Article

Mechanical Properties of Multi-Sized Porous Thermal Barrier Coatings at Micro and Nano Scales after Long-Term Service at High Temperature

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Abstract: Atmospheric plasma-sprayed multi-sized porous structures in thermal barrier coatings (TBCs) were constructed with hollow spherical (HOSP) 8YSZ powders and polypropylene pore formers. The mechanical properties of the multi-sized TBCs were investigated through the nanoin-dentation as comparisons of the as-sprayed coating and those serving at 1100 °C for a long-term. The results showed that the introduction of the multi-sized pores into TBCs could lead to the decrease of the hardness and modulus as well as the increase of fracture toughness. The hardness and modulus of the coating increased, and the fracture toughness of the coating decreased with the prolongation of the serving times at high temperatures. The mechanical properties of the coating became stable after 60 days’ serving at 1100 °C. The hardness, elastic modulus and fracture toughness of the TBCs increased to 6.51, 7.79, 10.04 GPa and 126.36, 135.13, 145.22 GPa as well as 1.049, 1.157, 1.255 MPa·m0.5, respectively, corresponding to the multi-sized porous TBCs with 0%, 10% and 15% PP powders. The nano-size pores disappeared gradually in the multi-sized TBCs during serving at 1100 °C. The macropores deposited between the ceramic particles penetrated with little diffusion and were not easy to disappear. The introduction of a multi-scale pore structure into the TBCs could improve the stress-strain tolerance of the TBCs.

Keywords: thermal barrier coatings; multi-sized pores; hardness; elastic modulus; fracture toughness

1. Introduction

The research, development and manufacturing capabilities of gas turbines and aero engines play an important role in the standard in the advanced industrial manufacturing level of a country [1]. It covers the most advanced science and technology in energy and power system design, automation control and advanced material manufacturing [1–3]. Up to now, the advanced gas turbine’s combustion temperature has exceeded 1500 °C, and the combustion temperature target of heavy-duty gas turbines may exceed 1700 °C in the future. Gas turbine’s high-temperature parts will experience a more severe working environment [2–5]. Therefore, it is necessary to use thermal barrier coatings (TBCs) to improve hot components’ high-temperature properties and the engines’ performances, including the reliability, durability and efficiency of advanced gas turbines and aero engines [4]. Zirconia ceramic is the preferred material for thermal barrier coatings due to its low thermal conductivity, low thermal expansion coefficient and high melting point, as well as excellent comprehensive mechanical properties [5]. However, zirconia will undergo a
phase transition from high temperature to low temperature, especially the transition from tetragonal phase to monoclinic phase [7–9], which will be accompanied by 5–7% volume expansion [10], resulting in high stress and finally cracks in the TBCs during thermal cycling. This phase transition can be solved by introducing a stabilizer into the zirconia lattice to form a substituted solid solution at the Zr site. For thermal barrier coatings, Y$_2$O$_3$ is the most excellent stabilizer [11–13]. There are two commonly used methods to prepare thermal barrier coatings, including electron beam physical vapor deposition (EB-PVD) and atmospheric plasma spraying (APS). The thermal barrier coatings prepared by these two methods have certain pores in the initial state [14]. Although the pores will reduce the coating’s mechanical properties, the stress can be released quickly during the crack propagation so as to absorb the energy during the crack’s initiation and hinder the crack’s propagation. Different sizes of pores can adjust the strength and toughness of the coating. Through the mutual cooperation of micro- and nanopores, their respective advantages can be exerted so that the coating has better comprehensive mechanical properties [15].

Pore formers, such as polypropylene (PP), polyether-ether-ketone (PEEK), high-density polyethylene (HDPE), polymethyl methacrylate (PMMA), mesocarbon-microbead (MCMB) carbon powder and so on, could be used to prepare porous TBCs with microns or tens of microns closed pores to adjust the properties of the TBCs [16]. Multi-sized porous TBCs at the nano- and micron-scale were prepared with nanopores retained from the nanostructured shells of hollow spherical YSZ powders (HOSP) and micro-sized pores from the deformed hollow structure of the HOSP YSZ powder in the work of Gao et al. [15]. Masayuki Arai et al. [17] prepared TBCs with 40% porosity, and tens of micron-sized large pores through a pore-former of polyester. Therefore, it will be helpful to improve the comprehensive mechanical properties of the TBCs with constructed pores.

Although pores often have negative effects in bulk constructional materials, seen as flaws or defects, they can have various positive effects on the basis of the serving environments in functional materials. Closed pores, filled with motionless air or vacuum, can act as thermal insulators with low thermal conductivity and relax the stress effectively, improving the strain tolerance of the material in thermal barrier coatings. Meanwhile, the pore size can have positive effects on thermal insulating [18–20]. Zhao et al. [20] prepared nano-sized YSZ coatings with a high content of nano/submicron pores through suspension plasma spray (SPS). Results indicated that increasing total porosity was an effective mean for reducing the heat transfer capability of SPS TBCs. Nano/submicron pores had a higher sensitive influence on thermal properties than that of large pores. When the porosities were certain, the interface quantities among pores and the deposited particles increased rapidly with the reduction of pore size, which relaxed the stress and improved the strain tolerance of the material furtherly [2,21]. Zhou et al. [21] investigated the nanoindentation creep behavior of plasma-sprayed nanostructured 8YSZ coatings using as-prepared nanostructured non-transformable tetragonal (t') feedstocks. The presence of pores could improve the strain tolerance of the material.

In general, the sintering of ceramics is a densification process, which will cause the pores to be healed. Meanwhile, although small pores are commonly looked upon as flaws, the sintering temperature can be reduced in some cases, and the sintering processing can be promoted [22]. When the pores were reduced to nano-size, the materials’ sintering activity became strong through finite element simulation [23,24]. The serving temperature becomes higher and higher, which might be near the sintering temperature in thermal barrier coatings [25]. F. Cernuschi et al. [26] investigated the microstructure of as-sprayed and sintered free-standing atmospheric plasma sprayed YPSZ TBC samples through infrared (IR) gas porosimetry, mercury intrusion porosimetry and image analysis. During the sintering of TBCs, the pores healed gradually. Nano-sized pores accelerated the sintering activation in YSZ ceramics, and the mechanism of pores inhibiting crack propagation was destroyed [27–30].

At present, the research concerning YSZ thermal barrier coating mainly focuses on the following aspects. The first is to obtain a stable YSZ thermal barrier coating using
preparation methods [31–35]. The second is to develop new stabilized materials for thermal barrier coatings [36,37]. The third is the microstructural design of thermal barrier coatings to adjust the thermal barrier coatings’ properties and performances, such as thermal conductivity, hardness, modulus, fracture toughness and thermal cycle lives [38–40]. The fourth is the performance of serving at high temperatures, such as the hot corrosion resistance of thermal barrier coatings [2]. The last is to evaluate the stress state and predict the serving lives of the thermal barrier [30]. In this work, the introduction of pores in the thermal barrier coating can not only reduce the thermal conductivity of the thermal barrier coating but also cause a decrease in the mechanical properties. In the previous work [16], the thermal conductivity of the multi-sized porous TBCs at micron and nano scales were investigated after continuous serving at 1100 °C for 60 days. Results showed that the thermal conductivities tended to be stable without obvious vibrations. Therefore, in this work, it is necessary to investigate the evolutions of the multi-sized pores on the mechanical properties of the TBCs after a long-term serving at high temperatures. In this work, atmospheric plasma sprayed TBCs with multi-sized pores were constructed with HOSP 8YSZ powders; different contents of polypropylene powders as pore formers. The influence of the porous structure evolution on the hardness, modulus and fracture toughness in the multi-sized porous structured TBCs were investigated during long-term serving at high temperatures.

2. Experimental Materials and Procedures

2.1. Feedstocks and Coating Preparation

8YSZ powders (Metco 204 NS, Oerlikon Metco, Schaumburg, IL, USA) with a hollow spherical structure, as shown in Figure 1, were chosen as feedstocks, which had been used in the previous work [16]. The mean size of the 8YSZ powder was about 80 μm. Figure 2 show the pore-forming agent of polypropylene powder from Guangdong Huachuang Plastic Chemical Industry Co. Ltd., Foshan, China. The polypropylene powder’s mean size was about 50 μm. Polypropylene powders and 8YSZ powders were commixed through ball milling with the ND7—04 (Nanda Tianzun Electronic Co., Ltd., Nanjing, China) at 120 rpm rotation speed for 24 h milling. The mixed powders were controlled in 0%, 10% and 15% polypropylene powder volumes. The substrate was Inconel 718 nickel alloy. Figure 3 show the microstructure of NiCoCrAlY powder (Amdry 997, Oerlikon Metco, Schaumburg, IL, USA) adapted as bond coat material. The Amdry 997 powder’s mean size was about 100 μm. The Inconel 718 substrate surface was sandblasted by brown corundum in 20–30 mesh at 0.8 MPa before coating deposition to clean the substrate surface. An atmospheric plasma-spraying system (ZB-80, Beijing Zhengbang Co. Ltd., Beijing, China) was adapted to prepare the thermal barrier coatings. Table 1 show the coating processing parameters. The primary gas and the secondary gas were argon and hydrogen with the pressure of 0.9 MPa and 0.3 MPa, respectively. The flow of argon and hydrogen were 38.1 and 2.7 SLPM for the bond coat and 36.5 and 3.4 SLPM for the top coat, respectively. The voltage and current were 67 V and 540 A for the bond coat and 70 V and 600 A for top coat, respectively. The powder feeding rates were 3.5 and 3.7 rad/min for the bond coat and the top coat, respectively.

2.2. High-Temperature Long-Term Service

According to the actual working conditions of the gas turbine, the multi-sized porous TBCs were set at 1100 °C for 1, 10, 20, 30, 60 and 90 days to evaluate the microstructures and properties evolutions.
Figure 1. Morphology (a) and cross-sectional microstructure (b) of the ceramic powder by SEM [16].

Figure 2. Morphology (a) and cross-sectional microstructure (b) of the polypropylene powder by SEM.

Figure 3. Morphology (a) and cross-sectional microstructure (b) of Amdry 997 powder by SEM.
Table 1. Coating deposition parameters through atmospheric plasma spraying.

| Coating     | Parameters                  |
|-------------|-----------------------------|
|             | Arc voltage (V) | 67          |
| Bond Coat   | Arc current (A) | 540         |
|             | H₂ pressure (MPa) | 0.3         |
|             | H₂ flow (SLPM)  | 2.7         |
|             | Ar pressure (MPa) | 0.9         |
|             | Ar flow (SLPM)  | 38.1        |
|             | Powder feeding rate | 3.5        |
| Top Coat    | Arc voltage (V) | 70          |
|             | Arc current (A) | 600         |
|             | H₂ pressure (MPa) | 0.3         |
|             | H₂ flow (SLPM)  | 3.4         |
|             | Ar pressure (MPa) | 0.9         |
|             | Ar flow (SLPM)  | 36.5        |
|             | Powder feeding rate | 3.7        |

2.3. Microstructures and Phases

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 Kα radiation in steps of 0.02° from 20° to 80° at a scanning speed of 2°/min.

2.4. Properties

A nanomechanical testing system (Hysitron TI Premier, Bruker, Billerica, MA, USA) was used to test the hardness and modulus of the coating. The indentation was applied with a prismatic indenter under a load of 10 mN. The loading time, holding time and unloading time were 5 s, 3 s and 5 s, respectively. Ten measurements were applied to ensure the data accuracy. Mean values and standard deviations were calculated statistically.

Radial cracks could be obtained in the low-load indentation test model. All of the cracks initiated in the tests were radial cracks. The crack length could be measured. Formula (1) reflects the relationship of fracture toughness and crack length according to the Nihhara relation [41]:

\[
K_{IC} = 1.073 \times \alpha \times \left( \frac{E}{H} \right)^{1/2} \times \left( \frac{P}{C^{3/2}} \right)
\]

where:
- P—the maximum indentation load (N);
- C—the crack length (m);
- \(\alpha\)—a coefficient related to the shape of the indenter (considered to be 0.016 [41]);
- E—the modulus (GPa);
- H—the hardness (GPa).

3. Results

3.1. Microstructure of the Deposited Porous TBCs

The cross-sectional microstructures of the multi-sized porous TBCs deposited with Metco 204NS powder and different contents of pore former are shown in Figure 4. It was found that the thicknesses of the ceramic layer of the TBCs were all about 150 microns. The top coatings were composed of both large and small pores. Through computer-aided
imaging processing and analysis of the TBCs figures, the porosities of the TBCs were 6.44%, 15.52% and 22.25%, respectively.

Figure 4. Microstructure of the deposited porous TBCs: (a) 0%; (b) 10%; (c) 15%.

Figure 5 show the area elemental map of TBCs with 0% pore former. It was found that the elements of the top ceramic layer were mainly composed of O, Zr and Y. Meanwhile, there were nonbonding areas among the deposited YSZ particles, which were seen as large pores.

The cross-sectional microstructures of the multi-sized TBCs with 0%, 10% and 15% percent pore formers after serving at 1100 °C for varying serving times are shown in Figures 6–8. The multi-sized pores disappeared partially along the deformed particles’ boundaries during serving at 1100 °C. Large pores, in microns and tens of microns, were not easy to disappear because the diffusion path among YSZ particles was too long for small YSZ particles to penetrate across the micro-sized pores easily, especially for tens of microns sized large pores. With the serving time reaching 30 days, the large pores gradually connected with each other in the coatings, as shown in Figures 6d, 7d and 8d. With the serving time reaching 60 days, the macropores connected completely, as shown in Figures 6e, 7e and 8e. At that moment, the coating’s porosity appeared to be stable and no longer changed with the extension of serving time.
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Figure 5. Area elemental map of TBCs with 0% pore former: (a) Area; (b) Zr element distribution; (c) O element distribution; (d) Y element distribution; (e) atomic percent and weight percent of each element.

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Figure 6. Cross-sectional microstructure of the deposited porous TBCs: (a) 0%, (b) 10%, (c) 15%.

Figure 7. Cross-sectional microstructure of the deposited porous TBCs: (a) 0%; (b) 10%; (c) 15%.

Figure 8. Cross-sectional microstructure of the deposited porous TBCs: (a) 0%; (b) 10%; (c) 15%.
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The cross-sectional microstructures of the multi-sized TBCs with 0%, 10% and 15% percent pore formers after serving at 1100 °C for varying serving times are shown in Figures 6–8. The multi-sized pores disappeared partially along the deformed particles’ boundaries during serving at 1100 °C. Large pores, in microns and tens of microns, were not easy to disappear because the diffusion path among YSZ particles was too long for small YSZ particles to penetrate a cross the micro-sized pores easily, especially for tens of microns sized large pores. With the serving time reaching 30 days, the large pores gradually connected with each other in the coatings, as shown in Figures 6d, 7d and 8d. With the serving time reaching 60 days, the macropores connected completely, as shown in Figures 6e, 7e and 8e. At that moment, the coating’s porosity appeared to be stable and no longer changed with the extension of serving time.

Figure 6. Cross-sectional microstructures of TBCs with 0% PP powder after serving at 1100 °C for: (a) 1 day; (b) 10 days; (c) 20 days; (d) 30 days; (e) 60 days; (f) 90 days.
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(a) 1 day; (b) 10 days; (c) 20 days; (d) 30 days; (e) 60 days; (f) 90 days.

Figure 7. Cross-sectional microstructures of TBCs with 10% PP powder after serving at 1100 °C for:
(a) 1 day; (b) 10 days; (c) 20 days; (d) 30 days; (e) 60 days; (f) 90 days.
Figure 7. Cross-sectional microstructures of TBCs with 10% PP powder after serving at 1100 °C for:
(a) 1 day; (b) 10 days; (c) 20 days; (d) 30 days; (e) 60 days; (f) 90 days.

Figure 8. Cross-sectional microstructures of TBCs with 15% PP powder after serving at 1100 °C for:
(a) 1 day; (b) 10 days; (c) 20 days; (d) 30 days; (e) 60 days; (f) 90 days.

Figure 9 shows the area elemental map of TBCs with 0% pore former after serving at 1100 °C for 30 days. The elements in the top ceramic layer were mainly composed of O, Zr and Y. There were little changes in element contents before and after high-temperature service.
Figure 8. Cross-sectional microstructures of TBCs with 15% PP powder after serving at 1100 °C for (a) 1 day; (b) 10 days; (c) 20 days; (d) 30 days; (e) 60 days; (f) 90 days.

Figure 9 shows the area elemental map of TBCs with 0% pore former after serving at 1100 °C for 30 days. The elements in the top ceramic layer were mainly composed of O, Zr and Y. There were little changes in element contents before and after high-temperature service.

Figure 9. Area elemental map of TBCs with 0% pore former after serving at 1100 °C for 30 days: (a) Area; (b) Zr element distribution; (c) O element distribution; (d) Y element distribution; (e) atomic percent and weight percent of each element.

The porosities of the TBCs were calculated through the image analysis method. There were four main steps, including grayscale transformation, image preprocessing, image binarization and porosity statistics. Table 2 show the statistics on the porosities of the
multi-sized TBCs after serving at 1100 °C for varying serving times. The porosities in the TBCs coating gradually decreased with the serving time’s extension until it stabilized after 60 days of service. The stabilization of the porosity of multi-scale porous TBCs can be attributed to the synergistic effect of the nanoscale small pores and microscale macropores in the coating. The nano-scale pores in the coating gradually disappeared with the service time, which was similar to the sintering process. Part of the micron-sized macropores in the coating formed through macropores with the prolongation of service time. When the service time reached 60 days, the nano-sized pores in the coating basically disappeared. At this time, the pores reached an equilibrium state and no longer changed. There were still some pores that existed steadily in the TBCs, which reflected that the multi-sized TBCs could still inhibit the sintering in some content after continuously serving at 1100 °C for 60 days.

Table 2. Statistics on the porosities of TBCs after service at 1100 °C for varying serving times.

| Time (Days) | TBCs with 0% Pore Formers | TBCs with 10% Pore Formers | TBCs with 15% Pore Formers |
|-------------|---------------------------|---------------------------|---------------------------|
| 0           | 6.440 ± 0.010%            | 15.524 ± 0.021%           | 22.250 ± 0.020%           |
| 1           | 6.356 ± 0.015%            | 15.433 ± 0.015%           | 22.037 ± 0.023%           |
| 10          | 6.113 ± 0.006%            | 15.174 ± 0.013%           | 21.871 ± 0.017%           |
| 20          | 5.966 ± 0.012%            | 14.888 ± 0.016%           | 21.582 ± 0.013%           |
| 60          | 5.572 ± 0.008%            | 14.486 ± 0.024%           | 21.143 ± 0.027%           |
| 90          | 5.564 ± 0.011%            | 14.467 ± 0.015%           | 21.138 ± 0.026%           |

3.2. Phases

Figure 10 show the X-ray diffraction patterns of the powder and coatings. According to the PDF card (No. 72-0597), 8YSZ powder played a part in the monoclinic phase at 27° and 32°. In the XRD patterns of the coating, the 8YSZ coating had a partial monoclinic phase too. The coating’s relative diffraction strength of the monoclinic phase was higher than that of the powder. After coating deposition, parts of the 8YSZ experienced phase changes from a tetragonal to monoclinic phase. More monoclinic phases formed after coating deposition. According to Formulas (2) and (3) regarding the calculation of content for each phase of 8YSZ using the X-ray diffraction peak intensity proposed by Miller et al. [42], the proportions of the m-phase and t-phase of the 8YSZ powder were calculated to be 33.5% and 66.5%, respectively. The proportions of the m-phase and t-phase of the 8YSZ coating were 49.6% and 50.4%, respectively. The ceramic powder was in a molten state at high temperatures during the plasma-spraying process, and the t-phase to m-phase transformation occurred during the rapid cooling after spraying.

\[ C_m = \frac{I_m(11\overline{1}T) + I_m(111)}{I_m(11\overline{1}T) + I_m(111) + I_t(111)} \]  

\[ V_m = \frac{PC_m}{1 + (P-1)C_m} \]

where \( C_m \) was the integrated intensity ratio of the monoclinic phase, \( I_m \) was the m-phase diffraction peak intensity, \( I_t \) was the t-phase diffraction peak intensity, \( P = 1.3 \) for tetragonal-monoclinic mixtures and \( V_m \) was the m-phase volume fraction [42].
3.3. Mechanical Properties of the Multi-Sized Porous TBCs

The hardness of the multi-sized porous TBCs after serving at 1100 °C for varying serving times is shown in Figure 11. The hardness of the multi-sized porous TBCs decreased with the increase of the polypropylene powder content. The addition of polypropylene increased the content of the coating’s large pores, which reduced the hardness to a certain extent. The hardness of the TBCs increased with the serving time’s prolongation. With the service time reaching 60 days, the coating’s hardness stabilized. This was because the pores in the coatings reached dynamic equilibrium and did not change obviously after 60 days’ serving at 1100 °C. The hardness reached the highest after the serving time reached 90 days with the highest microhardness of 10.06 GPa, 7.81 GPa and 6.53 GPa for the TBCs with 0%, 10% and 15% pore formers, respectively. Compared with the unserved coating, the microhardness increased by 17.11%, 22.99% and 12.98%, respectively.

Figure 11. The hardness of the multi-sized porous TBCs after serving at 1100 °C for varying serving times.
Figure 12 show the elastic modulus of the multi-sized porous TBCs after serving at 1100 °C for varying serving times. The elastic modulus of the TBCs decreased with the increase of the polypropylene powder content. The addition of polypropylene increased the content of the large pores in the TBCs. The introduction of pores reduced its elastic modulus to a certain extent. The elastic modulus of the TBCs increased with the increase of the serving times. With the service time reaching 60 days, the elastic modulus of the coating became stable. The pores in the TBCs reached dynamic equilibrium and did not change obviously after 60 days serving at 1100 °C. With the serving time reaching 90 days, the elastic modulus reached the highest with the highest elastic modulus of 145.29 GPa, 135.31 GPa and 126.41 GPa for the TBCs with 0%, 10% and 15% pore formers, respectively. Compared with the unserved coating, the elastic modulus increased by 5.63%, 3.62% and 8.67%, respectively.

![Elastic modulus vs Time](image-url)

**Figure 12.** The elastic modulus of the multi-sized porous TBCs after serving at 1100 °C for varying serving times.

Radial cracks could be obtained in the TBCs through the indentation test with the low-load indentation testing model. Figures 13–15 show the nanoindentation and cracks in the multi-sized porous TBCs after serving at 1100 °C for varying serving times. Table 3 show the fracture toughness values \( K_{IC} \) of the TBCs calculated with Equation (1). The fracture toughness of the TBCs increased with the increase of the polypropylene powder content. The addition of polypropylene increased the content of the large pores in the TBCs. The introduction of pores improved its fracture toughness to a certain extent. The fracture toughness of the TBCs decreased with the increase of the serving times. With the service time reaching 60 days, the coating’s fracture toughness became stable. With the serving time reaching 90 days, the fracture toughness reached the lowest with the values of 1.046, 1.155 and 1.252 MPa·m\(^{0.5}\) for the TBCs with 0%, 10% and 15% pore formers, respectively. Compared with the unserved coating, the fracture toughness decreased by 9.98%, 6.17% and 7.46%, respectively.
Figure 13. Nanoindentation with cracks in TBCs with 0% PP powder after serving at 1100 °C for: (a) 1 day; (b) 10 days; (c) 20 days; (d) 30 days; (e) 60 days; (f) 90 days.
Figure 14. Nanoindentation with cracks in TBCs with 10% PP powder after serving at 1100 °C for:
(a) 1 day; (b) 10 days; (c) 20 days; (d) 30 days; (e) 60 days; (f) 90 days.
Figure 15. Nanoindentation with cracks in TBCs with 15% PP powder after serving at 1100 °C for:
(a) 1 day; (b) 10 days; (c) 20 days; (d) 30 days; (e) 60 days; (f) 90 days.

Table 3. Fracture toughness of the multi-sized porous TBCs after serving at 1100 °C for varying serving times/MPa·m^0.5.

| Time (Days) | TBCs with 0% Pore Former | TBCs with 10% Pore Former | TBCs with 15% Pore Former |
|-------------|--------------------------|--------------------------|--------------------------|
| 0           | 1.162 ± 0.005            | 1.231 ± 0.008            | 1.353 ± 0.017            |
| 1           | 1.148 ± 0.002            | 1.217 ± 0.005            | 1.325 ± 0.014            |
Table 3. Fracture toughness of the multi-sized porous TBCs after serving at 1100 °C for varying serving times/MPa·m$^{0.5}$.

| Time (Days) | TBCs with 0% Pore Former | TBCs with 10% Pore Former | TBCs with 15% Pore Former |
|-------------|--------------------------|----------------------------|---------------------------|
| 0           | 1.162 ± 0.005            | 1.231 ± 0.008              | 1.353 ± 0.017             |
| 1           | 1.148 ± 0.002            | 1.217 ± 0.005              | 1.325 ± 0.014             |
| 10          | 1.135 ± 0.011            | 1.206 ± 0.006              | 1.297 ± 0.009             |
| 20          | 1.124 ± 0.004            | 1.192 ± 0.017              | 1.288 ± 0.005             |
| 30          | 1.093 ± 0.009            | 1.176 ± 0.015              | 1.276 ± 0.006             |
| 60          | 1.049 ± 0.012            | 1.157 ± 0.003              | 1.255 ± 0.012             |
| 90          | 1.046 ± 0.013            | 1.155 ± 0.003              | 1.252 ± 0.011             |

4. Discussion

4.1. The Influence Mechanism of Pore Evolution on Hardness and Elastic Modulus

Figure 16 show the schematic of the influence of the multi-sized pores on the hardness and elastic modulus of the coating. Hardness reflects the deformation resistance, which is often characterized by the indentation size in certain loads. When the pores were introduced into TBCs, the real contact area of the TBCs became small in certain loads so that the indentation size became larger and the apparent hardness became smaller than the dense one. The existence of pores made it easy to deform. However, the small pore size of the nanopore area dispersed the stress and disperse the energy, which was not enough to cause crack initiation and propagation. Due to the reduction of the pore size, the interface increased. The existence of the interface consumed the energy required for crack propagation. When the energy was consumed too much, there was no major damage, and no further deformation could occur. The size of the pores in the micron macropore area was large, and its ability regarding deformation resistance and deformation restoration was poor; therefore, the hardness and modulus decreased more obviously than those containing nanopores. Therefore, the hardness and elastic modulus of the 8YSZ coating decreased with the increase of the porosities. The hardness of the multi-sized TBCs with 0%, 10% and 15% polypropylene added into Metco 204NS powders were 8.59 GPa, 6.35 GPa and 5.78 GPa. After 60 days’ serving at 1100 °C, the hardnesses were 10.05 GPa, 7.81 GPa and 6.53 GPa, respectively. The elastic modulus of the multi-sized TBCs with 0%, 10% and 15% polypropylene added into Metco 204NS powders were 137.55 GPa, 130.58 GPa, 116.33 GPa. After 60 days’ serving at 1100 °C, the elastic modules were 145.29 GPa, 135.31 GPa and 126.41 GPa, respectively. With the prolongation of serving times, parts of the pores, especially nano-sized pores, disappeared along the boundaries around the deformed YSZ particles, which led to the simultaneous increase of the multi-sized TBCs’ hardness and elastic modulus. Large pores, in microns and tens of microns, made the YSZ particles diffuse with more difficulty across the large pores than the small nano-sized pores. Finally, the large pores were retained mainly after the long times’ serving at 1100 °C, which exhibited good sinter-resistance. Meanwhile, with the service time reaching 60 days, the pores in the coating became stable, which led to the hardness and elastic modulus of TBCs to remain unchanged. Ruiji Zhang et al. [28] prepared a hollow 8YSZ coating with hardness and elastic modulus of 5.28 GPa and 78.71 GPa. Thakarea J.G. et al. [43] prepared a 8YSZ thermal barrier coating by APS with a porosity of 13.2%, and its hardness and Young’s modulus were 8.95 GPa and 114.8 GPa, respectively. Keyvani et al. [44] prepared plasma-sprayed nanostructured and conventional YSZ thermal barrier coatings with a hardness of 10 GPa and 8 GPa; the elastic moduli were 125 GPa and 99.5 GPa, respectively. By comparison, it was found that the hardness and elastic modulus of the multi-scale porous thermal barrier coatings prepared by hollow YSZ powder and PP powder in this work were comparable to those prepared by conventional YSZ powder in similar total porosities. After 60 days of service, the hardness and elastic modulus of the coatings prepared in this work were comparable to the nanostructured YSZ coating.
4.2. The Influence Mechanism of Pore Evolution on Fracture Toughness

The fracture toughness of the multi-sized TBCs with 0%, 10% and 15% polypropylene added into Metco 204NS powders were 1.162 MPa·m$^{0.5}$, 1.231 MPa·m$^{0.5}$ and 1.353 MPa·m$^{0.5}$, respectively. After 60 days' serving at 1100 °C, the fracture toughnesses were 1.046 MPa·m$^{0.5}$, 1.155 MPa·m$^{0.5}$ and 1.252 MPa·m$^{0.5}$, respectively. The existence of pores could improve the fracture toughness of the materials. In the work of Ruiji Zhang et al. [28], thermal barrier coatings prepared with a hollow 8YSZ coating had a fracture toughness of 1.17 MPa·m$^{0.5}$. Although there was a slight decrease in fracture toughness after a long-term serving at 1100 °C, the multi-sized porous TBCs' fracture toughness was still kept at an equivalent level of the as-sprayed one in Zhang's work [28]. Figure 17 show the toughening mechanism of the multi-sized pores in the TBCs. The toughening of pores acts as a crack barrier and energy consumer. The existence of nanopores could absorb stress and disperse the stress into each pore, thereby reducing the occurrence of stress concentration. In addition, due to the influence of nanopores, the internal stress of the coating would be reduced during the spraying process, which would reduce the cracks of the coating and make the crack tips passivation. The size of micron pores was relatively large, and its deformation space was large. Therefore, when the crack propagated, it quickly released the stress and absorbed the energy of the crack propagation; this improved the fracture toughness of the ceramic material.

Figure 16. Schematic of the influence mechanism of pores on the coating’s hardness and elastic modulus: (a) before service; (b) after service.

Figure 17. Schematic of the toughening mechanism of the multi-sized porous TBCs.
Meanwhile, with the serving time was extended at high temperatures, the nanopores and the pores formed around the boundaries of the deposited particles gradually disappeared, and the micron-sized macropores connected with each other. As a result, the fracture toughness of the coating decreased. With the serving time reaching 60 days, the coating’s pores were in dynamic equilibrium and would not change obviously. The fracture toughness reached a stable status. At that moment, the presence of micro-pores in the coating would increase the stress and strain tolerance of the material to a certain extent and increase the toughness of the coating. Therefore, although the fracture toughness increased after service at 1100 °C for 90 days, the multi-sized TBCs with 15% PP added had the highest fracture toughness of 1.252 MPa·m$^{0.5}$. In Thakarea’s work, the 8YSZ thermal barrier coating had a fracture toughness of 0.55 MPa·m$^{0.5}$ [43]. Compared with the work of Thakarea et al. [43], although the introduction of multi-scale pore structure into the TBCs in this work would reduce its hardness, its Young’s modulus would be improved, and its fracture toughness would be greatly improved. The introduction of a multi-scale porous structure in the TBCs could also improve the stress–strain tolerance of the coating, which would be helpful for TBCs of turbine engines engaged in long-term continuous serving at high temperatures.

5. Conclusions

Atmospheric plasma-sprayed multi-sized porous structures in thermal barrier coatings (TBCs) were constructed with hollow spherical (HOSP) 8YSZ powders and polypropylene pore formers. The mechanical properties evolutions of the TBCs with multi-sized pores were investigated through nanoindentation after serving for varying times at 1100 °C. The following conclusions could be drawn:

1. The introduction of the multi-sized pores into TBCs could bring out the decrease of the hardness and modulus as well as the increase of the fracture toughness.
2. With the serving time’s extension at 1100 °C, the elastic modulus and hardness of the multi-sized porous TBCs increased, and the fracture toughness decreased.
3. When the serving time reached 60 days, the small nano-sized pores disappeared, and the large micron-sized pores were retained with good anti-sintering properties. The porous structure, hardness, elastic modulus and fracture toughness tended to be stable.

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