Microstructure and Properties of Densified Gd$_2$O$_3$ Bulk

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Abstract: In this work, Gd$_2$O$_3$ bulks were sintered at temperatures ranging from 1400 °C to 1600 °C for times from 6 h to 24 h, and their microstructure and properties were studied for a wider application of materials in thermal barrier coatings. The densification of the Gd$_2$O$_3$ bulk reached 96.16% when it was sintered at 1600 °C for 24 h. The elastic modulus, hardness, fracture toughness and thermal conductivity of the bulks all increased with the rise in sintering temperature and extension of sintering time, while the coefficient of thermal expansion decreased. When the Gd$_2$O$_3$ bulk was sintered at 1600 °C for 24 h, it had the greatest elastic modulus, hardness, fracture toughness and thermal conductivity of 201.15 GPa, 9.13 GPa, 15.03 MPa·m$^{0.5}$ and 2.75 W/(m·°C) (at 1100 °C), respectively, as well as the smallest thermal expansion coefficients of 6.69 × 10$^{-6}$/°C (at 1100 °C).

Keywords: Gd$_2$O$_3$ bulks; sinter; thermal conductivity; hardness; modulus; fracture toughness

1. Introduction

Thermal barrier coatings (TBCs) have been commonly applied to hot-end components in progressive gas turbines and aero engines to enhance engine dependability, durability as well as efficiency [1–3]. TBCs can effectively isolate the touch of the high-temperature working agent with the metal substrate, thus reducing the components’ surface temperature and weakening the heat transfer efficiency, which ultimately plays a role in protecting the metal substrate [4–6]. The top ceramic layer is essential in the thermal insulation of the thermal barrier coating, which is required to possess a high melting point, low heat exchange rate, stable crystal structure as well as good anti-sintering abilities. ZrO$_2$ is a commonly used material in TBCs for its high melting point (2680 °C), good anti-oxidation activity, stable chemical activity, high shock resistance and a coefficient of thermal expansion (CTE) close to metals (8–10.4 × 10$^{-6}$/°C). However, when it is used at high temperature, the phase structure will change, resulting in a change in volume, and the stress in the coating increases, which will cause the initiation of cracking, leading to the failure of the ceramic layer [7–13].

In Liu’s work, it was proposed that by adjusting the composition, thermal barrier coatings can be prepared with lower thermal conductivity and better high temperature performances than the commonly used ceramics materials [14]. The structure of zirconia TBCs can be modified by rare-earth oxide co-doped with trivalent or pentavalent compounds [15]. In lots of stabilizers of ZrO$_2$, Y$_2$O$_3$ is seen as the most suitable stabilizer when its doping amount lies from 6 to 12 wt%. Specially, 8 mol-YSZ has a single stabilized cubic structure with a thermal conductivity of 2.3 and 1.85 W/(m·°C) at room temperature and 1000 °C, respectively [16]. Conversely, once the serving temperature is higher than 1200 °C, ZrO$_2$ will be sintered quickly accompanied with phase changes. Rare-earth oxides...
become stable once they are oxidized because rare earth elements have a strong oxygen affinity [17,18]. The melting point of \( \text{Gd}_2\text{O}_3 \) is 2350 °C. Meanwhile, it possesses stable chemical activity, good anti-oxidation activity and good shock resistance, which makes it suited to serving in extreme environments [19–22]. The structure of TBCs can be modified and become stable via interaction with oxide co-doped yttrium oxide-stabilized zirconia ceramic materials. Moreover, Gd possesses a powerful ability of adsorbing rest elements, good chemical stability, and can be dissolved in ZrO\(_2\) cell [23–25]. Gao et al. [26] prepared quaternary GYYZO bulks with \( \text{Gd}_2\text{O}_3 \) and \( \text{Yb}_2\text{O}_3 \) added into 8YSZ. It was found that the addition of \( \text{Gd}_2\text{O}_3 \) reduced the thermal conductivity while improving the mechanical properties of the TBCs, with better comprehensive performance. Bobzin K et al. [27] prepared \( \text{Yb}_2\text{O}_3\cdot\text{Gd}_2\text{O}_3 \) co-doped YSZ high-porosity TBCs by atmospheric plasma spraying (APS), and thermally cycled the product at 1150 °C to study the sintering effects on the coatings’ microstructure and properties. The \( \text{Yb}_2\text{O}_3\cdot\text{Gd}_2\text{O}_3 \) co-doped YSZ coating has a relatively low thermal conductivity of 1.1 W/(m·K) (at 1100 °C). Zhang et al. [28] prepared \( \text{Yb}_2\text{O}_3 \) and \( \text{Gd}_2\text{O}_3 \) co-doped \( \text{SrZrO}_3 \) system with good properties through a traditional solid-state reaction. The SZYG/YGZO composite ceramics with \( \text{Yb}_0.3\text{Zr}_{0.5}\text{O}_1.75 \) and \( \text{SZO} \) phases possessed a thermal conductivity of 1.3 W/(m·K) (at 1000 °C), which was 40% less than the \( \text{SZO} \) ceramics’ at least. The CTE of the SZYG/YGZO composite ceramics reached \( 10.9 \times 10^{-6}\text{K}^{-1} \) (1250 °C). Meanwhile, the SZYG/YGZO composite ceramics’ fracture toughness was 30% higher than that of the \( \text{SZO} \) ceramic. Zheng et al. [29] deposited TBCs with Sm-doped \( \text{Gd}_2\text{Zr}_2\text{O}_7 \) through EB-PVD (electron beam physical vapor deposition: EB-PVD). The coating exhibited high CTE and long thermal shock lifetimes at 1100 °C. The TGO’s thickness was about 15 µm after thermal shock tests. Therefore, the addition of Gd elements could evidently improve the performance of \( \text{ZrO}_2 \) TBCs.

However, how does the added \( \text{Gd}_2\text{O}_3 \) enhance the material properties used in TBCs? This requires the properties of the pure \( \text{Gd}_2\text{O}_3 \), while there are few reports on the properties of \( \text{Gd}_2\text{O}_3 \) [19–23,25–29]. By consulting the relevant literature [19,21,22,29], it can be found that there are no detailed values for the thermal physical properties, including the thermal conductivity and thermal expansion coefficient, as well as mechanical properties, including elastic modulus, hardness and fracture toughness of the pure \( \text{Gd}_2\text{O}_3 \). Therefore, in this work, \( \text{Gd}_2\text{O}_3 \) bulks were made with which to study the microstructure, mechanical properties and thermal physical properties, which made the foundations for the wider application of materials in TBCs.

2. Experimental Materials and Procedures

2.1. Preparation of \( \text{Gd}_2\text{O}_3 \) Bulks

For the convenience of preparing the bulk, \( \text{Gd}_2\text{O}_3 \) powders were milled by ball milling with the type of NDL-04, which was made in Xianyang zunkai Co., Ltd., Xianyang, China. The ball milling rotation rate was controlled at 120 revolutions per minute. Table 1 showed the ball milling technology. During the milling of powders, the ball-to-powder ratio in weight was set as 10:1. Both the ball and jar consisted of agate in order to avoid contamination. The main component of agate was silicon dioxide with a Vickers hardness of 1213 ± 75. The powders were milled for 20 h. Sodium stearate was used as a wetting agent in one-percent solution during milling. The initial mean particle size of the \( \text{Gd}_2\text{O}_3 \) powder was about 100 µm. The ball-milled \( \text{Gd}_2\text{O}_3 \) powder’s mean size was 20 µm. The powders’ morphology and cross-sectional microstructure were shown in Figure 1. The powder had a globular shape. Then, the powders were cold-pressed into a green body in a size of \( \varnothing 13 \text{ mm} \times 3 \text{ mm} \) by an isostatic press with the type of TYP-60T, which was made in Taiyuan Xinzuo Co., Ltd., Taiyuan, China. The compacting pressure was kept at 200 MPa for 5 min. The detailed cold compaction parameters were given out in Table 2. Then, the preforms were sintered at 1400 °C, 1500 °C, 1600 °C for 6 h to 24 h in an air ambient muffle furnace, respectively. The sintering temperature was increased from room temperature to 600 °C at a heating rate of 10 °C/min. Then, the samples were heated from 600 °C to
1400 °C, 1500 °C and 1600 °C at a heating rate of 3 °C/min, respectively. The cooling method chosen was furnace cooling after heating.

Table 1. Ball-milling parameters of the powders.

| Processing Parameters | Powders | Gd$_2$O$_3$ |
|-----------------------|---------|-------------|
| Ball-to-powder ratio in weight | 10:1    | 1:1         |
| Grinding ball         | Agate ball | sodium stearate (1 wt.%) |
| Wetting agent         | sodium stearate (1 wt.%) | 120 revolutions per minute |
| Rotation rate         | 120 revolutions per minute | 20 h |
| Time                  | 20 h    | 20 h         |

Table 2. Parameters of isostatic press and sintering.

| Processing Parameters | Parameters |
|-----------------------|------------|
| Pressure              | 200 MPa    |
| Keeping time          | 5 min      |
| Sinter temperature    | 1600 °C, 1500 °C, 1400 °C |
| Sinter times          | 6, 12, 24 h |

2.2. Microstructures and Phases

The original powders’ morphology and the sintered bulks’ microstructure were characterized through a scanning electron microscopy conducted with the type of VEGA II-XMU, which was made in TESCAN, Brno, Czech Republic. X-ray diffraction was conducted with the D8 Discover, which was made in Bruker AXS GmbH, Germany, and was applied to characterize the powders’ and the bulks’ phases with Kα radiation of cooper. X-ray scanning was carried out with a step of 0.02°. The scanning was applied with 2θ from 20° to 80°. The scanning speed was controlled at 2°/min.

2.3. Properties

The bulk’s density was tested according to the Archimedes drainage method. The bulk’s mass was weighted through a balance with the type of PTY-504, which was made in Funing Huazhu Instrument Co., Ltd., Funing, Jiangsu, China. The balance’s accuracy was 0.0001 g. The density could be calculated through Formula (1):

$$\rho_s = \frac{m_1}{m_1 - m_2} (\rho_0 - \rho_L) + \rho_L$$  (1)

where $\rho_s$ indicated the sample’s density, $\rho_0$ indicated the water’s density of 0.998 g/cm$^3$, $\rho_L$ indicated the air’s density of $1.2 \times 10^{-3}$ g/cm$^3$, $m_1$ indicated the sample’s mass mea-
sured in air, and \( m_2 \) indicated the sample’s mass measured in water. The mean value of 10 measurements per sample was used for experimental data.

A laser thermal conductivity meter with the type of DLF-1200, which was made in TA, New Castle, DE, USA, was applied to test the thermal conductivity according to specifications of the laser flash heating technique. The thermal conductivity was estimated according to Formula (2):

\[
\lambda = DC_p\rho
\]  

(2)

where \( \lambda \) indicated the thermal conductivity (W·m\(^{-1}\)·K\(^{-1}\)), \( D \) indicated the thermal diffusivity (m\(^2\)·s\(^{-1}\)), \( C_p \) indicated the specific heat (J·kg\(^{-1}\)·K\(^{-1}\)), and \( \rho \) indicated the sample’s density at room temperature (kg·m\(^{-3}\)).

A thermal expansion meter (SDTA840, TA, New Castle, DE, USA) was applied to test the thermal expansion coefficient. The CTE was estimated through Formula (3):

\[
\alpha = \frac{(L_T - L_0)}{L_0(T - T_0)}
\]  

(3)

where \( \alpha \) represented the material’s CTE, \( L_T \) and \( L_0 \) represented the sample’s length at the temperature of \( T \) and \( T_0 \), and \( T_0 \) represented room temperature, respectively.

A nanomechanical testing system with the type of Hysitron TI Premier, which was made in Bruker, USA, was applied to measure modulus, hardness and fracture toughness. The used indenter in tests was a prismatic indenter. The force of 10 mN was loaded linearly in 5 s. The load of 10 mN was kept for 3 s. The load of 10 mN was unloaded linearly in 5 s. Radical cracks formed on the surface of the samples when the indentation test was used in a low-load model. All the formed cracks were radial cracks in this work. The crack length could be determined. The fracture toughness can be calculated through Formula (4) \[29\]:

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

(4)

where \( P \) represented the maximum press in load, \( C \) represented the crack length, and \( \alpha \) represented a correlation coefficient related to the indenter appearances; where \( 1.6 \times 10^{-2} \) was adopted, \( E \) represented the elastic modulus, and \( H \) represented the hardness. The mean values of the hardness, elastic modulus and fracture toughness were adopted on the base of ten measured results.

3. Results

3.1. Microstructure

Figure 2 shows the Gd\(_2\)O\(_3\) bulks’ microstructures as being sintered at 1400 °C, 1500 °C, 1600 °C, for 6 h to 24 h. The sintered Gd\(_2\)O\(_3\) bulks became dense gradually when the sintering time was extended at 1400 °C. In Figure 2a, when the Gd\(_2\)O\(_3\) bulk was sintered at 1400 °C for 6 h, there existed a lot of pores, while the number of pores in the bulk material decreased significantly when the fritting times reached 12 h and 24 h, as shown in Figure 2b,c. The bulks’ pores dissolved gradually with the fritting and densification of Gd\(_2\)O\(_3\). With the increase in the fritting temperature, the sintered Gd\(_2\)O\(_3\) bulk became dense. In Figure 2d, when the Gd\(_2\)O\(_3\) bulk was sintered at 1500 °C for 6 h, a lot of pores were also existed, while the number of pores in the bulk material decreased significantly when the fritting times reached 12 h and 24 h as shown in Figure 2e,f. As compared with the Gd\(_2\)O\(_3\) sintered at 1400 °C, the number of pores was lower in the one sintered Gd\(_2\)O\(_3\) at 1500 °C. The Gd\(_2\)O\(_3\) bulk sintered at 1600 °C had almost no pores. It reached a state of complete densification. With the sintering time extension at 1600 °C, the pore numbers did not change in the sintered Gd\(_2\)O\(_3\) bulk, as seen in Figure 2g–i, which was different to the densification of the sintered Gd\(_2\)O\(_3\) bulk at 1400 °C and 1500 °C.
Figure 2. The Gd$_2$O$_3$ bulk’s microstructure, sintered at 1400 °C for 6 h (a), 12 h (b), and 24 h (c); the Gd$_2$O$_3$ bulk’s microstructure, sintered at 1500 °C for 6 h (d), 12 h (e), and 24 h (f); the Gd$_2$O$_3$ bulk’s microstructure, sintered at 1600 °C for 6 h (g), 12 h (h), and 24 h (i).

The bulks’ porosities were processed through the image processing method with ImageJ Software®. Table 3 shows the porosities of the bulks. With the fritting time extension, the bulks’ porosities decreased gradually. There was the lowest porosity in the bulk sintered for 24 h. Meanwhile, the sintered Gd$_2$O$_3$ bulk at 1600 °C had almost no pores, and was reaching a state of complete densification. With the fritting time extension at 1600 °C, the change of the pores was not obvious in the sintered Gd$_2$O$_3$ bulk.

Table 3. The sintered bulks’ porosities analyzed through image processing.

| Bulks | 1400 °C | 1500 °C | 1600 °C |
|-------|---------|---------|---------|
| 6 h   | 17.9%   | 7.3%    | 0.9%    |
| 12 h  | 8.6%    | 3.8%    | 0.4%    |
| 24 h  | 4.5%    | 2.5%    | 0.2%    |
3.2. Phases

Figure 3 shows the X-ray diffraction patterns of the original powders and the sintered Gd$_2$O$_3$ bulks. On the bases of X-ray diffraction peaks identification, all of the peaks have been indicated. The Gd$_2$O$_3$ powder and sintered bulks consisted of both cubic and monoclinic structures. According to the Rietveld method, the ratios of cubic and monoclinic phases of Gd$_2$O$_3$ were 90.02% and 9.98%, respectively. Neither of the Gd$_2$O$_3$ powder and bulks were pure cubic or monoclinic, while the Gd$_2$O$_3$ powder and bulks were composed mainly of the cubic phase with about ten percent of monoclinic phase. The Gd$_2$O$_3$ bulks possessed the same phases as the original powder. The Gd$_2$O$_3$ bulk had no obvious phase transitions during sintering at 1400 °C, 1500 °C and 1600 °C. The characteristic peaks of the sintered Gd$_2$O$_3$ bulks were identical.

![Figure 3. X-ray diffraction patterns of the Gd$_2$O$_3$ powder and the sintered bulks.](image)

3.3. Densification

Table 4 shows the sintered Gd$_2$O$_3$ bulks’ real densities, tested according to the Archimedes drainage method. The sintered Gd$_2$O$_3$ bulk became dense gradually when the sintering temperature and the sintering time were increased. The density became larger and larger. The bulk had the maximum density of 7.394 g/cm$^3$ when it was sintered at 1600 °C for 24 h.

| Bulks | 1400 °C (g/cm$^3$) | 1500 °C (g/cm$^3$) | 1600 °C (g/cm$^3$) |
|-------|-------------------|-------------------|-------------------|
| 6 h   | 6.086             | 6.867             | 7.334             |
| 12 h  | 6.765             | 7.128             | 7.377             |
| 24 h  | 7.071             | 7.228             | 7.394             |

The theoretical densities of the pure monoclinic and cubic Gd$_2$O$_3$ were 8.350 g/cm$^3$ and 7.616 g/cm$^3$, respectively. The Gd$_2$O$_3$ bulks with 9.98% monoclinic and 90.02% cubic phases had a theoretical density of 7.689 g/cm$^3$ according to the contents of each phase. The sintered bulks’ densifications were determined according to the ratio of the real density to the theoretical one. The densifications of the Gd$_2$O$_3$ bulks sintered at different temperature for different times were given out in Table 5. With the rise in fritting temperature and the extension of fritting time, the sintered Gd$_2$O$_3$ bulk became dense, and the densification increased gradually. The Gd$_2$O$_3$ bulk had the maximum densification of 96.16% when it was
sintered at 1600 °C for 24 h. The reported density of the Gd$_2$O$_3$ bulk was 7.407 g/cm$^3$. The alumina was often added to Gd$_2$O$_3$ bulk to lower the sintering temperature and accelerate the sintering process. The alumina’s density was about 3.5 g/cm$^3$. Therefore, the reported Gd$_2$O$_3$ bulk’s density was lower than the theoretical one.

### Table 5. The Gd$_2$O$_3$ bulks’ densifications.

| Bulks | 1400 °C | 1500 °C | 1600 °C |
|-------|---------|---------|---------|
| 6 h   | 79.15%  | 89.21%  | 95.38%  |
| 12 h  | 87.98%  | 92.71%  | 95.94%  |
| 24 h  | 91.96%  | 94.01%  | 96.16%  |

3.4. Thermal Conductivity

As shown in Figure 4, the Gd$_2$O$_3$ bulks’ thermal conductivities were detected from room temperature to 1100 °C. With the extension of fritting time at a certain temperature, the bulk’s thermal conductivity increased gradually. The Gd$_2$O$_3$ bulk possessed the minimum thermal conductivity of 1.45 W/(m·k) (at 1100 °C) when it was sintered at 1400 °C for 6 h, which was much less than that of the one sintered at 1400 °C for 24 h, with its value of 2.11 W/(m·k) (at 1100 °C). The Gd$_2$O$_3$ bulk possessed the thermal conductivity of 1.84 W/(m·k) (at 1100 °C) when it was sintered at 1500 °C for 6 h, which was less than that of the one sintered at 1500 °C for 24 h with its value of 2.42 W/(m·k) (at 1100 °C). The Gd$_2$O$_3$ bulk sintered at 1600 °C for 6 h, 12 h, 24 h possessed the thermal conductivity of 2.68, 2.75 and 2.75 W/(m·k) at 1100 °C, respectively. When the fritting temperature was 1600 °C, the thermal conductivity was almost unchanged with the extension of fritting time, which was attributed to the fully densified state of the Gd$_2$O$_3$ bulk sintered at 1600 °C. The densified Gd$_2$O$_3$ bulk’s thermal conductivity was 2.75 W/(m·k) (at 1100 °C). With the increase in the sintering temperature, the pores or voids inside or among the Gd$_2$O$_3$ powders disappeared gradually. The motionless air in the pores or voids was a poor conductor of heat, with low thermal conductivity. With the decrease in the pores and voids during sintering, the sintered bulk’s Gd$_2$O$_3$ thermal conductivity was increased gradually.

![Figure 4. The sintered Gd$_2$O$_3$ bulks’ thermal conductivities.](image)

3.5. Thermal Expansion Coefficient

As shown in Figure 5, the Gd$_2$O$_3$ bulks’ CTEs were detected from room temperature to 1100 °C. Generally, all of the sintered bulks’ CTEs increased when the working
temperature elevated. The bulks’ CTEs decreased gradually with the rise in sintering temperatures and extension of times. The sintered Gd$_2$O$_3$ bulk possessed the minimum CTE of $6.69 \times 10^{-6}$/$^\circ$C (at 1100 $^\circ$C) when it was sintered at 1600 $^\circ$C for 24 h, which was 10.6% less than that of the one sintered at 1400 $^\circ$C for 6 h with its CTE of $7.48 \times 10^{-6}$/$^\circ$C (at 1100 $^\circ$C). The CTEs of the bulks sintered at 1600 $^\circ$C were almost unchanged, which was attributed to the fully densified state of the Gd$_2$O$_3$ bulk sintered at 1600 $^\circ$C. At 1100 $^\circ$C, the densified Gd$_2$O$_3$ bulk possessed a CTE of $6.69 \times 10^{-6}$/$^\circ$C. The increase in the bulk density with the increase in sintering temperature could be attributed to the decrease in pores or voids inside or among the Gd$_2$O$_3$ powders. With the densification process, the thermal expansion space became smaller, which restricted the thermal expansion and led to a low thermal expansion coefficient. With the decrease in the pores and voids during sintering, the sintered bulk’s thermal expansion coefficient decreased gradually.

![Figure 5. The sintered Gd$_2$O$_3$ bulks’ CTEs.](image)

3.6. Mechanical Properties

Figure 6 shows the hardnesses of the bulks sintered at 1400 $^\circ$C, 1500 $^\circ$C, 1600 $^\circ$C for 6 h, 12 h, and 24 h. With the rise in the sintering temperatures and extension of the fritting times, the sintered Gd$_2$O$_3$ bulks’ hardnesses were increased. The Gd$_2$O$_3$ bulk had the minimum hardness of 8.08 GPa when it was sintered at 1400 $^\circ$C for 6 h, which was 10.4% less than that of the sample sintered at 1400 $^\circ$C for 24 h, with its value of 9.02 GPa. The Gd$_2$O$_3$ bulk possessed the hardness of 8.43 GPa when it was sintered at 1500 $^\circ$C for 6 h, which was 7.4% less than that of the one sintered at 1500 $^\circ$C for 24 h, with its value of 9.10 GPa. The Gd$_2$O$_3$ bulks possessed the hardnesses of 9.12 GPa, 9.13 GPa and 9.13 GPa, respectively, when they were sintered at 1600 $^\circ$C for 6 h, 12 h and 24 h. The hardness was almost unchanged, which was attributed to the fully densified state of the Gd$_2$O$_3$ bulk sintered at 1600 $^\circ$C. The densified Gd$_2$O$_3$ bulk with the hardness of 9.13 GPa. With the extension of fritting times, the bulks’ densifications reached 99.82%, which was near the full densification and could indicate high hardness.
Figure 6. The sintered Gd$_2$O$_3$ bulks' hardnesses.

As Figure 7 shown, the bulks' elastic moduli were measured when they were sintered at 1400 °C, 1500 °C, 1600 °C for 6 h to 24 h. When the sintering temperature was raised and the sintering time was extended, the bulk’s elastic modulus increased. The Gd$_2$O$_3$ bulk possessed the minimum elastic modulus of 156.39 GPa when it was sintered at 1400 °C for 6 h, which was 19.5% less than that of the one sintered at 1400 °C for 24 h with its value of 194.39 GPa. The Gd$_2$O$_3$ bulk possessed the elastic modulus of 182.45 GPa when it was sintered at 1500 °C for 6 h, which was 8.5% less than that of the one sintered at 1500 °C for 24 h, with its value of 199.52 GPa. The Gd$_2$O$_3$ bulks possessed the elastic moduli of 200.56 GPa, 200.88 GPa, 201.15 GPa, respectively, when they were sintered at 1600 °C for 6 h, 12 h, 24 h. The elastic modulus was almost unchanged, which was attributed to the fully densified state of the Gd$_2$O$_3$ bulk sintered at 1600 °C. The densified Gd$_2$O$_3$ bulk’s elastic modulus was 201.15 GPa.

Figure 7. The sintered Gd$_2$O$_3$ bulks' elastic moduli.

As Figure 8 shown, the nanoindentations with cracks in the Gd$_2$O$_3$ bulks were labeled when the bulks were sintered at 1400 °C, 1500 °C, 1600 °C for 6 to 24 h. Table 6 shows the
bulks’ fracture toughnesses ($K_{IC}$) estimated on the basis of Formula (4). When the sintering time extended, the sintered Gd$_2$O$_3$ bulks’ fracture toughnesses all increased. Meanwhile, with the rise in the fritting temperature, the sintered Gd$_2$O$_3$ bulks’ fracture toughnesses increased. The Gd$_2$O$_3$ bulk possessed the minimum fracture toughness of 10.91 MPa·m$^{0.5}$ when it was sintered at 1400 °C for 6 h, which was 19.5% less than that of the one sintered at 1400 °C for 24 h, with its value of 13.50 MPa·m$^{0.5}$. The Gd$_2$O$_3$ bulk possessed the fracture toughness of 12.75 MPa·m$^{0.5}$ when it was sintered at 1500 °C for 6 h, which was 8.5% less than that of the one sintered at 1500 °C for 24 h with its value of 14.03 MPa·m$^{0.5}$. The Gd$_2$O$_3$ bulks possessed the fracture toughnesses of 14.97 MPa·m$^{0.5}$, 15.02 MPa·m$^{0.5}$ and 15.03 MPa·m$^{0.5}$, respectively, when they were sintered at 1600 °C for 6 h, 12 h and 24 h. The fracture toughness was almost unchanged, which was attributed to the fully densified state of the Gd$_2$O$_3$ bulk sintered at 1600 °C. The densified Gd$_2$O$_3$ bulk had the fracture toughness of 15.03 MPa·m$^{0.5}$.

![Indentations of the Gd$_2$O$_3$ bulks sintered at 1400 °C for 6 h (a), 12 h (b), and 24 h (c); indentations of the Gd$_2$O$_3$ bulks sintered at 1500 °C for 6 h (d), 12 h (e), and 24 h (f); indentations of the Gd$_2$O$_3$ bulks sintered at 1600 °C for 6 h (g), 12 h (h), and 24 h (i).](image-url)

**Figure 8.** Indentations of the Gd$_2$O$_3$ bulks sintered at 1400 °C for 6 h (a), 12 h (b), and 24 h (c); indentations of the Gd$_2$O$_3$ bulks sintered at 1500 °C for 6 h (d), 12 h (e), and 24 h (f); indentations of the Gd$_2$O$_3$ bulks sintered at 1600 °C for 6 h (g), 12 h (h), and 24 h (i).
4. Discussion

The melting point of Gd$_2$O$_3$ is 2350 °C, which is very high. Meanwhile, it possesses stable chemical activity, good oxidation resistance and good impact resistance, which makes it suited to serving in high-temperature and harsh circumstance. The crystal structure of TBCs can be modified and become stable by oxide co-doped yttrium oxide-stabilized zirconia. Moreover, Gd possesses a powerful affinity with rest elements and strong chemical stabilities and can be blended into ZrO$_2$ cell. Table 7 shows the lattice parameters of the unit cells and the space group of the phases calculated through the CrystalMaker software®. M-Gd$_2$O$_3$ had a monoclinic structure with space group C2/M, as well as the lattice parameters of a (14.095 nm), b (3.5765 nm), c (8.7692 nm) and $\beta = 100.08^\circ$. C-Gd$_2$O$_3$ had a cubic structure with space group Ia-3, and the lattice parameters of a (10.813 nm), b (10.813 nm) and c (10.813 nm) and $\alpha = \beta = \gamma = 90^\circ$. The crystalline structures of monoclinic and cubic Gd$_2$O$_3$ were shown in Figure 9. Cubic Gd$_2$O$_3$ had a large lattice constant, which was helpful for enhancing affinity with other elements. Therefore, Gd$_2$O$_3$ can be added to zirconia as a stabilizer to promote the material’s comprehensive properties used in TBCs.

Table 7. Lattice parameters of the unit cells and the space group of the monoclinic and cubic Gd$_2$O$_3$.

| Crystal Phase | Lattice (Å) | Space Group | Wyckoff Coordinates | Angle |
|---------------|-------------|-------------|---------------------|-------|
| M-Gd$_2$O$_3$ | a = 14.095  | C2/M        | Gd (0.25,0.25,0)   | $\alpha = \gamma = 90^\circ$ |
|               | b = 3.5765  |             | O (0,0,0)           | $\beta = 100.08^\circ$ |
|               | c = 8.7692  |             | O (0.5,0,0)         |       |
| C-Gd$_2$O$_3$ | a = b = c = 10.813 | Ia-3 | Gd (0.25,0,0)     | $\alpha = \beta = \gamma = 90^\circ$ |
|               |             |             | O (0.50,0.50,0.50)  |       |

Figure 9. Crystalline structures of the Gd$_2$O$_3$: (a) M-Gd$_2$O$_3$, (b) C-Gd$_2$O$_3$.

In this work, Gd$_2$O$_3$ bulks were sintered at 1400 °C, 1500 °C, 1600 °C for 6 h to 24 h to study the Gd$_2$O$_3$ bulks’ microstructure and properties to aid with wider the application of the materials in TBCs. The sintered Gd$_2$O$_3$ bulks were composed of monoclinic and cubic structures. Meanwhile, the cubic structure took about 90%. The main structure of the sintered Gd$_2$O$_3$ was cubic. The investigated mechanical properties included hardness, elastic modulus and fracture toughness. The thermal physical properties included the thermal expansion coefficient and thermal conductivity. It was found that the densification
of the Gd$_2$O$_3$ bulk reached 96.16% after 24 h sintering at 1600 °C. When the sintering temperature rose and sintering time extended, the elastic modulus, hardness, fracture toughness and thermal conductivity of the sintered bulks increased, and the CTE decreased gradually. Gd$_2$O$_3$ bulk possessed the greatest elastic modulus, hardness and fracture toughness of 201.15 GPa, 9.13 GPa and 15.03 MPa·m$^{0.5}$, respectively when it was sintered at 1600 °C for 24 h. Meanwhile, it had the highest thermal conductivity and the lowest CTE of 2.75 W/(m·K) and 6.69 × 10$^{-6}$/°C at 1100 °C. At present, the properties of the co-doped zirconia ceramics used in TBCs are shown in Table 8. The ZrO$_2$ bulk exhibited 12.0 GPa hardness, 210 GPa elastic modulus, a fracture toughness of 6 cMPa·m$^{0.5}$, 3.0 W/(m·K) (at room temperature (RT)) thermal conductivity and 9 × 10$^{-6}$/K (at 1100 °C) linear expansion coefficient, respectively [30,31]. The optimized 8YSZ bulk exhibited 13 GPa hardness, 230 GPa elastic modulus, a fracture toughness of 5.1 MPa·m$^{0.5}$, 1.85 W/(m·K) (at 1000 °C) thermal conductivity and 10 × 10$^{-6}$/K (at 1100 °C) CTE, respectively [31–34]. The 6GdSZ bulk stabilized by Gd$_2$O$_3$ had 10 GPa hardness, 200 GPa elastic modulus, 1.5 W/(m·K) (at 1100 °C) thermal conductivity and 11.5 × 10$^{-6}$/K (at 1100 °C) CTE, respectively [35,36]. The 15 wt.% Gd$_2$O$_3$-GYYZO bulk sintered at 1650 °C for 24 h possessed the hardness, elastic modulus, and fracture toughness, thermal conductivity and thermal expansion coefficient of 15.61 GPa, 306.88 GPa, 7.822 MPa·m$^{0.5}$, 1.04 W/(m·K) and 7.89 × 10$^{-6}$/°C (at 1100 °C), respectively [26]. The increase in the bulk density with the increase in sintering temperature could be attributed to the decrease in pores or voids inside or among the Gd$_2$O$_3$ powders. It could be assumed that the average grain size of the sintered sample increased moderately with the increase in sintering temperature [22]. For the effect of Gd$_2$O$_3$ and Yb$_2$O$_3$ co-doping on the sintering of 8YSZ, Gd$_2$O$_3$-Yb$_2$O$_3$-YSZ exhibited better sintering resistance than 8YSZ [37]. It was thought to be the case that sintering process was controlled by diffusion. On the one hand, the shrinkage of Gd$_2$O$_3$-Yb$_2$O$_3$-YSZ was lower than that of 8YSZ due to the incorporation of larger and heavier atoms in YSZ. On the other hand, the co-dopants could promote the formation of defect clusters in zirconia crystals. Gd$_2$O$_3$ will take great effect in adjusting the zirconia’s microstructure and properties to meet the serving environments. The properties of the sintered Gd$_2$O$_3$ bulk lay the foundation for the properties of Gd$_2$O$_3$-doped oxide ceramics and can adjust the performances of TBCs prepared with Gd$_2$O$_3$-doped oxide ceramics further.

5. Conclusions
(1) The Gd$_2$O$_3$ bulk became denser and denser when sintering temperature rose and sintering time extended. The densification of the Gd$_2$O$_3$ bulk reached 96.16% after sintering at 1600 °C for 24 h, which reached a near-fully dense state.
(2) There was no phase transformation during sintering of the preformed Gd$_2$O$_3$ bulks. All of the sintered Gd$_2$O$_3$ bulks were composed of about 90% cubic and 10% monoclinic structures.
(3) When sintering temperature rose and sintering time extended, the hardness, elastic modulus, fracture toughness and thermal conductivity of the sintered Gd$_2$O$_3$ bulk increased and the CTE decreased gradually. Gd$_2$O$_3$ bulk sintered at 1600 °C for 24 h possessed the maximum elastic modulus, hardness, fracture toughness and thermal conductivity.

Table 8. Properties of Gd$_2$O$_3$ and co-doped zirconia ceramics used in TBCs.

| Bulks              | Hardness (GPa) | Elastic Modulus (GPa) | Fracture Toughness (MPa·m$^{0.5}$) | Thermal Conductivity W/(m·k) | Thermal Expansion Coefficient (at 1100 °C) |
|--------------------|----------------|-----------------------|------------------------------------|-----------------------------|------------------------------------------|
| Gd$_2$O$_3$        | 9.13           | 201.15                | 15.03                              | 2.75 (at 1100 °C)           | 6.69 × 10$^{-6}$/°C                     |
| ZrO$_2$            | 12.0 [31]      | 210 [31]              | 6.0 [31]                           | 3.0 (at RT) [30]            | 9 × 10$^{-6}$/K [30]                     |
| 8YSZ               | 13 [31]        | 230 [32]              | 5.1 [33]                           | 1.85 (at 1000 °C) [16]      | 10 × 10$^{-6}$/K [34]                    |
| 6GdSZ              | 10 [35]        | 200 [35]              | —                                 | 1.5 (at 1100 °C) [36]       | 11.5 × 10$^{-6}$/K [36]                  |
| 15 wt%Gd$_2$O$_3$-GYYZO | 15.61 [26]    | 306.88 [26]           | 7.822 [26]                         | 1.04 (at 1100 °C) [26]      | 7.89 × 10$^{-6}$/K [26]                  |
conductivity of 201.15 GPa, 9.13 GPa, 15.03 MPa·m^0.5 and 2.75 W/(m·K) (at 1100 °C), and the minimum CTE of 6.69 × 10^{-6}/°C (at 1100 °C).

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