Phase Structure and Phase Stability Studies of La-Y Co-doped HfO$_2$ Materials and Coatings

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Abstract. In this study, the 30 mol% La-Y co-doped HfO$_2$ was prepared by solid-phase synthesis and the effect of the doping content of La element on the phase structure and high temperature phase stability was investigated by XRD. The results show that LaYSH is pyrochlore p-phase + fluorite c-phase when the doping content of La element is 6 and 9 mol%, and a single fluorite c-phase when the doping content is 0-3 mol%. After sintering at 1600 °C for 50 h, 0, 1 and 2 LaYSH remained as a single fluorite c-phase, 3 LaYSH produced 2.54 wt% pyrochlore p-phase, and the pyrochlore p-phase content in 6 and 9 LaYSH decreased to varying degrees. The prepared 0, 1 and 2 LaYSH coatings all had a single c-phase and remained unchanged in the single c-phase when sintered at 1600°C for 50 hours, demonstrating their good high temperature phase stability.

1. Introduction

Thermal barrier coatings provide thermal protection to the alloy from the internal heat flow of the engine. The most common one in use today is 7-8 wt% Y$_2$O$_3$ partially stabilised ZrO$_2$ (8YSZ), which is stable up to 1200°C for long service in the operating environment [1]. However, beyond 1200°C, the problems of 8YSZ gradually become apparent, mainly in the following aspects: (1) the t phase is a non-equilibrium phase, which decomposes into c phase + t phase above 1200°C[2]. The generation of c phase reduces the fracture toughness of the coating, while the t phase transforms into m phase during the cooling process, leading to cracking as well as spalling of the coating [3-5]. (2) The sintering resistance of 8YSZ is poor. Under high temperature, the grains will grow rapidly and the holes and cracks will gradually shrink and close, generating large sintering stresses; at the same time, the decrease in porosity will lead to an increase in thermal conductivity, and the thermal insulation effect will be affected. Therefore, the optimum operating temperature of 8YSZ is below 1200°C, which does not give the best performance in engines with higher inlet temperatures. In response to the above problems many scholars have carried out a lot of research on new thermal barrier coatings.

Hf and Zr belong to the same IV subgroup, and their oxide crystal structure are relatively similar[6], which provides a reference for the study of HfO$_2$ thermal barrier coating materials. Similar to ZrO$_2$, HfO$_2$ has m, t and c phases and a reversible phase transition between the three phases, but its phase transition temperature is higher than that of ZrO$_2$: the m phase will change to the t phase at around 1720°C and the t phase to the c phase at 2600°C.

Because of this, the researchers proposed the use of HfO$_2$ as a replacement for 8YSZ to solve the problem of phase change of 8YSZ above 1200°C and to enhance the high temperature phase stability of the coating. First principles calculations show[7] that the phase structure of HfO$_2$ is influenced by the atomic radius of the dopant, e.g. when oxides of elements with small atomic radii such as Si, Ti and Al are used as dopants, the doped hafnium oxide obtained t-phase, whereas when oxides of rare earth elements with larger atomic radii are used as dopants, HfO$_2$ will be easily stabilised in the c-phase. Unlike ZrO$_2$, the t and m phase transitions of HfO$_2$ produce only a 1% volume expansion[8]. Ramana, C.V.[9] prepared Gd$_2$O$_3$-doped HfO$_2$ with a c-phase phase structure. Zhu, D.[10-12] prepared Y$_2$O$_3$-doped HfO$_2$ coatings with Y$_2$O$_3$ content ranging from 5 to 25%. As the Y$_2$O$_3$ content increased, the phase structure gradually changed from the m+c phase to the c phase, the thermal conductivity of the coatings gradually decreased and the lifetime of the coatings at 1600°C improved. Li, C. et al. used APS to prepare 8 wt% Y$_2$O$_3$-stabilised HfO$_2$ coatings with a conventional structural coating that transforms from t phase to m-phase HfO$_2$ and c phase YSH after thermal exposure at 1300 °C[13].

In this paper, a study of La$_2$O$_3$ and Y$_2$O$_3$ co-doped HfO$_2$ materials as well as coatings was carried out, focusing on the effect of La elemental doping on the phase structure of HfO$_2$.

2. Experimental

xLa(30-x)YHfO$_{1.88}$ (x = 0, 3, 6, 9 mol%) was prepared by solid phase synthesis method and noted as YSH, 3LaYSH, 6LaYSH and 9LaYSH respectively. La$_2$O$_3$, Y$_2$O$_3$ and
HfO$_2$ powders (purity $\geq$ 99.9%, 1-3 $\mu$m, ENO material, Co. Qinhuangdao, China) were used to prepare the samples. The powders were weighed and mixed with ethanol and poured into a planetary ball mill for mixing (350 rpm, 24 h) according to the corresponding stoichiometric ratios. The mixture was dried in an oven at 120°C for 10 hours. The mixture was then calcined at 1600°C for 20 hours. Finally, the material was ground in ethanol by means of a planetary ball mill (350 rpm, 48 hours) and the fine powder was screened using a 200 mesh sieve.

The phase structure were analyzed by X-ray diffraction (Rigaku Ultima-IV X-Ray Powder Diffractometer, Rigaku, Japan). The overall scanning range was 20°-80° and the scanning rate was 3°/min. The local scanning range was 28-32° with a scanning rate of 0.5°/min.

The graphite sheet is sprayed as a substrate and can be peeled off after cooling to obtain a separate coating tissue. The spray thickness is set to 1 mm and the resulting specimen is ready for direct determination of the phase structure by X-ray diffraction.

### 3. Results and discussion

#### 3.1 Phase structures and phase stability of powders

The phase structures of xLa$_x$Y$_{30-x}$SH (x = 0, 3, 6, 9 mol%) were prepared as shown in Fig. 1. The phase structures of both YSH and 3LaYSH correspond well with the PDF card of c-phase HfO$_2$, demonstrating that both materials are in a single c-phase. However, compared to the PDF standard card, the positions of the diffraction peaks do not correspond well and all six diffraction peaks are at smaller angles than those indicated on the PDF standard card.

![Fig. 1 phase structure of LaYSH](image)

From the Table 1, it can be obtained that when La and Y are doped into the HfO$_2$ lattice, it is impossible for La and Y to enter the interstices of the lattice because their ionic radii are larger than that of Hf. Therefore, La and Y must be substituted for Hf to form a replacement solid solution. The doping of La and Y also increases the volume of the cell and the lattice constant becomes larger. According to the Bragg equation, when the lattice constant becomes larger, the crystal plane spacing becomes wider and the d value increases, therefore, the 2θ value decreases and the corresponding diffraction angle has to become smaller, which is reflected in the XRD pattern as a leftward shift of the diffraction peak, proving that the lattice constant of HfO$_2$-based ceramics increases due to doping, in accordance with Vegard’s law.

As shown in Fig. 2, the phase structures of 6LaYSH and 9LaYSH differ significantly from YSH and 3LaYSH. A smaller diffraction peak appears to the left of each of the four higher intensity diffraction peaks for c-phase HfO$_2$. The four diffraction peaks were identified using the standard card library and found to belong to La$_2$Hf$_2$O$_7$ in the pyrochlore p-phase (PDF#37-1040). This suggests that the solid phase synthesis of 6LaYSH and 9LaYSH is fluorite c-phase + pyrochlore p-phase.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Atomic mass</th>
<th>Ionic radius(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>138.91</td>
<td>1.061</td>
</tr>
<tr>
<td>Y</td>
<td>88.91</td>
<td>0.9</td>
</tr>
<tr>
<td>Hf</td>
<td>178.49</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Table 1. Lattice constant and theoretical density of each compound.
The samples were sintered at 1600°C for 50h to characterise their phase stability at high temperatures. The results are shown in Fig. 3. From the XRD patterns, it can be seen that the phase structure of YSH did not change after 50h of holding at 1600°C. The pyrochlore p-phase diffraction peaks of 6LaYSH and 9LaYSH did not disappear, indicating that the presence of pyrochlore p-phase was not related to the sintering time.

A slow scan of the main diffraction peak region from 28 to 32° reveals a smaller diffraction peak at 28.6°, which

The noteworthy aspect here is that 3LaYSH underwent a change in phase structure, as shown in Fig. 4.

**Fig. 2** phase structure of 6,9LaYSH, (a) 2θ = 20-80°, (b) 6LaYSH, 2θ = 28-32°, (c) 9LaYSH, 2θ = 28-32°.

**Fig. 3** phase structure of xLa(30-x)YHfO1.88 (x = 0, 3, 6, 9 mol%) after sintered at 1600°C for 50h, (a) 2θ = 20-80°, (b) 6LaYSH, 2θ = 28-32°, (c) 9LaYSH, 2θ = 28-32°.
can be derived as the (222) characteristic peak of the pyrochlore p-phase by checking the PDF card. This indicates that the phase structure of 3LaYSH changes after sintering at 1600°C for 50h, from a single fluorite c-phase to a fluorite c-phase + pyrochlore p-phase.

![Fig. 4 phase structure of 3LaYSH after sintered at 1600°C for 50 h](image)

The pyrochlore p-phase content of several materials is shown in Fig. 5. After sintering at 1600°C for 50h, 3LaYSH produced 2.54wt% pyrochlore p-phase, 6LaYSH changed from 11.8% to 10.16% pyrochlore p-phase and 9LaYSH from 19.2% to 11.21%. After a long period of sintering, the pyrochlore p-phase content of the materials with different La doping levels changed. 3LaYSH originally had no pyrochlore p-phase, while 6LaYSH and 9LaYSH both had varying degrees of reduction in pyrochlore p-phase.

![Fig. 5 Variation of pyrochlore p-phase content of xLa(30-x)YHfO1.88 (x = 0, 3, 6, 9 mol%) before and after sintering at 1600°C for 50h](image)

The phase structure of hafnium oxide depends mainly on the radius ratio of the dopant ion to Hf⁴⁺. When A³⁺:B⁴⁺ is less than 1.46, the phase structure is fluorite phase, and between 1.46 and 1.78, it is pyrochlore phase; after exceeding 1.78, it becomes monoclinic phase. The ratio of cation radii is 1.31 for 6LaYSH and 1.33 for 9LaYSH, neither of which exceeds 1.46, and it is theoretically impossible to produce a pyrochlore p-phase. The ionic crystals consist of numerous individual crystals, which are chemically homogeneous on a macroscopic scale. However, when viewed on a smaller scale, there are more defects, such as vacancies and dislocations. The chemical composition at the defects is not homogeneous and has the potential to deviate from pre-determined stoichiometric ratios, which is likely to cause the ionic radius ratio of trivalent and tetravalent cations to exceed 1.46 somewhere within the material, this results in the formation of the pyrochlore p-phase. The sintering of the material at 1600 °C for 50 h resulted in the formation of pyrochlore p-phase in 3LaYSH, which indicates that the sintering process, with sufficient diffusion and migration of the material, does not prevent the concentration of components on a smaller scale, but rather exacerbates this phenomenon. The content of pyrochlore p-phase will remain at a low level after a long sintering period, so the presence and content of pyrochlore p-phase is more related to the doping content of La elements than to the sintering time.

When the doping content of La is greater than or equal to 3 mol%, LaYSH materials with a single-phase structure and stable at high temperatures are not obtained, therefore, a reduction of the doping content of La is considered.

1LaYSH and 2LaYSH were prepared using the same process, the XRD patterns are shown in Fig. 6. After reducing the doping content, no diffraction peaks of pyrochlore p-phase were found in 1LaYSH and 2LaYSH, proving that the synthesized 1LaYSH and 2LaYSH have a single-phase c-phase structure. After sintering at 1600 °C for 50 h, the phase structures are shown in Fig. m, which are consistent with those before sintering, with a single c-phase, proving that the materials have good high-temperature phase stability.
3.2 Phase structures and phase stability of coatings

The phase structure of the coatings was determined and the results are shown in the Fig. 7. The XRD pattern shows that the coatings all contain six distinct diffraction peaks, which correspond to the PDF#53-0560 for c-phase HfO$_2$, proving that the HfO$_2$-based materials in the sprayed state all have a single c-phase and that no other phase structures exist. According to the X-ray diffraction pattern after sintering at 1600°C for 50h, the phase structure of the coatings remained unchanged and was consistent with the single c-phase before sintering, proving the good phase stability of the coatings.

4. Conclusion

In this paper, the effect of the doping content of La element on the phase structure of 30 mol% La-Y co-doped HfO$_2$ was investigated, and the prepared materials and coatings were sintered at 1600 °C for 50 h to study their high-temperature phase stability. The results are as follows:

(1) The doping content of La element affects the phase structure of HfO$_2$-based ceramics. When the doping content is in the range of 0-3 mol%, the solid phase synthesized samples are all in a single fluorite c phase, and when the doping content is raised to 6 and 9 mol%, the phase structure changes to pyrochlore p-phase + fluorite c phase.

(2) After sintering the samples at 1600°C for 50 hours, 0-2LaYSH remained as a single c-phase, 3LaYSH produced 2.54 wt% pyrochlore p-phase, 6LaYSH reduced pyrochlore p-phase from 11.8% to 10.16% and 9LaYSH reduced from 19.2% to 11.21%.

(3) The 0-2LaYSH coating samples were prepared by air plasma spray, and their phase structures were all in a single c-phase. After sintering at 1600°C for 50 h, the single c-phase remained unchanged, demonstrating the good phase stability of the coating samples at high temperatures.

Rare earth doped hafnium oxide materials and coatings with a single phase structure were obtained by controlling the doping content of La elements. None of them changed their phase structure after sintering at 1600°C for 50h, which avoided the possible adverse effects of multiphase structures as well as phase changes.
on the coatings in the service environment. After this study, the focus should be on the thermophysical properties of the coatings in order to meet the corresponding performance specifications.

References