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Preparation and Thermophysical Properties of New Multi-Component Entropy-Stabilized Oxide Ceramics for Thermal Barrier Coatings

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Abstract: Five kinds of multi-component entropy-stabilized oxide ceramics were prepared by a solid-state reaction method for thermal barrier coatings, namely $\text{La}_{0.125}\text{Y}_{0.125}\text{Yb}_{0.125}\text{Gd}_{0.125}\text{Zr}_{0.5}\text{O}_{1.75}$ (LaYYbGdZr), $\text{Y}_{0.125}\text{Yb}_{0.125}\text{Gd}_{0.125}\text{Ta}_{0.125}\text{Zr}_{0.5}\text{O}_{1.875}$ (YYbGdTaZr), $\text{La}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{Gd}_{0.1}\text{Ta}_{0.1}\text{Zr}_{0.5}\text{O}_{1.85}$ (LaYYbGdTaZr), $\text{Y}_{0.125}\text{Yb}_{0.125}\text{Gd}_{0.125}\text{Ta}_{0.125}\text{Hf}_{0.25}\text{Zr}_{0.25}\text{O}_{1.875}$ (YYbGdTaHfZr), and $\text{La}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{Gd}_{0.1}\text{Ta}_{0.1}\text{Hf}_{0.25}\text{Zr}_{0.25}\text{O}_{1.85}$ (LaYYbGdTaHfZr). Many properties of the materials were studied, such as their microscopic morphology, crystal structure, thermophysical properties, and ablation resistance. The results show that the oxide ceramics synthesized in this paper have a uniform single-phase defect fluorite structure, and can still maintain this structure after high-temperature treatment at 1500 °C. The YYbGdTaHfZr coatings had the lowest thermal conductivity ($0.61\sim0.89\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), which was much lower than that of YSZ. The ceramic blocks also exhibited excellent thermal expansion properties. The thermal expansion coefficient of LaYYbGdTaZr could reach $11.09 \times 10^{-6}\text{ K}^{-1}$ (1400 °C), which was slightly higher than that of 8YSZ ($11.0 \times 10^{-6}\text{ K}^{-1}$). The antioxidant ablation results proved that the YYbGdTaHfZr coating showed the best heat-insulating property. All the results showed that the YYbGdTaHfZr coating is a promising thermal barrier coating.

Keywords: high entropy; thermal barrier coatings; thermal conductivity; thermal expansion coefficient



Citation: Li, W.; Zhu, Y.; Wang, X.; Zhao, L.; Chu, Y.; Chen, F.; Ge, C.; Fang, S. Preparation and Thermophysical Properties of New Multi-Component Entropy-Stabilized Oxide Ceramics for Thermal Barrier Coatings. *Coatings* **2023**, *13*, 937. <https://doi.org/10.3390/coatings13050937>

Academic Editor: Andreas Killinger

Received: 18 April 2023

Revised: 10 May 2023

Accepted: 12 May 2023

Published: 17 May 2023



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1. Introduction

Aerospace engines are exposed to ultra-high temperatures during service. Especially in recent years, to obtain greater driving force, the engine has developed in the direction of a high thrust-to-weight ratio and high gas temperatures, and further requirements have been put forward for the high-temperature resistance of engine materials [1–3]. Thermal barrier coatings (TBCs) are a layer of ceramic materials coated on the metal surface of the engine, which can provide thermal shielding for metal parts working at high temperatures, protect the working parts, and prolong their service life [4]. The thermal barrier coating's ceramic material must have the characteristics of a high melting point (>2000 °C), no phase transition in the operating temperature range (room temperature to 1500 °C), low thermal conductivity, and a thermal expansion coefficient matching the matrix material. Currently, yttrium oxide partially stabilized zirconia ((6–8) wt% Y_2O_3 stabilized zirconia, YSZ) coatings are commonly used, and phase transition occurs above 1200 °C [5]. The phase-change volume difference causes the coatings to peel off from the substrate, so it is necessary to develop new materials with better properties to meet the development needs.

In 2015, Rost [6] first reported a rock-salt structure (MgNiCoCuZn)O high-entropy ceramic (HECs) material. At present, various types of new high-entropy ceramics in different fields are being widely used. High-entropy ceramics are a series of single-phase ceramics

designed by multi-principal high-entropy alloying. Each core element in the system is in an equiatomic percentage or a near-equiatomic percentage. Compared with traditional ceramic materials, high-entropy ceramics exhibit significant differences in composition, structure, or properties. They provide a new idea for obtaining new thermal barrier coating materials with ultra-low thermal conductivity, a large thermal expansion coefficient, and excellent mechanical properties. The studies of Jien-Wei Yeh [7] and others [8–11] found that the performance of high-entropy ceramics is affected by four processes: high entropy, lattice distortion, sluggish diffusion, and the cocktail effect.

In recent years, many kinds of high-entropy oxides have been studied. Yao [12] reported a double tetragonal phase high-entropy oxide ceramic ($\text{Zr}_{1-4x}\text{Y}_x\text{Yb}_x\text{Ta}_x\text{Nb}_x\text{O}_2$), a multi-ceramic material with excellent high-temperature stability and excellent thermomechanical properties. Sun et al. [13] prepared a cubic phase structure high-entropy oxide ($5\text{RE}_{0.2}\text{O}_3$ ($\text{RE} = \text{Sm}, \text{Eu}, \text{Er}, \text{Lu}, \text{Y}, \text{Yb}$)), whose thermal expansion coefficient is close to Y_2O_3 and Al_2O_3 , has good CMAS resistance, and is expected to be used in environmental barrier coating materials. Chen et al. [14] reported a new fluorite-type high-entropy oxide ($\text{Ce}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{O}_2$), which has reversible changes between low-temperature multi-phase and high-temperature single-phase states; its room temperature thermal conductivity is $1.28 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is only half the size of 7YSZ, indicating that the material can be used in the field of thermal insulation.

Some studies have found that the small-radius ions Ta^{5+} doped into YSZ can reduce the degree of distortion of the crystal tetragonal phase, improve the phase stability of the material, and prevent phase transitions during heating and cooling. Bhattacharya [15] and Pitck [16] each studied the $\text{ZrO}_2\text{-YO}_{1.5}\text{-TaO}_{2.5}$ system. The solubility of Ta^{5+} ions in ZrO_2 is limited. When Y^{3+} and Ta^{5+} are doped simultaneously, there is a strong interaction between the two ions, which leads to a significant increase in the solubility of YTao_4 , and a uniform single-phase structure is finally obtained [17]. The strong interaction of the two ions reduces the material's reactivity, so the corrosion resistance is also excellent. Therefore, the zirconia composite co-stabilized by $\text{YO}_{1.5}$ and $\text{TaO}_{2.5}$ improves the phase stability and corrosion resistance, and the obtained metastable t' phase can exist stably below 1500°C without phase transition [15]. However, the stable tetragonal region in the $\text{ZrO}_2\text{-YO}_{1.5}\text{-TaO}_{2.5}$ phase diagram is very narrow [18], and the compositions and phases may easily deviate from their original states after high-temperature operation, which severely limits their application in TBCs.

The goals of this study were to obtain a new thermal barrier coating material for aerospace engines through high-entropy design, further reduce the thermal conductivity of the coating, improve the coefficient of thermal expansion, and achieve high temperature stability. Therefore, this study drew on the research ideas of Pitck et al. [16] to introduce Ta^{5+} into high-entropy oxides. Due to the presence of the high entropy effect, the resulting material is still a single-phase structure. The defect association between smaller Ta^{5+} and larger Y^{3+} in the ZrO_2 lattice improves stability [15]. At the same time, the introduction of trivalent ions will produce oxygen ion vacancies, while pentavalent Ta^{5+} can inhibit the formation of oxygen vacancies and improve the fracture toughness and phase stability of the material [17]. At the same time, a variety of other oxides, such as rare earth element oxides (RE_2O_3 , $\text{RE} = \text{La}, \text{Y}, \text{Yb}, \text{Gd}$), HfO_2 , and Ta_2O_5 , together with the following multi-component entropy-stabilized oxide ceramics, were prepared: $\text{La}_{0.125}\text{Y}_{0.125}\text{Yb}_{0.125}\text{Gd}_{0.125}\text{Zr}_{0.5}\text{O}_{1.75}$ (LaYYbGdZr), $\text{Y}_{0.125}\text{Yb}_{0.125}\text{Gd}_{0.125}\text{Ta}_{0.125}\text{Zr}_{0.5}\text{O}_{1.875}$ (YYbGdTazr), $\text{La}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{Gd}_{0.1}\text{Ta}_{0.1}\text{Zr}_{0.5}\text{O}_{1.85}$ (LaYYbGdTazr), $\text{Y}_{0.125}\text{Yb}_{0.125}\text{Gd}_{0.125}\text{Ta}_{0.125}\text{Hf}_{0.25}\text{Zr}_{0.25}\text{O}_{1.875}$ (YYbGdTahfzr), $\text{La}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{Gd}_{0.1}\text{Ta}_{0.1}\text{Hf}_{0.25}\text{Zr}_{0.25}\text{O}_{1.85}$ (LaYYbGdTahfzr). Additionally, the structure, thermophysical properties, and thermal shock resistance of multi-component entropy-stabilized oxides were studied to ensure that the material has good development prospects in thermal barrier coatings.

2. Materials and Methods

2.1. Raw Materials and Preparation

Five oxide ceramic powders were synthesized by high-temperature solid-phase synthesis, all with an analytical grade, from the Sinopharm Chemical Reagent Co., Ltd., and they could be used without further processing. The experimental process was as follows: first, the oxide powder with the metrological ratio was mixed with absolute ethanol and, then, mixed by ball milling at $400 \text{ r} \cdot \text{min}^{-1}$ for 5 h. The obtained slurry was dried in an oven at 80°C for 12 h, sieved with an 80-mesh sieve, and collected. The resulting powder was then sintered at 1500°C for 5 h. After cooling, the sample was crushed and ground to obtain ceramic powder, after passing through an 80-mesh screen. The prepared ceramic materials were sprayed and granulated to obtain a powder with good fluidity, which can be used to prepare thermal barrier coatings (TBCs) by atmospheric plasma spraying (APS, MultiCoat, Oerlikon metco). The spraying parameters were as follows: current, 570 A; Argon, 50 NLPM; hydrogen, 7 NLPM; spray distance, 128 mm; and speed, 400 mm/s.

A $50 \text{ mm} \times 50 \text{ mm} \times 5 \text{ mm}$ superalloy sheet was used as the substrate. First, $100 \mu\text{m}$ NiCoCrAlY coatings were sprayed and, then, ceramic coatings of $500 \mu\text{m}$ were prepared.

Part of the adhesive (polyvinyl alcohol solution, 8 wt.%) was added to the pre-sintered ceramic powder, pressed into a $\phi 19 \times 5 \text{ mm}$ block ceramic under 10 MPa pressure, and degummed at 400°C for 2 h. After sintering at 1500°C for 5 h, a dense ceramic block (cut as $10 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm}$) was formed to measure the coefficient of thermal expansion.

2.2. Sample Characterization

The phase analysis of the ceramic powder and spray coatings was carried out by X-ray diffractometer (XRD, Rigaku SmartLab 9 kW, Tokyo, Japan). The test conditions were Cu target, $K\alpha$ rays, a tube voltage of 40 kV, and a tube current of 30 mA. The step size was 0.02° , the scanning speed was $20^\circ/\text{min}$, and the scanning range was $5\sim 90^\circ$. Lattice parameters were calculated according to XRD Rietveld refinement. The refinement data were tested with a step width of 0.02° and a step size of $4 \text{ s} \cdot \text{step}^{-1}$. High-resolution field emission scanning electron microscopy (SEM, JSM-7800 (Prime), Japan) was used to analyze the morphology of the powder samples and the structure of the coatings surface and interface. The content ratio of each element was analyzed using an X-ray energy spectrometer (EDS, X-MaxN50 Aztec, Oxford, UK). The test parameters of SEM were EHT = 2.00 kV, WD = 10.00 mm and 6.00 mm; the test parameters of EDS were EHT = 15.00 kV, WD = 10.00 mm. A laser thermal conductivity tester (LFA427, NETZSCH, Selb, Germany) was used to test the thermal conductivity of the samples. The samples were ceramic sheets of $\phi 12.5 \times (1.0\sim 1.5) \text{ mm}$, prepared by spraying. The thermal diffusivity and constant pressure heat capacity were tested at six temperature points of room temperature— 300°C , 600°C , 900°C , 1200°C , and 1500°C —and the thermal conductivity curve and specific heat capacity curve of the coatings were obtained. The measurement errors of the instruments and equipment used were as follows: NETZSCH laser thermal conductivity tester (LFA427), $\pm 3\%$; coefficient of thermal expansion (PCY-1700), $\pm 0.1\%\sim 0.5\%$.

3. Results and Discussion

3.1. Phase Structure

Figure 1 shows XRD images of various oxide ceramics that were prepared, including LaYYbGdZr, YYbGdTaZr, LaYYbGdTaZr, YYbGdTaHfZr, and LaYYbGdTaHfZr. The synthesized ceramic powder mainly showed a c-ZrO₂ structure (Fm3m). The characteristic peaks correspond, from left to right, to the crystal planes (111), (200), (220), (311), (222), (400), (331), and (420), respectively, and no other crystal phases were formed. Comparing the powder XRD diffraction peak with the diffraction peak (PDF#96-210-1235) of the standard c-ZrO₂ crystal phase, the diffraction peak shifted to a small angle as a whole. This was because more RE³⁺ with a larger radius was added, and less Ta⁵⁺ with a smaller radius was added. The overall doping effect increased the lattice constant. Using the Bragg

equation $d\sin\theta = n\lambda$, it can be seen that when n and λ were unchanged, a larger d caused θ to decrease; that is, the diffraction peak shifted to a small angle. From the difference curves in the $28\text{--}36^\circ$ and $48\text{--}61^\circ$ 2θ -theta regions, it can be seen that the diffraction peaks of the three ceramics containing La^{3+} ions shifted more by small angles. This result also validated the interpretation of the Bragg equation. The phase composition and structure of five ceramics were demonstrated by XRD combined with Rietveld refinements (Figure 2). As shown, the five ceramics had a cubic single-phase structure (Fm3m) with a lattice parameter: (a) LaYbGdZr , $a = 5.178 \text{ \AA}$, (b) YbGdTaZr , $a = 5.179 \text{ \AA}$, (c) LaYbGdTaZr , $a = 5.168 \text{ \AA}$, (d) YbGdTaHfZr , $a = 5.171 \text{ \AA}$, and (e) LaYbGdTaHfZr , $a = 5.171 \text{ \AA}$.

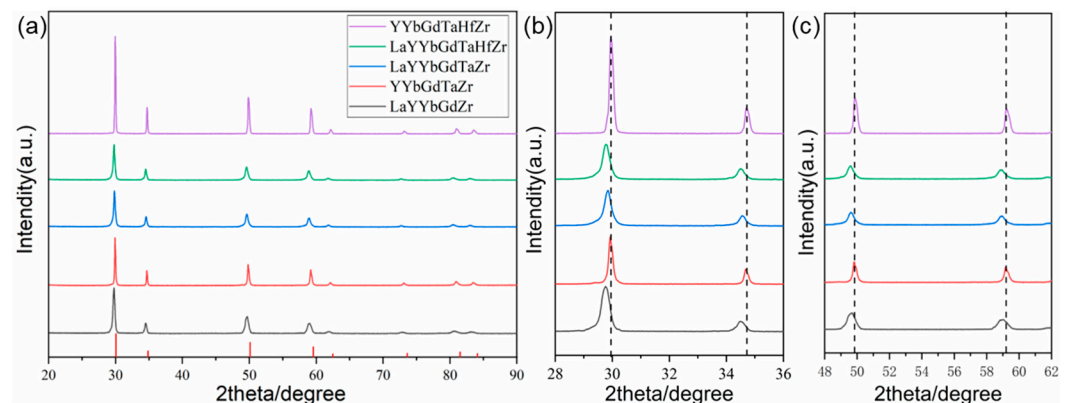


Figure 1. XRD patterns of five ceramic powders: (a) $20^\circ \leq 2\theta \leq 90^\circ$, characteristic peaks of (b) $28^\circ \leq 2\theta \leq 36^\circ$ and (c) $48^\circ \leq 2\theta \leq 61^\circ$.

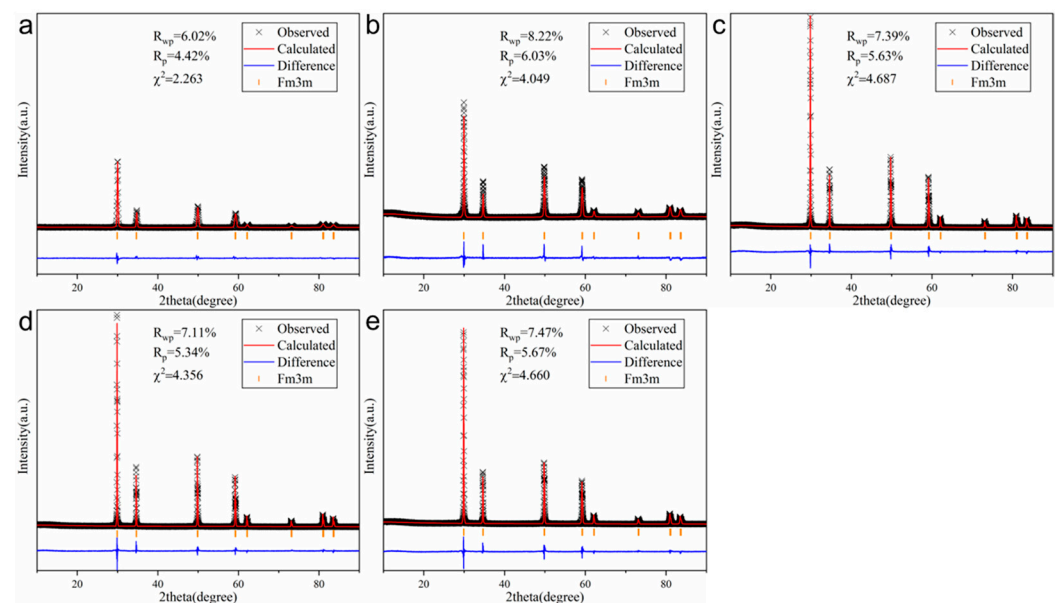


Figure 2. Rietveld XRD refinement of five ceramic powders: (a) LaYbGdZr , (b) YbGdTaZr , (c) LaYbGdTaZr , (d) YbGdTaHfZr , and (e) LaYbGdTaHfZr .

Figure 3 shows the XRD patterns of five ceramic coatings after thermal cycling from room temperature to 1500°C . It was found that both before and after heat treatment, the coatings all had the Fm3m space group structure, the positions of each diffraction peak could correspond one-to-one, and the crystal structure did not change. Thus, these results proved that the thermal stability of the material is very good, and the crystal structure will not be changed due to heating. This is because the slow diffusion effect in high-entropy ceramics hinders the diffusion of cations and oxygen vacancies [19], requiring

more energy to change the material structure. This enables the material to withstand higher temperatures, enhancing its high-temperature stability.

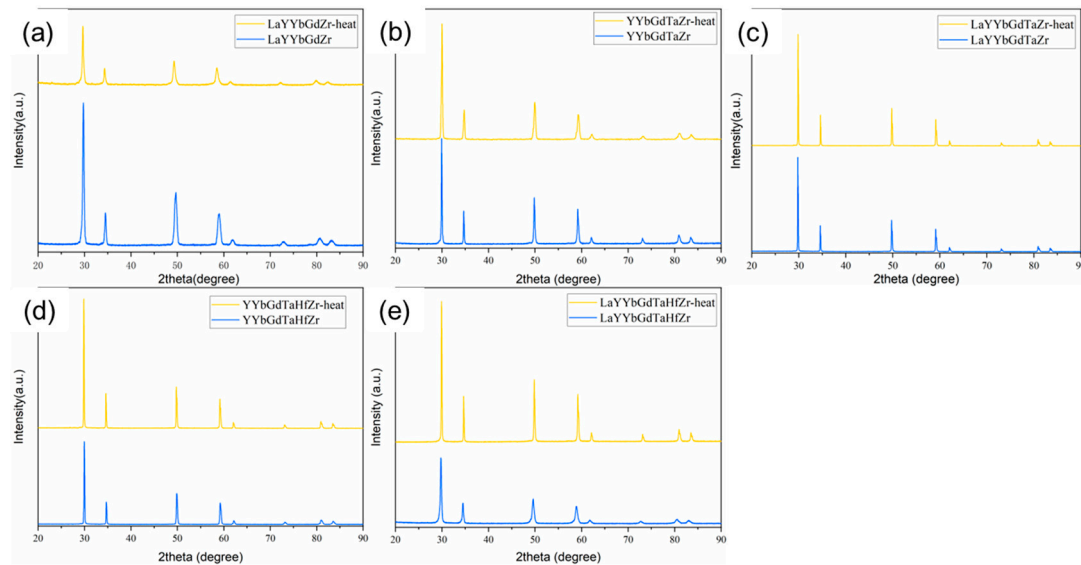


Figure 3. XRD patterns of the five ceramic coatings before and after thermal cycling from room temperature to 1500 °C: (a) LaYYbGdZr, (b) YYbGdTaZr, (c) LaYYbGdTaZr, (d) YYbGdTaHfZr, and (e) LaYYbGdTaHfZr.

3.2. Microstructure

The coating of each component was prepared by plasma spraying, and the topography of the coating section was characterized by scanning electron microscopy. Figures 4 and 5 show SEM images of the cross-section of each component of ceramic coatings. As shown in Figure 4, the thickness of the coating was about 500 μm , and the thickness was uniform. The coating formed by spraying did not have a high density, and there were many pores and microcracks inside the coating. However, the overall molding effect of the coating was good, the coating powder deposited after melting was tightly bonded, and there was no big defect. No obvious delamination could be seen in the overall topography of the coating at 500 μm , but in the enlarged image of the coating section in Figure 5b, it can be seen that the topography of the different layers in the coating was different. As shown in Figure 5b, there was a large solidified accumulation of particles inside the coating. During the coating formation, the coating powder particles were not completely melted, so a coating of such a structure was formed during the deposition process. Figure 5c–e shows a further enlarged topography of the coating cross-section, from which many pores and incompletely molten ceramic particles can be observed to accumulate inside the coating. These pores and microcracks provide the coating with good tolerance against thermal strain [20].

During plasma spraying, molten particles were ejected with the flame and deposited layer-by-layer on the substrate. When high-speed particles were sprayed out, lateral flattening, rapid solidification, and cooling occurred. At the same time, there were many splash components, which eventually formed a disk-shaped block deposited on the substrate. The pores formed by the imperfect stacking of different particles in the layer are called intra-sheet pores, and the imperfect combination between layers is called an interlayer crack. Interlayer cracks and intra-sheet pores are interconnected to form a unique plasma-sprayed layered structure [21,22]. The composition of each element in the sample was analyzed by EDS (Figure 6), and it was found that the distribution of various elements was uniform, and there was no component segregation phenomenon. Within the error range, the content of each element was basically consistent with the theoretical amount added (Table 1).

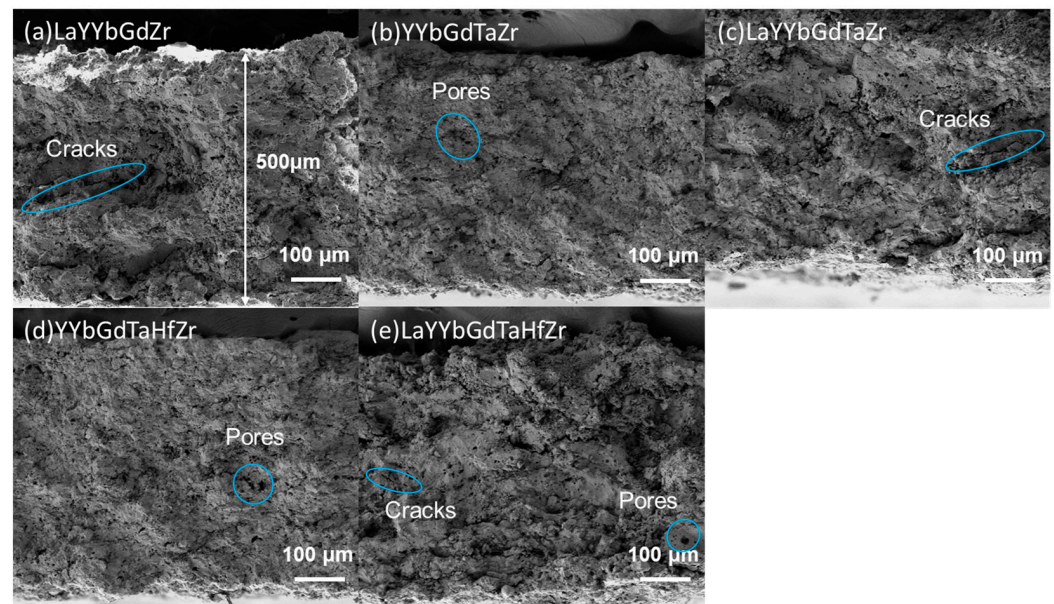


Figure 4. Cross-sectional SEM images of five ceramic coatings, with a coating thickness of about 500 μm . (a) LaYYbGdZr, (b) YYbGdTazr, (c) LaYYbGdTazr, (d) YYbGdTahfZr, and (e) LaYYbGdTahfZr.

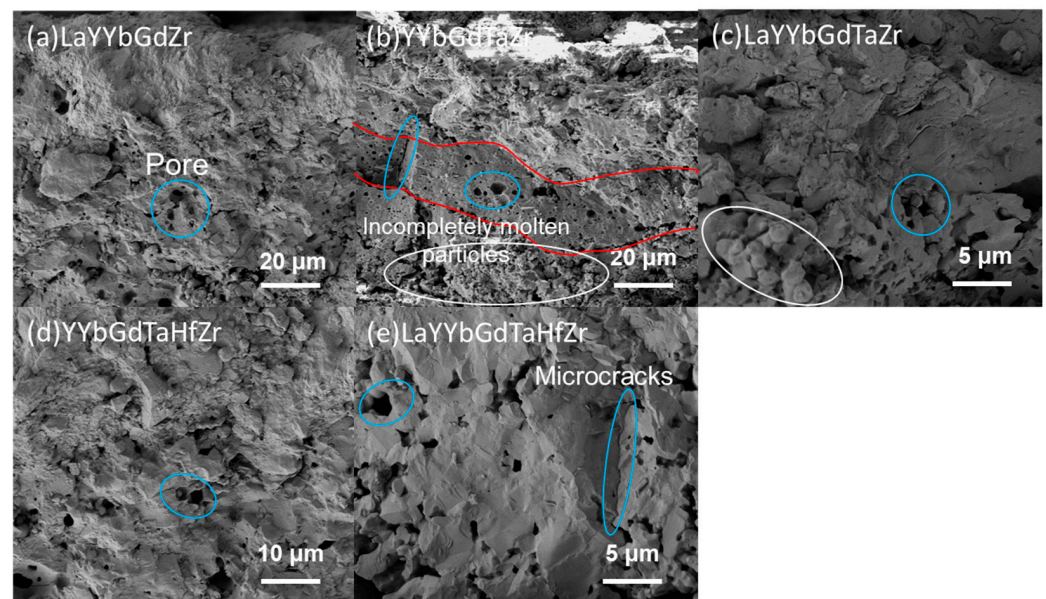


Figure 5. Cross-sectional SEM enlarged images of five ceramic coatings, as well as delamination, pores, and microcracks in the coatings. (a) LaYYbGdZr, (b) YYbGdTazr, (c) LaYYbGdTazr, (d) YYbGdTahfZr, and (e) LaYYbGdTahfZr.

Table 1. The content of each element in the sample (at%) and the error (%) with the theoretical addition amount.

Element	LaYYbGdZr		YYbGdTazr		LaYYbGdTazr		YYbGdTahfZr		LaYYbGdTahfZr	
	at%	Error %	at%	Error %	at%	Error %	at%	Error %	at%	Error %
O	64.84	1.89	66.82	2.46	66.27	2.09	65.55	0.52	64.23	−1.04
Zr	16.75	−7.86	16.58	−4.66	16.57	−5.56	8.72	0.24	8.97	2.26
La	4.79	5.48	0.00	0.00	3.35	−4.65	0.00	0.00	3.75	6.94
Y	4.93	8.48	4.51	3.74	3.56	1.49	4.47	2.84	3.69	5.07
Gd	4.55	0.16	4.03	−7.29	3.40	−3.10	4.24	−2.38	3.78	7.72
Yb	4.13	−9.14	4.08	−6.18	3.48	−0.72	4.51	3.64	3.70	5.41

Table 1. Cont.

Element	LaYYbGdZr		YYbGdTaZr		LaYYbGdTaZr		YYbGdTaHfZr		LaYYbGdTaHfZr	
	at%	Error %	at%	Error %	at%	Error %	at%	Error %	at%	Error %
Hf	0.00	0.00	0.00	0.00	0.00	0.00	8.30	−4.51	8.35	−4.83
Ta	0.00	0.00	3.98	−8.44	3.37	−3.87	4.21	−3.26	3.53	0.63
	100.00		100.00		100.00		100.00		100.00	

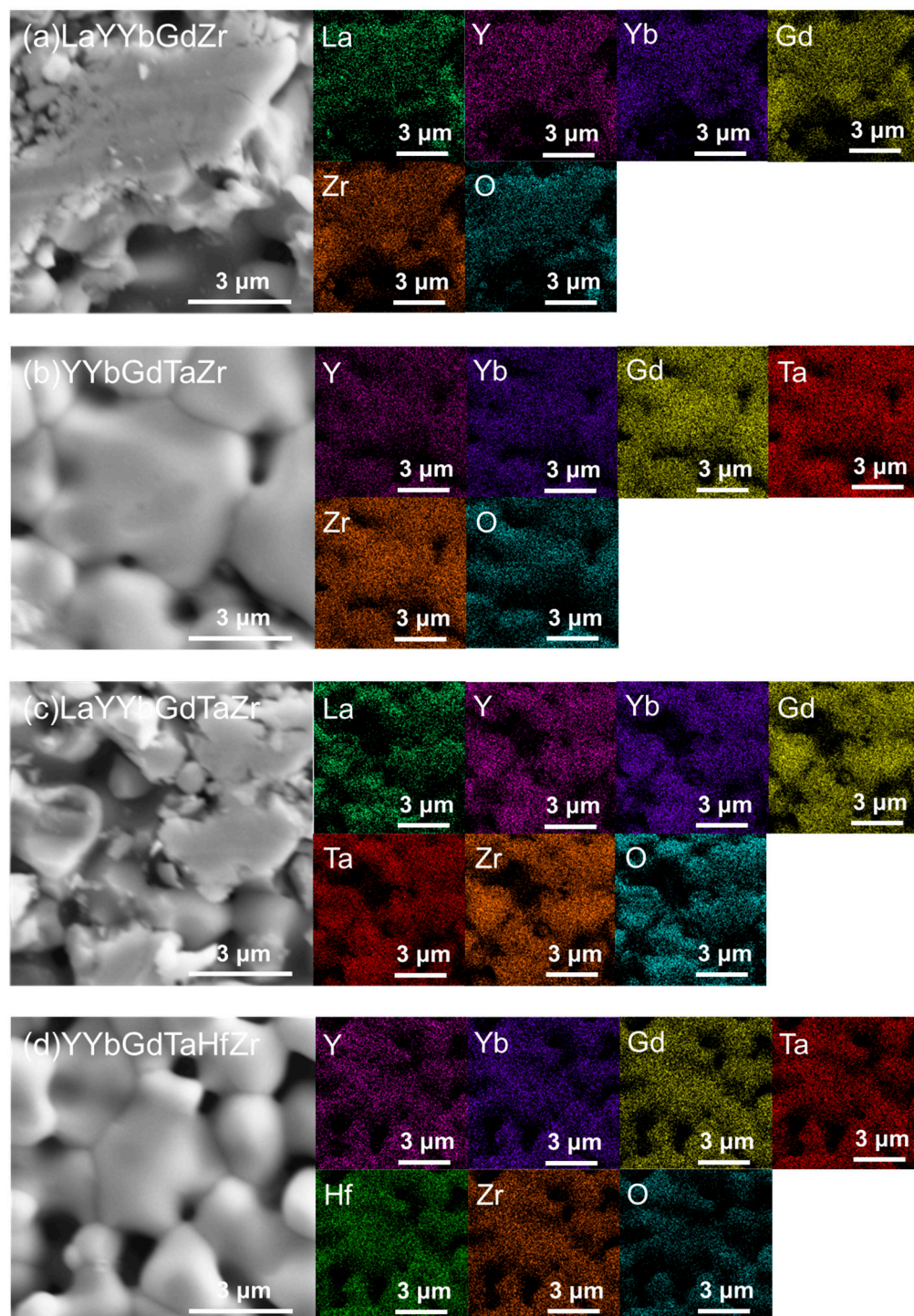


Figure 6. Cont.

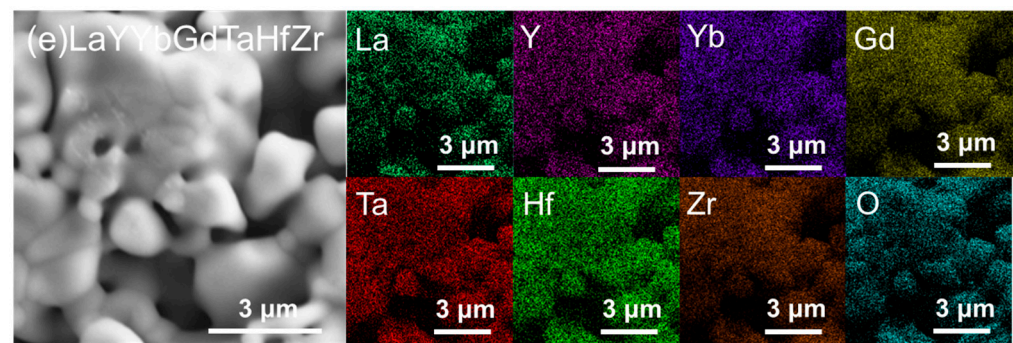


Figure 6. Five ceramic oxides corresponding to EDS mapping of Zr, Ta, Yb, Y, Hf, O, La and Gd elements, respectively. (a) LaYYbGdZr, (b) YYbGdTaZr, (c) LaYYbGdTaZr, (d) YYbGdTaHfZr, and (e) LaYYbGdTaHfZr.

3.3. Thermal Conductivity of the Coatings

The thermal conductivity of thermal barrier coatings prepared by APS was tested. According to the theory of solid heat conduction, the heat conduction of materials is mainly carried out by electrons and phonons, and photons are involved at high temperatures [23]. However, for ceramic materials with high resistivity, the contribution of electrons to thermal conductivity can be ruled out [24]. Therefore, phonon thermal conduction and photon thermal conduction are mainly considered. Figure 7a shows the intrinsic thermal diffusivity changes in the five multi-component entropy-stabilized ceramic components, YSZ, and $\text{La}_2\text{Zr}_2\text{O}_7$ (LaZr). From room temperature to 1500 °C, the thermal diffusivity of several different coatings gradually decreased below about 900 °C with increasing temperature, and increased again above 900 °C. This was because phonon scattering increases with increasing temperature due to phonon diffusion control at low temperatures, resulting in a decrease in thermal conductivity [25–27]. The photon thermal conductivity gradually increases at high temperatures, so the thermal diffusivity turns into growth when the temperature is too high. The high-entropy disordered configuration of the material can significantly enhance the anharmonic lattice vibration, enhance phonon scattering, and lead to a large decrease in thermal diffusivity. Thus, the thermal diffusivity of the five multi-component entropy-stabilized materials was significantly lower than that of YSZ and LaZr. As can be seen in Figure 7b, the specific heat capacity of the material increased as the temperature increased, mainly due to large volume expansion and enhanced phonon scattering [28]. The thermal conductivity k of a material could be calculated by the following formula:

$$k = C_p \cdot \lambda \cdot \rho$$

C_p ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$) is the measured specific heat capacity, λ ($\text{mm}^2 \cdot \text{s}^{-1}$) is the measured intrinsic thermal diffusivity, and ρ (g/cm^3) is the actual density of the sample.

The law of the thermal diffusion rate of materials conforms to the thermal conduction mechanism of solid materials. When Ta^{5+} is introduced into ceramic materials, the difference in radius and mass between Ta^{5+} and rare earth ions is larger than the difference between rare earth ions. At the same time, the oxides of pentavalent cations introduce additional oxygen ions into the crystal, and O^{2-} filling the lattice introduces cationic voids and further disrupts the charge distribution [29,30]. Lattice distortions and crystal defects established by these factors can enhance phonon scattering, resulting in a further decrease in the thermal conductivity of ceramic materials. Therefore, using Ta^{5+} to replace La^{3+} for doping can significantly reduce the thermal diffusion rate of the material, while stabilizing the lattice and providing phase stability. The introduction of Hf^{4+} ions into the material to replace Zr^{4+} in the lattice, in addition to the mass disorder caused by the increase in atomic species, also causes lattice distortion, enhances phonon scattering, and reduces the thermal diffusion rate [31,32].

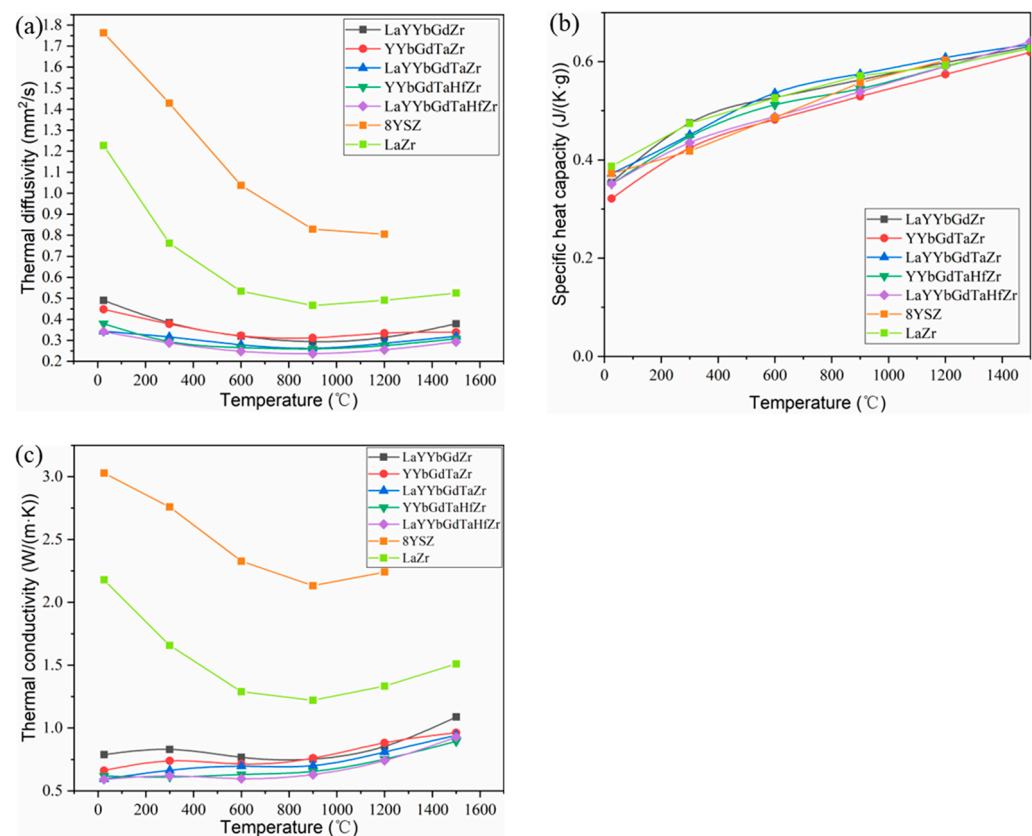


Figure 7. Thermophysical properties of multi-component entropy-stabilized ceramics, 8YSZ and $\text{La}_2\text{Zr}_2\text{O}_7$: (a) thermal diffusivity; (b) specific heat capacity; (c) thermal conductivity.

The thermal conductivity of five multi-component entropy-stabilized ceramics coatings was $0.79\sim1.09\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (LaYYbGdZr, $25\sim1500\text{ }^\circ\text{C}$), $0.66\sim0.96\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (YYbGdTaZr, $25\sim1500\text{ }^\circ\text{C}$), $0.59\sim0.94\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (LaYYbGdTaZr, $25\sim1500\text{ }^\circ\text{C}$), $0.61\sim0.89\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (YYbGdTaHfZr, $25\sim1500\text{ }^\circ\text{C}$), $0.59\sim0.93\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (LaYYbGdTaHfZr, $25\sim1500\text{ }^\circ\text{C}$), which was greatly improved, compared to YSZ ($\sim2.3\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $1000\text{ }^\circ\text{C}$) [33] and $\text{La}_2\text{Zr}_2\text{O}_7$ ($\sim1.51\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $1500\text{ }^\circ\text{C}$) materials. The low thermal conductivity of the material is mainly attributed to several reasons. One reason is the large number of point defects in ceramics, mainly a large number of oxygen vacancies in the defective fluorite structure, which greatly enhances the phonon scattering rate and reduces the free path of phonon scattering, thereby reducing thermal conductivity. The second reason is that the cocktail effect enhances the synergy of multi-component elements, increases the number of scattering centers, and reduces thermal conductivity [34].

3.4. Thermal Expansion Coefficient

One of the main reasons for the failure of the coatings is the mismatch of the thermal expansion coefficient between the ceramic layer and the bonding layer. During the heating-cooling cycle, the coefficient of thermal expansion differs between the coating and the metal substrate, and a large amount of thermal stress is generated inside the coatings. The accumulated thermal stress causes a large number of cracks in the coating during cooling, which eventually leads to coating failure [35,36]. It can be seen in Figure 8 that the thermal expansion coefficients of several ceramic blocks increased with the increase in temperature in the range of $200\sim1400\text{ }^\circ\text{C}$. This is because the thermal expansion coefficient is inversely proportional to the lattice energy, which is proportional to the average electronegativity difference between anions and cations and inversely proportional to the atomic spacing [37–39]. For the same kind of ceramics, the atomic spacing increases with

the increase in temperature, so the thermal expansion coefficient also increases with the increase in temperature.

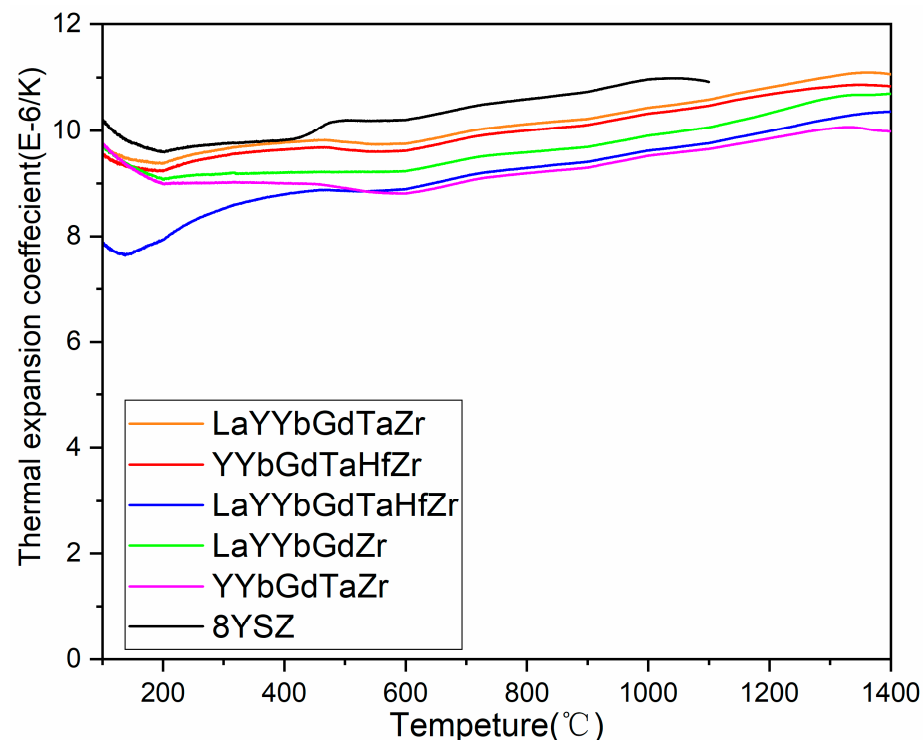


Figure 8. Thermal expansion performance curve of multi-component entropy-stabilized ceramic blocks and 8YSZ.

Multi-component entropy-stabilized ceramics can improve the thermal expansion coefficient by changing the type of doping atoms to affect the lattice distortion. The introduction of Gd^{3+} , Y^{3+} , Yb^{3+} , and La^{3+} with larger radii into ZrO_2 increases the particle spacing in the ceramic material, reduces the lattice energy, and increases the thermal expansion coefficient [40]. Due to the obvious cocktail effect, disordered and controllable mixed structures can effectively induce thermal expansion coefficient increases [41]. It can be seen in Figure 8 that the ceramic material with the highest thermal expansion coefficient was LaYYbGdTaZr, while the lowest was YYbGdTaZr. The thermal expansion coefficients were $11.09 \times 10^{-6} K^{-1}$ (LaYYbGdTaZr, 1400 °C), $10.86 \times 10^{-6} K^{-1}$ (YYbGdTaHfZr, 1400 °C), $10.36 \times 10^{-6} K^{-1}$ (LaYYbGdTaHfZr, 1400 °C), $10.70 \times 10^{-6} K^{-1}$ (LaYYbGdZr, 1400 °C), $10.07 \times 10^{-6} K^{-1}$ (YYbGdTaZr, 1400 °C). They all had high thermal expansion coefficients, which were close to that of 8YSZ ($11.0 \times 10^{-6} K^{-1}$, 1000 °C) [33]. However, when used for a long time at more than 1200 °C, the 8YSZ coating underwent a phase change and lost its effect. The use temperature of multi-component entropy-stabilized materials is much higher than that of 8YSZ, and it can still maintain a high coefficient of thermal expansion at high temperatures.

According to the Rietveld refinement results in Figure 2, the lattice constant of the five ceramics differed very little ($\sim 0.01 \text{ \AA}$), so the change of lattice energy after the formation of crystals was not obvious. Moreover, the same entropy stable oxide was stable at high temperature, so the change in its thermal expansion coefficient could not be judged from the change of lattice energy. Therefore, it can also be seen from the figure that comparing the thermal expansion coefficient of LaYYbGdTaZr and LaYYbGdZr, the thermal expansion coefficient increased after doping Ta^{5+} . Comparing the thermal expansion coefficients of YYbGdTaZr and YYbGdTaHfZr, LaYYbGdTaZr and LaYYbGdTaHfZr, the thermal expansion coefficient increased and decreased after doping Hf^{4+} ions. Therefore, the doping of Ta^{5+} and Hf^{4+} ions did not improve the thermal expansion performance obviously.

3.5. Ablation Properties of Coatings

Coatings must be exposed to ultra-high temperature conditions, so exploring the service life of coatings at high temperatures is also an important part of coatings' performance characterization. The thermal barrier coating ablation experiment uses ultra-high temperature flames to hit the coating surface. The ablation performance of the coating can be obtained by observing the morphology change in the coating after the ablation-cooling cycle process.

The prepared ceramic material was coated on the superalloy substrate by plasma spraying, including a 100 μm primer layer (MCrAlY) and a 500 μm ceramic layer (multi-component entropy-stabilized oxides). Using a plasma flame as a heating source, the surface of the coatings was ablated at 1500 $^{\circ}\text{C}$ for 300 s, then cooled to room temperature naturally in the air to observe the morphology change of the surface coatings. If the coatings did not crack, the process was repeated until the coatings cracked significantly or the coatings began to fall off, and the number of thermal cycles was recorded. The ablation test device is made by relevant professionals to ensure the professionalism of the equipment. The ablation test setup is periodically calibrated with the specimen to minimize test errors and ensure the accuracy and repeatability of the test process.

Figure 9 shows that coatings of several different formulation materials exhibited different results for high-temperature flames. Among them, YYbGdTaNfZr could withstand six thermal cycles without obvious cracking, showing good ablation resistance. This was mainly because the YYbGdTaNfZr coating had a higher thermal expansion coefficient, which matched well with that of the bond layer, and good thermal insulation; this also proved that the YYbGdTaNfZr coating had lower thermal conductivity. Several other coatings cracked or peeled off after two to three thermal cycles.

Figure 10 shows the surface morphology change in ceramic coatings after ablation. The original coating contained pores, microcracks, and unmelted particles. These morphologies were changed in the ablative coating. After ablation, microcracks and pores that were originally present in the coating propagated and joined together to form larger cracks [42] (Figure 10a–c). While the unmelted particles present in the layer were sintered together, the pores expanded and joined together (Figure 10c). Cracks (Figure 10d) or larger pores (Figure 10e) appeared after ablation in the originally dense areas of the coatings. After sintering, the thermal conductivity of the coatings increased, and the thermal insulation performance decreased. Sintering also caused the coatings to harden, creating sintering stress that could lead to cracks.

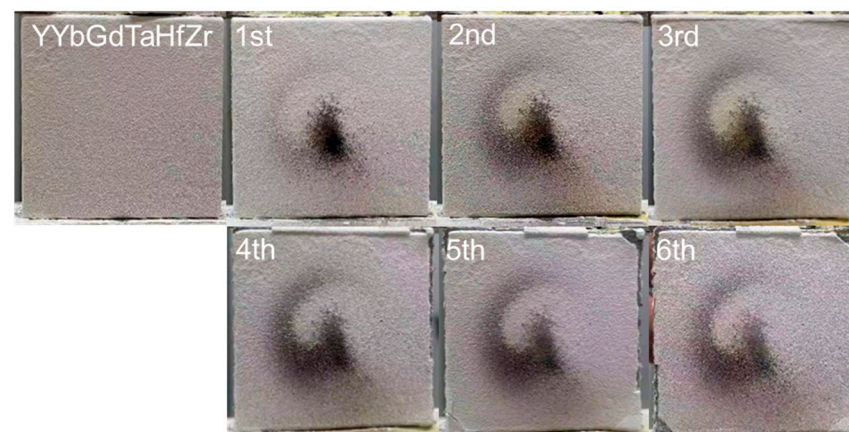


Figure 9. Cont.

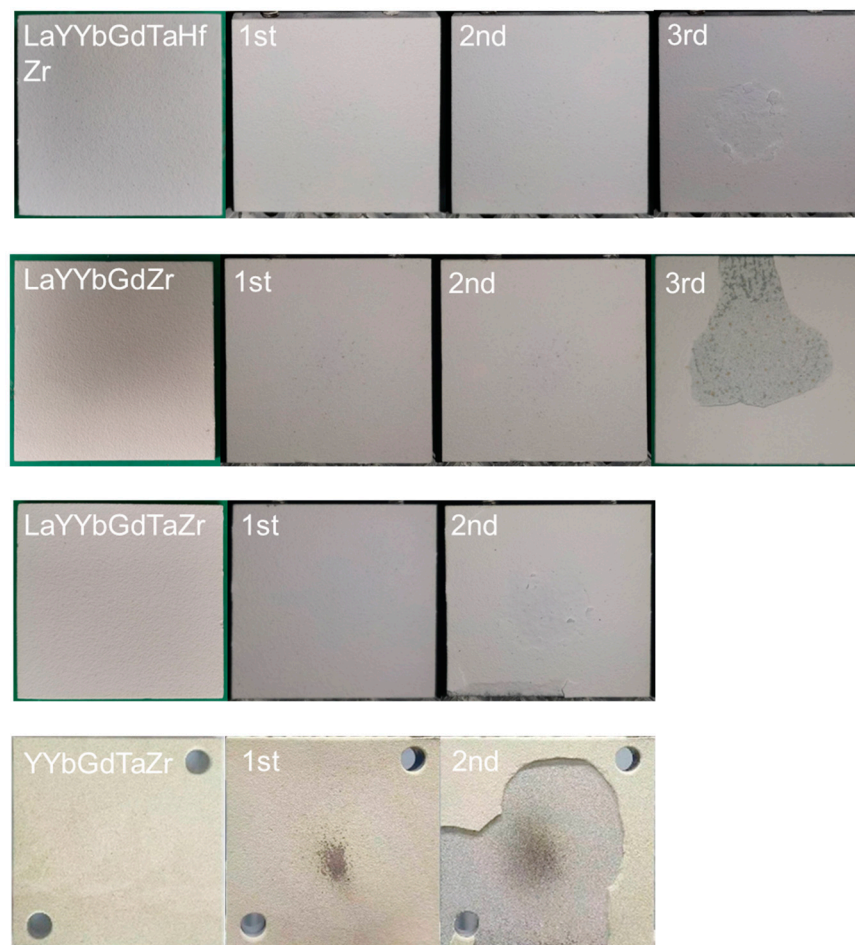


Figure 9. Surface change in the multi-component entropy-stabilized ceramic coatings ablation experiment.

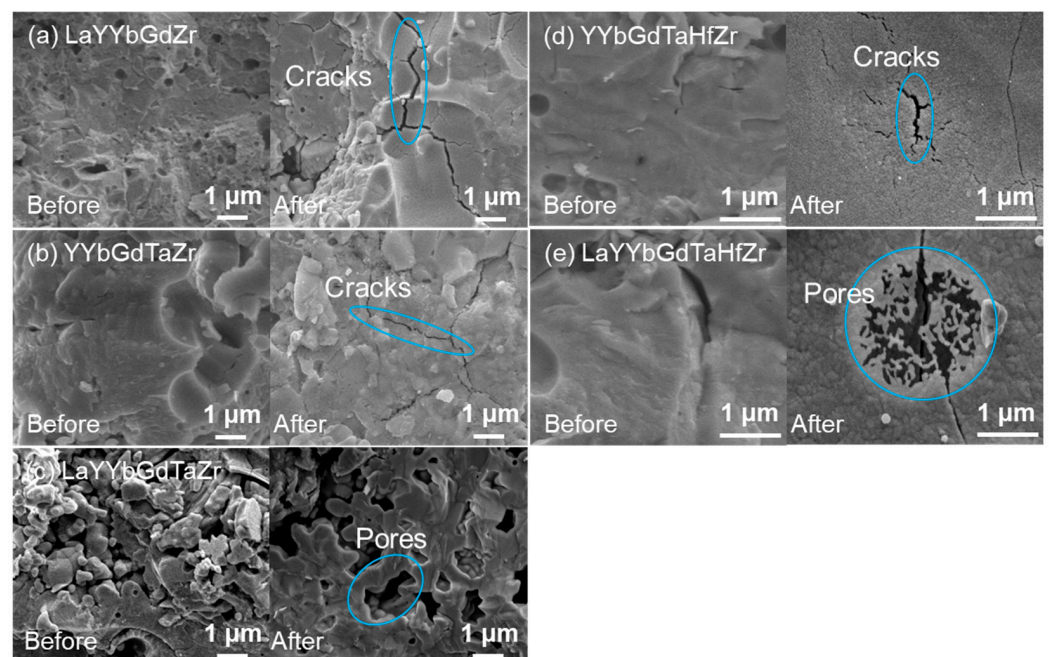


Figure 10. Surface morphology change in ceramic coatings after ablation. (a) LaYYbGdZr, (b) YYbGdTazr, (c) LaYYbGdTazr, (d) YYbGdTahfZr, (e) LaYYbGdTahfZr.

Slow diffusion is a major feature of high-entropy ceramics, which leads to slow grain growth in the coating, anti-sintering, low volume shrinkage, etc. During the ablation-cooling process, accompanied by the sintering process of the coating, sintering leads to a decrease in the porosity in the coating and reduces the thermal strain tolerance of the coating. However, the slow diffusion effect of the high-entropy coating slows down the sintering process, and the grain growth is slow, which improves its ablation resistance.

4. Conclusions

Five kinds of multi-component medium entropy and high entropy oxide ceramics were successfully prepared by using the high entropy design concept. On the basis of the inclusion of four rare earth elements, Ta⁵⁺ and Hf⁴⁺ were added to co-doping to obtain ceramics with defective fluorite structures. The material had good high temperature stability and could still maintain the phase structure after treatment at 1500 °C. The lattice distortion effect caused by the doping of multiple ions increased the phonon scattering site in the ceramics and greatly reduced the thermal conductivity of TBCs. The YbGdTaHfZr coatings had the lowest thermal conductivity, ranging from 0.61 to 0.89 W·m⁻¹·K⁻¹ between room temperature to 1500 °C, well below that of 8YSZ (~2.3 W·m⁻¹·K⁻¹, 1000 °C). Multi-component entropy-stabilized oxide ceramics also had a high thermal expansion coefficient, among which the thermal expansion coefficient of LaYbGdTaZr could reach $11.09 \times 10^{-6} \text{ K}^{-1}$ (1400 °C), which was slightly higher than that of commonly used YSZ materials. After the high-temperature plasma flame ablation test, the YbGdTaHfZr coating could undergo 6 thermal cycles under the experimental conditions of 1500 °C, without obvious cracking. With its excellent performance, the material has broad application prospects in aerospace engines, automobile and ship engines, and other fields.

Author Contributions: Conceptualization, Y.Z. and X.W.; methodology, Y.Z., X.W. and W.L.; software, F.C. and Y.C.; validation, Y.Z., X.W. and W.L.; formal analysis, W.L.; investigation, X.W. and W.L.; resources, W.L., C.G. and L.Z.; data curation, W.L.; writing—original draft preparation, W.L.; writing—review and editing, Y.Z. and X.W.; visualization, W.L.; supervision, Y.Z.; project administration, X.W.; funding acquisition, Y.Z. and S.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article.

Conflicts of Interest: The authors declare no conflict of interest.

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