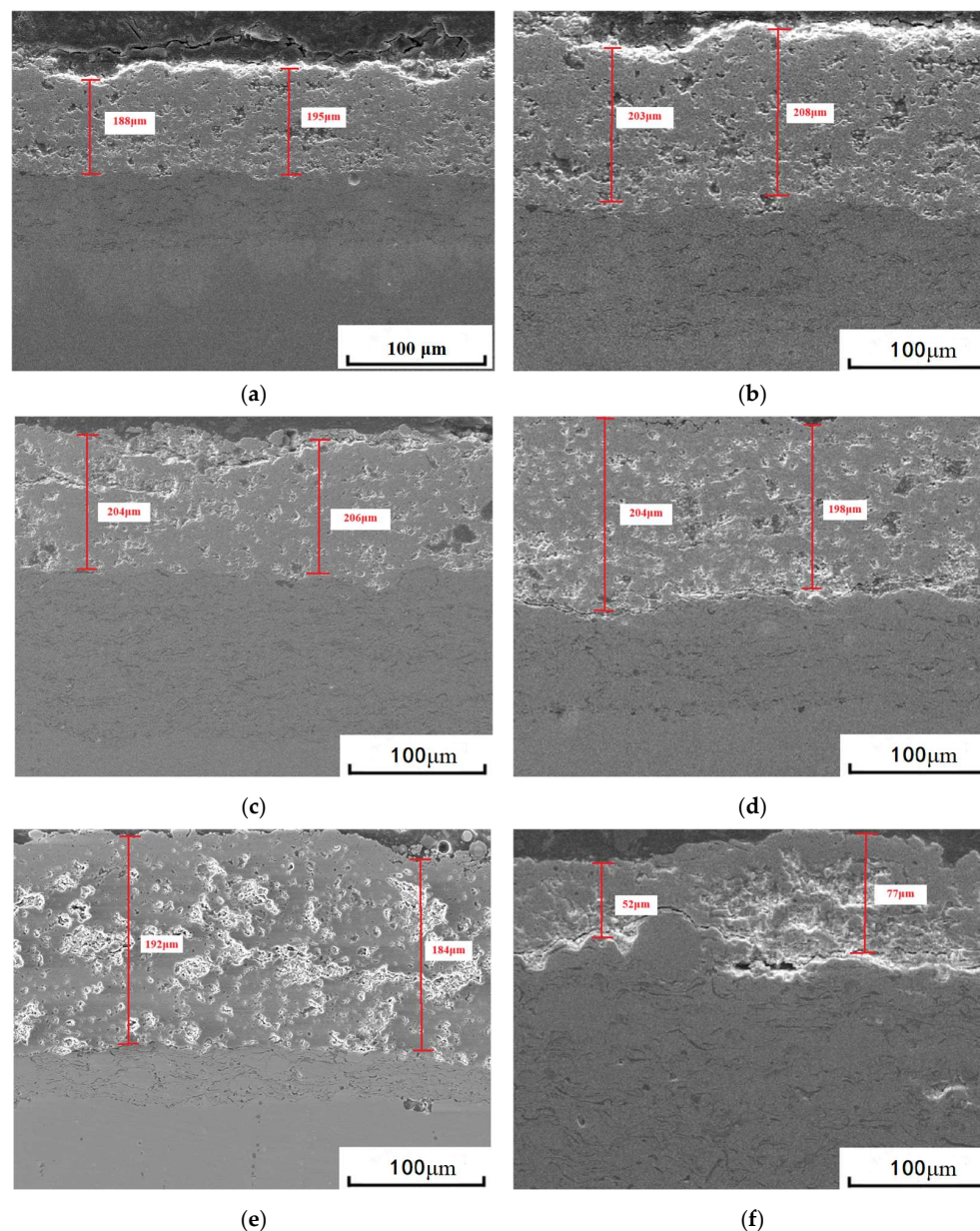


Figure 5. Cross-sectional morphologies of 10GYYZO TBCs before and after service: (a) without cycling; (b) 10 cycles; (c) 30 cycles; (d) 60 cycles; (e) 90 cycles; (f) 150 cycles.

3.2. Phase Analysis

Figure 6 presents the X-ray diffraction (XRD) patterns of the powders (a) and coatings (b) employed in the experiment. From the patterns, it can be observed that the XRD pattern of the 8YSZ powder exhibits partial monoclinic phase peaks at 27° and 32° (PDF card No. 72-0597). In contrast, no monoclinic phase is detected in the GYYZO powders; instead, only the tetragonal phase is present (PDF card No. 71-1282). This indicates that the addition of Gd_2O_3 (PDF card No. 24-0430) and Yb_2O_3 (PDF card No. 74-1981) can replace part of Y_2O_3 (PDF card No. 20-1412), thereby enhancing the stability of 8YSZ. In the XRD patterns of the coatings, the 8YSZ coating still shows partial monoclinic phase peaks at 27° and 32° , with diffraction intensity higher than that of the 8YSZ powder. This suggests that after the coating is fabricated via plasma spraying, part of the tetragonal phase in 8YSZ

undergoes a phase transformation, leading to the formation of more monoclinic phase. However, no monoclinic phase is observed in any of the GYYZO coatings, which maintain the same phase structure as the corresponding GYYZO powders. This confirms that the GYYZO powders do not undergo phase transformation after plasma spraying, and the incorporation of Gd_2O_3 and Yb_2O_3 can improve the stability of 8YSZ.

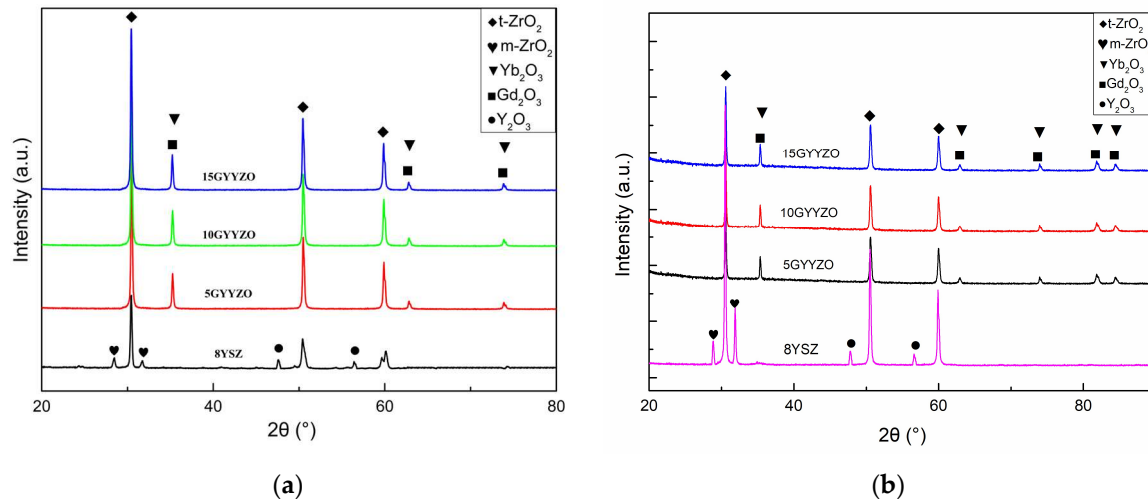


Figure 6. XRD analysis of powders and coatings: (a) powders [24]; (b) coatings.

During the phase transformation between the tetragonal phase (t-phase) and monoclinic phase (m-phase), the variation range of chemical composition is relatively narrow. Therefore, in most studies characterizing this phase transformation process, the volume fraction is generally calculated using the integrated intensity of diffraction lines. By employing the formulas (2) and (3) proposed by Taylor et al. to calculate the phase content of yttria-stabilized zirconia (YSZ) via X-ray diffraction peak intensity [26], the phase contents of the powders and coatings were obtained, as presented in Table 4. It can be observed from Table 4 that after the coating was prepared by plasma spraying, a portion of the t-phase in 8YSZ underwent phase transformation, resulting in the formation of a greater amount of the m-phase. However, the phase content of the GYYZO powder remained essentially unchanged without any phase transformation occurring. This indicates that the addition of Gd_2O_3 and Yb_2O_3 can enhance the phase stability of 8YSZ.

$$C_m = \frac{I_m(11\bar{1}) + I_m(111)}{I_m(11\bar{1}) + I_m(111) + I_t(111)} \quad (2)$$

$$V_m = \frac{PC_m}{1 + (P - 1)C_m} \quad (3)$$

where C is the integrated intensity ratio of the phase, I is the peak intensity of the phase, V is the volume fraction of the phase, and $P = 1.3$.

Table 4. Phase contents of powders and coatings.

Sample Type	Sample	m-Phase Content (%)	t-Phase Content (%)
Powders	8YSZ	27.9	72.1
	5GYYZO	4.3	95.7
	10GYYZO	1.5	98.5
Coatings	8YSZ	39.2	60.8
	5GYYZO	4.4	95.6
	10GYYZO	1.7	98.3

3.3. Evolution Mechanism of Thermal Conductivity Before and After Thermal Cycling

Figure 7 presents the thermal conductivity variation curves of thermal barrier coatings (TBCs) before and after thermal cycling, where (a) corresponds to the 8YSZ TBC, (b) to the 5GYYZO TBC, and (c) to the 10GYYZO TBC. It can be observed that the three types of coatings exhibit the same trend in thermal conductivity evolution after thermal cycling. Prior to thermal cycling, the thermal conductivity of the 10GYYZO TBC at 1100 °C was 0.59 W/(m·K), while that of the 5GYYZO TBC at the same temperature was 0.72 W/(m·K), and the 8YSZ TBC had a thermal conductivity of 2.02 W/(m·K) at 1100 °C. This indicates that doping Gd_2O_3 and Yb_2O_3 into 8YSZ can effectively reduce the thermal conductivity of the TBC. During exposure to hot gas impingement, a lower thermal conductivity of the TBC corresponded to a better thermal insulation effect. Comparing the coating cross-sectional morphologies before and after thermal cycling, the number of nanoscale small pores in the coating decreases significantly, while the number and content of micron-scale larger pores remain essentially unchanged. This phenomenon is analogous to self-healing during the high-temperature thermal insulation process of the ceramic layer, which is equivalent to the effect of sintering. However, this has an adverse impact on the thermal conductivity reduction performance of the TBC, leading to a continuous increase in the coating's thermal conductivity after thermal cycling.

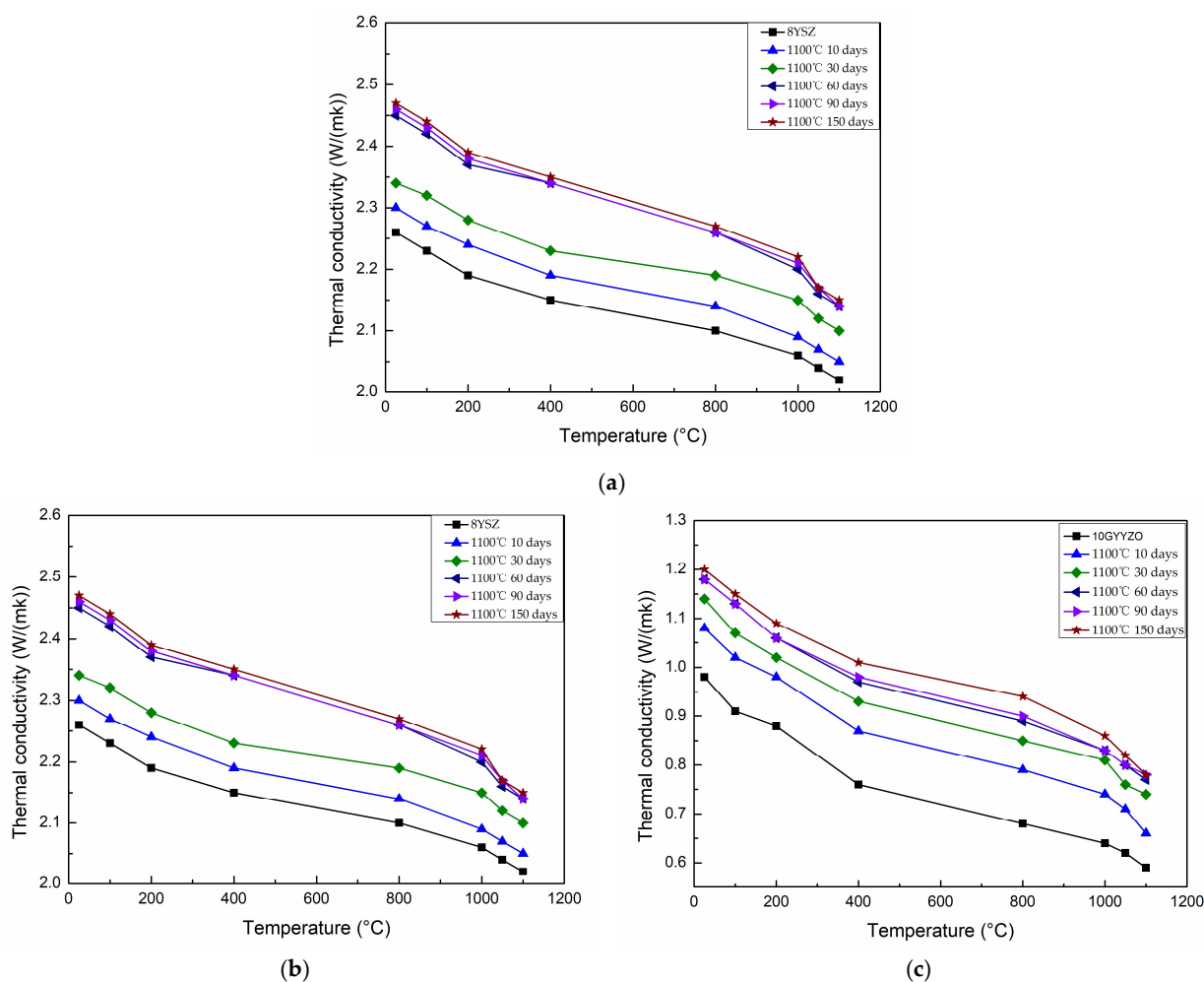


Figure 7. Thermal conductivity Variation Curves of TBCs Before and After Thermal Cycling: (a) 8YSZ; (b) 5GYYZO; (c) 10GYYZO.

Combined with the cross-sectional morphologies of the TBCs, it is found that the thermal conductivity of all coatings tends to stabilize after 60 cycles of thermal cycling. The

reason is that the internal pressure of the coating continuously increases during the thermal cycling process. As the internal pressure of the coating rises to a certain level, closed pores with sizes ranging from tens to hundreds of nanometers are crushed into open pores, and their sizes further decrease. Under the action of long-term high-temperature cycling, the open pores at the interfaces of ceramic particles further shrink with the diffusion of interface atoms and interface migration, until the interface pores are completely pushed to the larger pores. With the reduction in the number of heat exchange interfaces between nanoscale pores and the ceramic matrix, a partial rebound in the thermal conductivity of the TBCs occurs after long-term high-temperature thermal cycling, which degrades the thermal insulation performance of the TBCs. When the nanoscale small pores completely disappear, the thermal conductivity tends to stabilize. After 150 cycles, the thermal conductivities of the three coatings reach their maximum values: 2.15 W/(m·K) for 8YSZ at 1100 °C, 0.84 W/(m·K) for 5GYYZO at 1100 °C, and 0.78 W/(m·K) for 10GYYZO at 1100 °C.

4. Discussion

4.1. Mechanism of ZrO_2 Stabilization by Gd_2O_3 , Yb_2O_3 , and Y_2O_3

The core insight of this study lies in the synergistic stabilization effect of Gd^{3+} , Yb^{3+} , and Y^{3+} on ZrO_2 , which fundamentally addresses the phase instability issue of traditional 8YSZ coatings. As revealed by the XRD results (Figure 6, Table 3), 8YSZ powders and coatings exhibit partial m-phase peaks at 27° and 32°, while all GYYZO systems (5GYYZO, 10GYYZO, 15GYYZO) retain a pure t-phase, even after plasma spraying. This stabilization mechanism builds on key factors supported by prior research.

The ionic radii matching effect aligns with the fundamental principle of rare-earth stabilization of zirconia, as Gd_2O_3 and Yb_2O_3 are recognized as effective ZrO_2 stabilizers due to their ionic radius compatibility with Zr^{4+} . More specifically, Gd^{3+} (0.0938 nm) and Yb^{3+} (0.0868 nm) show minimal lattice mismatch with Zr^{4+} (0.084 nm), enabling substitution in the ZrO_2 lattice to form limited solid solutions [20]. This substitution disrupts lattice regularity and generates oxygen vacancy defects for charge neutrality. These defects act as “diffusion barriers” to inhibit Zr^{4+} and O^{2-} migration, which improves the phase stability of zirconia at high temperatures. In contrast, 8YSZ relies solely on Y^{3+} doping. Evans et al. noted that single Y^{3+} doping achieves only limited defect concentration, failing to fully suppress phase transformation during thermal cycling [27]. This finding is consistent with our observation of m-phase formation and cracking in 8YSZ after 60 cycles (Figure 3).

4.2. Microstructure and Material Properties

Thermal conductivity tests (Figure 7) show that 10GYYZO exhibits the lowest initial thermal conductivity (0.59 W/(m·K) at 1100 °C), far lower than 5GYYZO (0.72 W/(m·K)) and 8YSZ (2.02 W/(m·K)). This superiority stems from two microstructure-related effects. First, image analysis reveals that 10GYYZO has moderate porosity (15.36%), higher than 8YSZ (6.44%) and 5GYYZO (10.52%). Nanoscale pores act as “thermal barriers” to scatter phonons, the primary heat carriers in ceramics. However, excessive Gd_2O_3 (15 wt%) leads to abnormal porosity (43.55%) and unmelted grains (Figure 2d), causing spallation. This aligns with Gao et al.’s [24] findings that porosity above 30% destroys coating integrity, though GYYZO reaches this threshold at higher rare-earth content than single-doped systems. Second, oxygen vacancies and complex aggregates in GYYZO further scatter mid-frequency phonons. Compared to 8YSZ, GYYZO has higher defect density, which intensifies scattering. Johannes Essmeister et al. report that defect-induced phonon scattering reduces thermal conductivity by 30–40% in multi-doped TBCs [28]. During cycling, all coatings show increased thermal conductivity (10GYYZO rises to 0.78 W/(m·K) after 150 cycles) due to nanoscale pore sintering. Notably, GYYZO’s post-cycling thermal conductivity

remains 63% lower than 8YSZ ($2.15 \text{ W}/(\text{m}\cdot\text{K})$), whereas Zhang J X et al. reported only 40% reduction in dual-doped (Yb-Y) systems, confirming that Gd addition enhances long-term insulation stability [25].

The thermal cycling life order ($10\text{GYYZO} > 5\text{GYYZO} > 8\text{YSZ}$) links directly to phase stability and pore evolution, with clear advantages over reported coatings:

For 8YSZ (Figure 3), $t \rightarrow m$ phase transition causes 3–5% volume expansion, generating stress that cracks the coating, consistent with Evans et al.'s classic failure mechanism. Micron pores connect into cracks after 60 cycles, leading to spallation [27].

For 5GYYZO (Figure 4), pure t-phase avoids volume expansion, but lower porosity (10.52%) provides limited stress relief—failing after 90 cycles. For 10GYYZO (Figure 5), the combination of pure t-phase and moderate porosity (15.36%) extends life to 150 cycles. Its thickness remains $200 \mu\text{m}$ until 90 cycles, far more stable than 8YSZ ($100 \mu\text{m}$) and even exceeding the 120-cycle life of Yb-Y co-doped coatings reported by Cao et al. [29]. This confirms that Gd addition optimizes the “phase stability–porosity balance” critical for thermal cycling resistance.

5. Conclusions

In this study, 8 wt% Y_2O_3 and 5 wt% Yb_2O_3 were doped with 5 wt%, 10 wt%, and 15 wt% Gd_2O_3 to stabilize zirconia powders. GYYZO thermal barrier coatings (TBCs) were fabricated via atmospheric plasma spraying (APS). Subsequently, the GYYZO coatings with different Gd_2O_3 addition amounts were subjected to continuous thermal shock cycling at 1100°C for 10, 30, 60, 90, and 150 cycles. The results indicate the following:

- (1) Co-doping Gd_2O_3 , Yb_2O_3 , and Y_2O_3 enables ZrO_2 to form a stable pure t-phase. By substituting Zr^{4+} and generating oxygen vacancy defects/complex aggregates, this system completely suppresses $t \rightarrow m$ transformation, outperforming single Y^{3+} doping and dual Yb-Y doping in phase stability.
- (2) 10GYYZO balances porosity (15.36%) and defect density, achieving $0.59 \text{ W}/(\text{m}\cdot\text{K})$ thermal conductivity and 150-cycle life. Its thermal cycling life is 2.5 times that of 8YSZ. This “composition–microstructure–performance” tuning strategy advances beyond structural optimization approaches.
- (3) 10GYYZO coatings exhibit superior insulation, long life, and APS compatibility, making them a promising 8YSZ replacement. Avoiding excessive Gd_2O_3 and verifying CMAS resistance will accelerate industrial adoption.

This study provides a new paradigm for high-performance TBC design via rare-earth co-doping, offering actionable insights for improving high-temperature equipment reliability.

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