Preparation and Thermal Properties of LaPO₄ Ceramics

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Abstract. Ceramic thermal barrier coatings (TBCs) are widely used on the gas turbine engine. As one of the candidate TBC materials, LaPO₄ has attracted much attention. In the present study, the bulk LaPO₄ was prepared by spark plasma sintering (SPS). The effect of different preparation conditions on the properties of the obtained LaPO₄ ceramic was studied. The phase composition, microstructure, thermal expansion and thermal conductivity of the LaPO₄ ceramic with heat treatment at 1450°C for different time were studied by XRD and SEM.

1. Introduction
Ceramic thermal barrier coatings (TBCs) are widely used on the hot-section metal components of gas turbine engine, due to their low thermal conductivity, high melting point and good corrosion resistance [1]. State-of-the-art TBCs are based on 8wt% yttria partially stabilized zirconia (8YSZ), that cannot meet the demands of design and operation of turbine blades in the next generation high-performance aero engines, due to phase transitions and sintering effect above 1200°C [2]. Therefore, development of new ceramic TBC materials has become one of the key issues for the next generation high-performance aero engines. As one of the candidate TBC materials, LaPO₄ has attracted much attention [3-10].

2. Experimental methods

2.1. Sample preparation
The LaPO₄ powder used in this paper is a precursor powder prepared using La(NO₃)₃ and NH₄H₂PO₄ as a raw material by chemical precipitation method, and then sintered at a temperature of 1000°C. Weigh an amount of LaPO₄ powder and put into a graphite mold, pre-press it for 20 min under a pressure of 15 MPa using tablet machine, and then perform sintering at 1300°C for 3 minutes at a pressure of 40 MPa by spark plasma sintering (SPS) or by pressureless sintering at 1600°C for 2 h.

2.2. Ceramic composition and properties analysis
The phases were determined by X-ray diffraction analysis (D/MAX-2500/PC), which was performed with Cu irradiation (1.5406 Å) at a scanning rate of 3° min⁻¹ in 20 range between 20° and 80°. In this
paper, FESEM (Quanta FEG 650, FEI Co. Ltd., USA) was used to compare the morphology of ceramic bulks.

Determination of density of Ceramic coating is by drainage method with computational formula equation (1).

\[ \rho = \frac{A}{A-B}(\rho_0 + \rho_L) + \rho_L \]  

\( \rho \), measurement density; \( A \), mass of the sample in air; \( B \), mass of the sample in liquid; \( \rho_0 \), liquid density; \( \rho_L \), air density.

The microhardness tester used in this paper is HXD-1000TM/LCD type digital display microhardness meter. The fracture toughness \( K_{IC} \) is calculated by equation (2).

\[ K_{IC} = 0.16 \cdot H \cdot a^{1/2} (c/a)^{3/2} \]  

\( a \), indentation half-length; \( c \), half-length of indentation crack; \( H \), microhardness.

The thermal expansion coefficient of ceramic bulk was measured by Netzsch DIL 402E equipment. The Thermal diffusion coefficient of ceramic materials was measured using a NETZSCHLFA-427 laser thermal conductivity instrument.

3. Results and discussion

3.1. Effect of Sintering method

Figure 1 is XRD patterns of the LaPO₄ ceramic at different sintering method. In this figure, it can be shown that the XRD results of LaPO₄ ceramic after pressureless sintering and spark plasma sintering are consistent with the results of the LaPO₄ powder after the sintering at 1000°C. All of them are monoclinic phase LaPO₄. The crystallization of the ceramic prepared by the two sintering methods is good. In particular, the diffraction peaks of LaPO₄ ceramic by spark plasma sintering are more sharp and higher than that of by pressureless sintering, which indicates that the crystallization by spark plasma sintering is better.

![Figure 1. XRD patterns of the LaPO₄ ceramic at different sintering method: (a) LaPO₄ powder, (b) Pressureless sintering, (c) Spark Plasma Sintering.](image)

Compared with the XRD spectra, The relative intensity of the diffraction peak of the ceramic sintered by SPS on the(210) plane at \( 2\theta = 29.7^\circ \) was significantly increased. And, the relative intensity
of the diffraction peak of the (112) plane at 31.0° decreases obviously. It is possible that the texture of ceramic sintered by SPS has occurred.

The effect of SPS sintering and pressureless sintering on the texture of LaPO₄ ceramic samples was characterized by the ratio of the integral area of the (210) plane to the peak integral area of the (120) plane (α = S(210) / S(120)) and the ratio of the (112) plane to the (120) plane (b = S(112) / S(120)). The calculated results are as shown in Table 1. In this experiment, the α in SPS sintering, pressureless sintering, powder and standard card is 0.1818, 0.1497, 0.1559 and 0.1601, b is 0.3587, 0.7778, 0.8147 and 0.7771, respectively. It can be seen that there is obvious texture in SPS sintered LaPO₄ ceramic samples.

Table 1. Peak area ratio of different sintering method.

| Sample                        | α = S(210)/S(120) | b = S(112)/S(120) |
|-------------------------------|-------------------|-------------------|
| PDF Card                      | 0.1601            | 0.7771            |
| LaPO₄ powder                  | 0.1559            | 0.8147            |
| LaPO₄ Ceramic by pressureless  | 0.1497            | 0.7778            |
| SPS                           | 0.1818            | 0.3587            |

Figure 2 shows the SEM of fracture microstructure of LaPO₄ ceramic. It can be seen from Figure 2a that the sintered grain is small granule, while the morphology observed in Figure 2b is layered structure. The results show that the directional growth and flake structure of LaPO₄ ceramic occur in the process of SPS sintering, which is consistent with the analysis results of XRD spectra. In addition, though the sintering temperature of spark plasma sintering is lower than that of pressureless sintering, but the pore is obviously lower than that of pressureless sintering. Via the drainage method, the measurement density of ceramic obtained by pressureless sintering and spark plasma sintering was measured respectively. And the theoretical density of the corresponding ceramic material is calculated according to the cell parameters, then the relative density (ρ measurement density / ρ theoretical density) × 100% could be got. The results are shown in Table 2. The relative density of LaPO₄ ceramic sintered by SPS is obviously higher than that of LaPO₄ ceramic sintered by pressureless sintering.

Table 2. The relative densities of the LaPO₄ ceramic at different sintering method.

| Sintering method | Sintering temperature (°C) | Heating rate (°C/min) | Dwelling time (min) | Theoretical density (g/cm³) | Measurement density (g/cm³) | Relative density (%) |
|------------------|-----------------------------|-----------------------|---------------------|----------------------------|-----------------------------|----------------------|
| Pressureless sintering | 1600                        | 3                     | 120                 | 5.0732                     | 4.8329                      | 95.26                |
| SPS              | 1300                        | 100                   | 3                   | 5.0732                     | 5.0388                      | 98.89                |
3.2. Effect of Sintering temperature

Figure 3 shows XRD spectra of LaPO₄ ceramic by SPS at different temperatures. It can be seen that the LaPO₄ ceramic is monoclinic phase sintered at 1300°C and 1600°C. The difference is that the peak area of the (020) plane is increased after calcination at 1600°C. The ratios of the integral area (α = s (210) / s (120)) sintered at 1300°C and 1600°C are calculated to be 0.250 and 0.335, respectively.

![Figure 3. XRD patterns of SPS sintered LaPO₄ ceramics under different temperature.](image)

Figure 4 shows the fracture morphology of SPS sintered LaPO₄ ceramic at different temperatures. It can be seen that the LaPO₄ ceramic bulk sintered at 1300°C are dense and uniform in grain size (Figure 4a). When the sintering temperature reaches 1350°C, as shown in Figure 4b, it can be seen that
the grain size is obviously delamination. The grain size of the upper layer of the bulk material is similar to that of the Figure 4a, but the grain size of the lower layer is obviously increased. As shown in Figure 4c, no grains can be observed when the sintering temperature reaches 1600°C. The analysis shows that the optimum sintering temperature of LaPO₄ ceramic by SPS is 1300°C.

3.3. Thermal Properties of LaPO₄

3.3.1. Mechanical Behavior under High Temperature of LaPO₄ Ceramic. The operating temperature of aero-turbine engine is higher than 1400°C, so it is of great practical significance to study the mechanical properties of LaPO₄ ceramic materials after heat treatment at 1450°C for different times. Figure 5 shows the microhardness, fracture toughness and relative density of LaPO₄ ceramic sintered by SPS after heat treatment at 1450°C for different times.

LaPO₄ ceramic bulk before heat treatment are called as preparation state. In Figure 5a, the microhardness of LaPO₄ ceramic in preparation state is 4.65 ± 0.28 GPa. With the increase of heat treatment time, the microhardness increases. The microhardness of LaPO₄ ceramic was 5.30 ± 0.38 GPa after holding at 1450°C for 216 h. The increase of microhardness with the increase of heat treatment time is not significant due to the high density and low porosity of LaPO₄ ceramics prepared by SPS.

![Figure 5](image-url)

Figure 5. (a) microhardness, (b) fracture toughness and (c) relative density of the sintered LaPO₄ bulks after heat treatment at 1450°C for different times.

From Figure 5b and 5c, it can be seen that the fracture toughness of LaPO₄ ceramic bulk in preparation state is 1.02 ±0.03 MPa·m¹/², the relative density is 98.89%. At the early heat treatment at 1450°C, the fracture toughness and relative density decreased obviously. It may be due to the fact that
during the heat treatment process, the sintering phenomenon will occur, which will lead to the increase of pores caused by the shrinkage of the bulk material. With the increase of heat treatment time, there is a significant increase in fracture toughness and relative density. It may be due to the increase of grain growth and densification. Figure 6 shows the fracture morphology of LaPO$_4$ ceramic block after heat treatment at 1450°C for different time.

![Fracture morphology of LaPO$_4$ ceramic block after heat treatment at 1450°C for different time: (a) Preparation state; (b) 72h; (c) 144 h; (d)216h.](image)

**Figure 6.** Fracture morphology of LaPO$_4$ ceramic block after heat treatment at 1450°C for different time: (a) Preparation state; (b) 72h; (c) 144 h; (d)216h.

![XRD patterns of LaPO$_4$ ceramic bulk after heat treatment at 1450°C for different time.](image)

**Figure 7.** XRD patterns of LaPO$_4$ ceramic bulk after heat treatment at 1450°C for different time.

Figure 7 shows the XRD spectra of LaPO$_4$ ceramic after heat treatment at 1450°C for different time. It can be seen that the ceramics treated by heat treatment are still monoclinic phase LaPO$_4$, which indicates that the ceramics have good stability at high temperature, and means that LaPO$_4$ ceramic can work at 1450 for a long time.
3.3.2. Thermophysical Properties of LaPO₄ Ceramic. Figure 8 shows the TECs of LaPO₄ ceramic bulk after heat-treatment for different time at 1450°C. It can be seen that the thermal expansion coefficient of the LaPO₄ ceramic in preparation state is $7.49 \times 10^{-6} \text{K}^{-1}$ at normal temperature. When the heat treatment temperature increases at 1200°C, the thermal expansion coefficient of the ceramic bulk reaches $9.56 \times 10^{-6} \text{K}^{-1}$. During the whole heating process, the thermal expansion coefficient of LaPO₄ ceramic blocks increases with the increase of temperature, and there is no obvious inflection point, which indicates that there is no phase transition of LaPO₄ in the whole heating process.

Compared with preparation state, the coefficient of thermal expansion decreased at the heat treatment for 72h and increased at the heat treatment for 144h and 216h. This is due to the increase of pore in the early stage of heat treatment, which leads to the decrease of thermal expansion coefficient, the decrease of porosity in the material at the later stage of heat treatment, and the increase of thermal expansion coefficient with grain growth. The thermal expansion coefficient of the ceramic bulk with heat treatment for 144h and 216h reaches $10.25 \times 10^{-6} \text{K}^{-1}$ at 1200°C.

![Figure 8. The TECs of LaPO₄ ceramic bulk after heat-treatment for different time at 1450°C.](image1)

![Figure 9. Thermal diffusion coefficient curve of LaPO₄ ceramic bulk after heat treatment for different times at 1450°C.](image2)
Thermal diffusion coefficient is one of the important thermophysical properties of thermal barrier coating materials, which can characterize whether the materials have good thermal insulation. Figure 9 is the diagram of thermal diffusion coefficient of LaPO₄ ceramic after heat treatment at 1450°C for different time. It shows that the thermal diffusion coefficient of the LaPO₄ ceramic bulk in preparation state is 0.32mm²·s⁻¹ at 1000°C. When the temperature is lower than 1000°C, the thermal diffusion coefficient of LaPO₄ ceramic bulk decreases with the increase of temperature. When the temperature is between 1000°C and 1200°C, the thermal diffusion coefficient of ceramics increases. This may be due to the fact that the heat conduction of ceramics at low temperature is mainly phonon conduction, while the photonic conduction dominates at high temperature. After heat treatment at 1450°C for a long time, the thermal diffusion coefficient of LaPO₄ ceramic bulk is similar to that of 0.6mm²·s⁻¹ at 1000°C.

The thermal conductivity of LaPO₄ ceramic bulk after heat treatment at 1450°C for different time is shown in Figure 10. The change trend is consistent with the trend of the thermal diffusion coefficient in Figure 9. When the temperature is lower than 1000°C, the thermal conductivity of LaPO₄ ceramic bulk decreases with the increase of temperature, and the thermal conductivity of ceramic bulk increases when the temperature is above 1000°C. On the whole, the heat treatment of LaPO₄ ceramic bulk at 1450°C for a long time has little effect on its thermal conductivity. At 1000°C, the thermal conductivity of LaPO₄ ceramic bulk is between 1.24 W/(m·K) and 1.5 W/(m·K). Therefore, the thermal conductivity of LaPO₄ ceramic bulk is 32% lower than that of 8YSZ bulk (2.1-2.2 W/(m·K) [11]). This means that LaPO₄ materials have better thermal insulation performance.

4. Conclusions
LaPO₄ ceramic bulk with a lamellar structure were prepared by SPS at 1300°C. The hardness, fracture toughness and relative density of LaPO₄ ceramic bulk were 4.65 ±0.28GPa, 1.02±0.03MPa·m¹/₂ and 98.89%, respectively. After heat treatment at 1450°C, with the increase of heat treatment time, the microhardness of LaPO₄ ceramic bulk increases gradually, and the fracture toughness and the relative density are similar, which decreases at first and then increases. The thermal expansion coefficient decreases at first and then increases, and the curve trend of the thermal diffusion coefficient is consistent with that of the thermal conductivity, and all of them change suddenly at 72 h. The thermal expansion coefficient of LaPO₄ ceramic bulk is 9.56×10⁻⁶K⁻¹ at 1200°C, and the thermal conductivity is 1.24W/(m·K) at 1000°C. The thermal expansion coefficient and thermal conductivity, after long time heat treatment at 1450°C are 10.25×10⁻⁶K⁻¹ and 1.5W/(m·K), respectively.
Acknowledgements
This work was supported by the National Natural Science Foundation of China (No.51865044), the Natural Science Foundation of Inner Mongolia Autonomous Region (2017MS0503), and the Inner Mongolia Key Laboratory of Thin Film and Coatings.

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