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Structural Evolution and Mechanical Behavior of Ytterbia Doped Hafnia Biphasic Ceramics under Annealing at 1500 °C

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Abstract: HfO₂ has become a promising thermal barrier coating material due to its similarity in structure and chemical properties with ZrO₂ and its higher phase structure transition temperature. However, the fracture toughness of HfO₂ is not ideal, greatly limiting its application. In this report, we find a special sandwich structure of ceramics, comprising a cubic (C) phase /monoclinic (M) phase/cubic (C) phase. The microstructural evolution and mechanical properties of these ceramics were investigated under annealing at 1500 °C. The results indicate that, with an increase in annealing duration, there was a gradual augmentation in the proportion of the monoclinic (M) phase and the fracture toughness increased from 2.18 MPa·m^{0.5} to 2.83 MPa·m^{0.5} after 48 h of annealing, which is higher than many potential TBC materials. The residual compressive stress present in the M phases during the progression of crack propagation served to facilitate the bridging and deflection of cracks. As such, this process led to the alleviation of stress concentration at the crack tip, ultimately enhancing the toughening effect.

Keywords: TBCs; Ytterbia stabilized hafnia (YbSH); sandwich structure; fracture toughness

1. Introduction

Thermal barrier coatings (TBCs) are widely used in aviation engine turbine blades due to their ability to block high-temperature gases from the superalloy matrix, enhancing engine service temperature and thermal efficiency [1–3]. Currently, the most universally used TBC material is 6–8 wt.% yttria stabilized zirconia (8YSZ), which boasts relatively high melting temperature (~2700 °C), high fracture toughness, low thermal conductivity (2.3 W m⁻¹ K⁻¹) at 1000 °C for dense bulk, and high coefficient of thermal expansion (CTE, ~11 × 10⁻⁶ K⁻¹), contributing to an excellent service life below 1200 °C [4–7]. However, when the service temperature is above 1200 °C, 8YSZ undergoes a phase transition from metastable tetragonal to monoclinic and cubic phases, resulting in 3–5% volume expansion and residual stress that causes the coating to peel off. In addition, severe sintering will occur above 1200 °C, leading to an increase in thermal conductivity and Young's modulus, hindering its use at higher temperatures [8–10]. Therefore, searching for new TBC materials with a better high-temperature phase stability and lower thermal conductivity has become an urgent research problem and receives constant attention.

Hf and Zr belong to the fourth subfamily, and the chemical properties and crystal structures of HfO₂ and ZrO₂ are similar. Moreover, HfO₂ has a higher phase transition temperature and better high-temperature resistance, suggesting its potential use as a TBC material [11,12]. However, unlike YSZ, which can improve fracture toughness through the ferroelastic toughening mechanism of tetragonal phase [13,14], poor toughness is a key factor limiting the application of hafnium oxide in TBCs. Many efforts have been



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). dedicated to improving its fracture toughness from many perspectives, including rare earth oxide doping [15–19]. Nonetheless, Lee demonstrated through first principles theory calculations that rare earth element doping can hardly stabilize monoclinic hafnium oxide into the tetragonal phase, because the critical grain size (4-10 nm) of HfO₂ to maintain a metastable tetragonal phase at room temperature is much smaller than that of ZrO_2 (about 30 nm) [20-22]. Li also found no tetragonal phase in hafnium oxide doped by 8% mol Y₂O₃ stabilized HfO₂ by experimental methods, and only 53% (volume fraction) monoclinic phase and 47% cubic phase were present in the system [23]. When the doping amount reaches 20%, doping with rare earth oxides such as Y_2O_3 can stabilize hafnium oxide to a cubic phase, but the fracture toughness of the cubic phase is low, leading to a decrease in the service life of the coating [24,25]. Although it is not possible to enhance fracture toughness in hafnium oxide through martensitic transformation, the differences of thermal expansion in monoclinic and cubic phase ceramics can generate residual stress at grain boundaries, which may also improve fracture toughness [26,27] Additionally, phase stability of both M phase and C phase are excellent below 1700 °C [21], indicating that ceramics with biphasic hafnium oxide structure will serve as a potential TBC material. There are still several questions to be considered: First, how to prepare a relatively dense microstructure with tightly bound monoclinic and cubic phases, the evolution of its mechanical properties during long-term high-temperature service. Third, the influence of microstructure on its fracture toughness and its toughening mechanism.

In this study, we prepared 10 mol% Yb³⁺ doped HfO₂ (10YbSH) nano powder using the precipitation-hydrothermal method, and formed ytterbium partially stabilized hafnium ceramics with C (cubic phase)/M (monoclinic phase)/C (cubic phase) sandwich structure through cold pressing sintering. The dense C/M phase boundary was mainly formed by the diffusion of rare earth elements in the C phase nano powder at high temperatures. The effect of different annealing time at 1500 °C on the mechanical properties of hafnium oxide materials was studied, providing a new approach for toughening hafnium oxide materials. As it was expected that this dual phase sandwich-structured ceramic material would improve the thrust to weight ratio of aircraft engines, it was proposed that this ceramic material would be used as a thermal barrier coating material on turbine blades with service temperatures above 1200 °C.

2. Materials and Methods

2.1. Specimen Preparation

10YbSH nano-powders were synthesized using the hydrothermal method. HfCl₄ (99.99%, Jinghui Zirconium Hafnium New Material Jiangxi, Ganzhou, China) and Yb₂O₃ (99.99%, Aladdin Biochemical Technology Co., Ltd., Shanghai, China) were weighed at a stoichiometric ratio of 9:1 and then dissolved in deionized water to obtain the desired compositions. The prepared solutions were slowly titrated into an ammonia solution that was continuously stirred. The pH was maintained above 12 by continuous addition of concentrated NH₄OH. The obtained precipitate was washed several times with deionized water and alcohol until a neutral pH of 7 was achieved. The obtained precipitate was heated at 220 °C for 2 h to facilitate a hydrothermal reaction. The hydrothermal nano powders were dried and calcined at 1200 °C for 2 h to obtain the final powder sample.

The synthesized powder was sieved through a 200 mesh sieve, pre-pressed into shape, and then subjected to cold isostatic pressing. The powder samples were compressed under 200 MPa pressure into circular green samples with diameter of 15 mm and thickness of 2.5 mm. Finally, the samples were sintered at 1600 °C for 6 h to form dense ceramic bricks. After cold isostatic pressing, the densified 10YbSH ceramics were annealed at 1500 °C for 3 h, 6 h, 12 h, 24 h, and 48 h, respectively, to investigate the effects of thermal aging on the microstructure and mechanical properties of the sandwich structures.

2.2. Microstructure and Properties Characterization

The phase compositions of specimens were characterized by X-ray diffraction (PANalytical, X'Pert Pro MPD, Panaco Analytical Instruments, Almelo, The Netherlands) in the 2 θ range of 20–90° operating with Cu K α radiation (λ = 0.15406 nm) generated at 40 kV and 40 mA. For the purpose of learning about the phase compositions and qualify the weight fraction of each phase, the XRD data were further refined through the Rietveld method by using the GSAS software (GSAS-II).

The microstructure of densified ceramic bulks was examined by using scanning electron microscopy (Gemini 300, Zeiss, Oberkochen, Germany) equipped with an energy dispersive spectrometer (EDS, Ultim MAX, Oxford, UK). The elastic modulus of the ceramic materials was determined using the ultrasonic method by UMS ultrasonic echo material testing system (UMS-100, EDAN, Beijing, China) with the following equation.

$$E = \rho v_t^2 \frac{4v_t^2 - 3v_l^2}{v_t^2 - v_l^2}$$
(1)

$$E_0 = \frac{E}{\left(1 - \varphi^{\frac{3}{2}}\right)^{1.21}}$$
(2)

where v_t and v_l are the transverse and longitudinal wave speeds, respectively. ρ and φ are the density and the porosity measured using the Archimedean drainage method, respectively. *E* and *E*₀ represent the experimental elastic modulus and the theoretical elastic modulus [28].

The hardness (H_V) of ceramic bulks was measured by the microhardness tester (TMVP-1, Beijing Times Peak Technology Co., Ltd., Beijing, China), and the fracture toughness (K_{IC}) and fracture energy (Γ) were calculated by the indentation method [29].

$$K_{IC} = 0.016 \times \left(\frac{E_0}{H_V}\right)^{\frac{1}{2}} \frac{P}{C^{\frac{3}{2}}}$$
(3)

$$\Gamma = 2\xi^2 P \frac{d^2}{c^3} \tag{4}$$

where *c*, *d*, *P*, and $\xi = 0.016$ stand for the crack length from crack tip to the indentation center, half of the diagonal length, loading force, and the geometry factor of the Vickers penetrator, respectively.

3. Results and Discussion

3.1. Formation of Hafnium Oxide Ceramic Sandwich Structure

As shown in the XRD patterns (Figure 1), the diffraction peak of 10YbSH powder prepared by hydrothermal method only contained a single metastable cubic phase of HfO₂. At the same time, the diffraction peak exhibited low intensity, while the full the width at half maxima (FWHM) appeared relatively large. These observations collectively suggest the presence of a small grain size in the material. Meanwhile, there were no extra diffraction peaks in the diffraction pattern, indicating sufficient atomic diffusion and successful pre synthesis Upon calcination at 1200 °C for 2 h, a monoclinic phase of HfO₂ appeared in the powder, with an increase in diffraction peak intensity and a decrease in FWHM, which could be attributed to the critical grain size effect in hafnium oxide [21]. When the grain size was smaller than the critical size, a relatively lower rare earth doping concentration could also stabilize monoclinic hafnium oxide to cubic phase. Despite the relatively low rare earth dopant concentration in the powder subjected to hydrothermal treatment, it remained at the nanometer scale, and notably smaller than the critical size. The surface effects associated with the nano powder also contributed to its stabilization in the metastable cubic phase [20]. During the calcination process at 1200 °C, the grains gradually grew and exceeded the critical grain size. The metastable system could not reach equilibrium, and monoclinic hafnium oxide began to appear in the powder.



Figure 1. XRD patterns of 10YSH hydrothermal powders before and after annealing at 1200 °C for 2 h.

To further investigate the process of nano powder phase transformation, high-temperature XRD testing was conducted, and the X-ray diffraction patterns from 1000 °C to 1200 °C were obtained, as presented in Figure 2. At temperatures above 1000 °C, cubic phase nanocrystals began to grow, the critical grain size of hafnium oxide powder was disrupted, and M phases began to precipitate in the system. At 1050 °C, there was a gradual emergence of diffraction peaks associated with the M phase at 28.38° and 31.42°. As the temperature continued to rise to 1100 °C, 1150 °C, and 1200 °C, the intensity of these diffraction peaks corresponding to the M phase progressively increased. The ratio of diffraction peak intensity between the M phase and C phase gradually increased, indicating an increase in M phase content. Such findings could be attributed to the fact that at temperatures above 1000 °C, the grain size of the metastable C phase gradually increased, exceeding the critical grain size, thereby causing a phase transition from C phase to M phase to occur.



Figure 2. High temperature XRD diffraction patterns of 10YbSH hydrothermal nano powder.

The SEM image of 10YbSH dense ceramics after cold pressing and sintering is shown in Figure 3. Through EDS analysis of cations in the system (Figure 3b–d), findings were made that the Yb content on both sides of the sandwich structure was significantly higher than that of the middle plate prism structure. Notably, the content of rare earth elements could also be used to determine the crystal structure of YbSH ceramics [30]. The M phase content remained below 2%, while the C phase content exceeded 9% (but does not form rare earth hafnate). Additionally, the contrast in rare earth element distribution on either side of the sandwich structure further substantiates the presence of the C/M/C sandwich structure. Figure 4 shows the schematic diagram of the formation process of the interlayer structure. The metastable C phase hafnium oxide powder, synthesized through the hydrothermal method, undergoes a significant transformation when subjected to calcination temperatures exceeding 1000 °C. At these elevated temperatures, two larger metastable C phase grains make contact with each other, initiating ion diffusion and subsequent sintering processes at the grain boundaries. Yb³⁺ with higher chemical activity tended to move from the neck towards the interior of the grains, leaving a low Yb³⁺ region in the area where the grains came into contact, promoting the nucleation of the M phase at low concentrations of Yb³⁺. Meanwhile, the cation Hf⁴⁺ with low chemical activity moved from the interior of the grain towards the neck region, achieving densification. Since the stable M phase crystal formed in the neck region belongs to the monoclinic prism type, the energy on the base plane was conducive to nucleation, and the growth rate is far higher than that of the prism surface. As such, the lath-shaped M phase morphology was formed [31]. Further, considering the anisotropy of M phase during grain growth, a C/M/C sandwich structure was formed.



Figure 3. (**a**) Microscopic structure and element distribution on both sides of the sandwich structure. (**b**) overall element distribution, (**c**) Yb distribution, (**d**) Hf distribution.



Figure 4. Schematic diagram of the formation process of the sandwich structure [32].

3.2. Microstructure Evolution during Thermal Aging

Figure 5 shows the XRD patterns of the densely sintered 10YbSH ceramics at various annealing time. After being pressed and sintered at 1600 °C for 6 h, the powder experienced an increase in contact area, resulting in more even elemental diffusion. Thus, the metastable cubic phase was destroyed. There was obvious monoclinic hafnium oxide in the unannealed ceramics. Meanwhile, as the annealing time prolongs, the diffraction intensity of M phase became strong (confirmed by the relative intensity to the (111) peak of C phase), which demonstrates that the weight fraction of the M phase increased. The weight fractions of the M and C phases calculated using the Rietveld method are shown in Table 1. After annealing for 3 h, the weight fraction of the M phase increased sharply from 41.8% to 47.6%. As the annealing time increases from 6 h to 48 h, the weight fraction of M phase continued to increase; however, the rate of change in its content notably diminished, only increasing from 48.9% to 49.8%. The precipitation of the M phase in the metastable C phase was found to be mainly controlled by Yb³⁺ ion diffusion, and the phase transformation progress was fast in the first 3 h of annealing, ultimately stabilizing to the two-phase equilibrium point. In contrast, the non-diffusive martensitic transformation of $T \rightarrow M$ occurred in YSZ cooling from 1200 °C, causing a substantial 3% to 5% volume expansion, ultimately leading to coating failure [33]. The $C \rightarrow C + M$ in hafnium oxide represents a diffusive phase transition that did not entail abrupt volume changes. This is also a critical basis for rare earth doped hafnium oxide coatings as YSZ improved materials.



Figure 5. XRD patterns of the 10YbSH ceramics after annealing at 1500 °C for different time.

Table 1. Weight fractions of the M phase and C phase in the 10YbSH ceramics.

Annealing Time	M Phase	C Phase
0 h	41.8%	58.2%
3 h	47.6%	52.4%
6 h	48.9%	51.1%
12 h	49.0%	51.0%
24 h	49.5%	50.5%
48 h	49.8%	50.2%

Figure 6 shows SEM images of 10YbSH ceramics after annealing at 1500 °C for different time. The ceramic bulks sintered by nano powder were relatively compact and the microstructure is relatively uniform. In comparison to the unannealed samples depicted in Figure 6a, the annealing process from Figure 6b–f reveals a more pronounced growth of hafnium oxide bulk grains with clearer grain boundaries. With the increase of annealing time, certain grains progressively enlarged, leading to the emergence of larger grains characterized by flat surfaces. However, as analyzed earlier, at 1500 °C, the system contains a partial phase transition from the C phase to the M phase, resulting in the transformation of large-sized C phase grains into small-sized M phase grains, and the grain growth effect was not significant obvious. The grains in the microstructure could be generally divided into three categories: (I) C phase/M phase/C phase sandwich structure, (II) M phase cluster-like grains, and (III) surface flat C phase grains, as shown in Figure 6d. The grain size of M phase with rough surface $(0.5-1 \ \mu m, Figure 6e, f)$ is smaller than that of C phase with flat surface (more than 2 μ m, Figure 6c–f), indicating that the sintering resistance of the C phase is worse than the M phase [23]. The oxygen vacancy introduced by Yb³⁺ doping is the main reason for the poor sintering resistance of C phase. Firstly, oxygen vacancies provide a rapid route for cation diffusion, leading to faster grain boundary movement than the M phase. Secondly, cation diffusion occurs through the cation gap mechanism, thus the diffusion of Yb^{3+} and Hf^{4+} occurs more easily due to the lattice relaxation caused by the oxygen vacancy. Notably, the sandwich structure formed after sintering remained intact and did not disappear with extended annealing time. Based on the difference in Yb³⁺ content between the M phase and the C phase mentioned earlier, grains with low Yb content (<2 wt.%) were attributed to the M phase, whereas grains with elevated Yb content were associated with the C phase [30]. The anisotropic growth of M phase crystals contributed to the relatively flat nature of the interfaces in the sandwich structure. When subjected to high temperatures, one of the modes of grain growth observed in 10YbSH crystals involved the formation of these sandwich structures. Moreover, Yb³⁺ in the particles moved towards adjacent particles, resulting in a low concentration of Yb³⁺ in the original particles, while the concentration of Yb³⁺ in the surrounding particles was relatively high. This was the reason for the formation of separated M phase and C phase grains. Further, the proportion of sandwich structures in the microstructure is not high, indicating during the annealing process at 1500 $^{\circ}$ C, the predominant mode of growth involves the independent growth of the M phase and the C phase.

3.3. Hardness and Fracture Toughness

Exceptional and well-rounded mechanical properties play a vital role in ensuring the long-term and efficient performance of TBC materials. Enhancing the hardness of coating materials is essential for withstanding particle impacts and extending the service life of the coatings. Additionally, improving the fracture toughness of these coating materials effectively mitigates crack propagation during service, reducing damage caused by collisions. The Vickers hardness of 10YbSH ceramics was measured by the indentation method at different annealing times, as shown in Figure 7a. With the increase in annealing time, the Vickers hardness of the ceramics gradually decreased. During the first 6 h of annealing, the hardness rapidly decreased from 732.9 H_V to 610 H_V . After annealing for over 6 h, the changing amplitude of hardness significantly decreased, and remained at 583 H_V after 48 h of annealing. On the one hand, according to the phase content change data calculated by XRD testing, the difference in C phase content change was relatively small from 6 h to 48 h of annealing. In the crystal structure of hafnium oxide, the M phase was categorized as a ductile phase, whereas the C phase was considered a hard and brittle phase, with the primary contribution to micro-hardness stemming from the C phase. Therefore, as the hafnium oxide content in the C phase diminished, there was a reduction in Vickers hardness. On the other hand, due to the thermal residual stress caused by the difference in thermal expansion coefficients between the M and C phases, as the annealing time increased, the bonding strengths of the M phase and C phase grains were enhanced. Both of these factors contributed to higher residual stress within the ceramics and a decrease in hardness as the annealing time prolongs.



Figure 6. SEM images of 10YbSH ceramics under different annealing time: (**a**) 0 h; (**b**)3 h; (**c**) 6 h; (**d**) 12 h, (I) C phase/M phase/C phase sandwich structure, (II) M phase cluster-like grains, and (III) surface flat C phase grains (**e**) 24 h, (**f**) 48 h.

As shown in Figure 7b, with the increase in annealing time, the fracture toughness of 10YbSH ceramics gradually increased, and the overall fracture energy also exhibited the same trend. Such findings can be attributed to the gradual increase in the content of toughness phase M during the annealing process. It is worth noting that in hafnium oxide ceramics with a dual phase sandwich structure, the fracture toughness reached 2.18 MPa·m^{0.5}, which is higher than many potential thermal barrier coating materials, such as Gd₂Zr₂O₇, La₂Ce₂O₇, and LaPO₄ (fracture toughness of 0.8 MPa·m^{0.5}, 1.4 MPa·m^{0.5}, and 1.1 MPa·m^{0.5}, respectively. All were measured using the same indentation method as in this experiment) [34–36]. Moreover, as the annealing time increased, the fracture toughness could increase to 2.83 MPa·m^{0.5}. Compared to ceramics before annealing, it increased by 29.86%. The fracture energy exhibited an increase from 27.48 N·m⁻¹ to 45.12 N·m⁻¹, marking a notable increment of 64.20% when compared to the pre-annealing state. This substantial improvement contributed to a more effective impediment against crack propagation. Hence, these findings underscore the potential of dual-phase ceramics as promising TBC materials.



Figure 7. (a) Hardness and (b) fracture toughness and fracture energy of 10YbSH ceramics under different annealing time.

3.4. The Toughening Mechanisms

The influence of residual stress resulted in varying strains corresponding to the inclination angles of the same crystal plane in different directions within different grains. This variation in strain is reflected in the changes observed in the crystal plane spacing in XRD measurements. The formula used is as follows:

$$\frac{d_{\psi} - d_0}{d_0} = (1+v)\frac{\sigma_{\varphi}}{E}\sin^2\psi$$
(5)

where ψ , *E* and *v* are the sample tilt angle, elastic modulus, and Poisson's ratio, respectively. d_{ψ} , and d_0 represent the interplanar spacing at a tilt angle of ψ and the interplanar spacing under stress free conditions [37].

For the 10YbSH ceramic polishing surfaces, Figure 8a shows the changes in interplanar spacing of M phase and C phases. With the increase in $\sin^2\psi$, the overall interplanar spacing gradually decreased. Through linear fitting, its slope was negative, representing σ_{φ} as negative and indicating the occurrence of residual compressive stress. In Figure 8b, the interplanar spacing of the cubic phase (111) increased in pace with $\sin^2\psi$, suggesting the presence of tensile stress. The stress mismatch between the two phases enhanced the fracture toughness of this special structural ceramic [38].



Figure 8. Changes in interplanar spacing of (a) M phase and (b) C phase on polished surfaces.

The results of observing surface cracks using SEM are shown in Figure 9. The predominant fracture mode observed was primarily transcrystalline rupture (Figure 9a–c). The fractures exhibited relatively straight patterns, with occasional bending observed in a few areas, indicating a tendency toward intergranular fracture (Figure 9d). As seen in Figure 9a, when the crack extended in ceramics, crack bridging occurred, which is a type of crack wake effect. In cases where the crack did not propagate through, but instead rotated around the reinforcement, stress accumulated behind the crack tip, causing the two crack surfaces to move closer to each other. This led to an increase in the stress field intensity factor as the crack continued to expand. When the crack entered the grain of the sandwich structure, due to the presence of residual compressive stress in the M phase, the crack plane would be reoriented perpendicular to the direction of applied tensile stress. At the same time, as the crack propagation path increases, the crack tip decreased [39]. Additionally, crack deflection is another significant factor for the toughening of 10YbSH. Owing to the difference in thermal expansion properties ($6.3 \times 10^{-6} \text{ K}^{-1}$ and $10.4 \times 10^{-6} \text{ K}^{-1}$, respectively [23]), and

elastic modulus between the M phase and C phase, cracks tended to deflect towards the junction of the C phase and M phase grain boundaries when passing through the interlayer structure, as shown in Figure 9c,d. The direct effect of crack deflection was to increase the apparent fracture surface energy of the material, thereby reducing the sensitivity of cracks and achieving a toughening effect.



Figure 9. SEM images of crack propagation. (a) crack bridging, (b–d) crack deflection.

4. Conclusions

In this study, the precipitation hydrothermal method was employed to prepare partially stable 10YbSH, and cold isostatic pressing + sintering was adopted to produce densified ceramics. The effect of varying annealing durations at 1500 °C on both hardness and fracture toughness was examined. The toughening mechanism was analyzed, and the following conclusions were drawn:

(1) The nano powder prepared by the coprecipitation hydrothermal method was found to consist of a metastable cubic phase, which gradually precipitated the monoclinic phase when calcined above 1000 $^{\circ}$ C, forming a special C/M/C sandwich structure during sintering;

(2) With the increase in annealing time at 1500 °C, the M phase in 10YbSH gradually increased. The fracture toughness increased from 2.18 MPa \cdot m^{0.5} to 2.83 MPa \cdot m^{0.5}, remaining at a relatively high level;

(3) The difference and residual stress between the two phases in the C/M/C sandwich structure caused cracks to bridge and deflect during the propagation process, releasing stress concentration at the crack tip and achieving a toughening effect.

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