Phase evolution, interdiffusion and failure of La$_2$(Zr$_{0.7}$Ce$_{0.3}$)$_2$O$_7$/YSZ thermal barrier coatings prepared by electron beam–physical vapor deposition

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**A B S T R A C T**

La$_2$(Zr$_{0.7}$Ce$_{0.3}$)$_2$O$_7$ (LZ7C3) has attracted great interest for thermal barrier coatings (TBCs) because it presents extremely low thermal conductivity, high thermal stability and is more resistant to sintering than yttria stabilized zirconia (YSZ). In the present study, an LZ7C3/YSZ double-ceramic-layer (DCL) TBC was deposited by electron beam–physical vapor deposition (EB–PVD) and the TBC system was investigated for its phase evolution, interdiffusion and failure pattern though thermal shock test at 1373 K. X-ray diffraction and Raman spectra results indicate that the as-deposited LZ7C3 coating transforms from fluorite to pyrochlore structure upon thermal shocking between 373 K and 1373 K. It seems that this phase change may have affected the durability of the DCL TBCs. The EDS mapping analysis indicates that some diffusion of Y from YSZ to LZ7C3 layer is occurred after thermal shock test. Additionally, an obvious outward diffusion of Cr from bond coat into LZ7C3 layer takes place due to the chemical reaction of LZ7C3 and Cr. The phase transformation of LZ7C3, the abnormal oxidation of bond coat, and the outward diffusion of Y and Cr alloying element into LZ7C3 coating would be the primary factors for the spallation of LZ7C3/YSZ thermal barrier coating.

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1. Introduction

Thermal barrier coatings (TBCs) have been extensively used in advanced gas turbine engines to protect hot components such as combustion chambers and turbine blades from high temperature gas aggression [1]. The application of TBCs enables engines to be operated at higher gas inlet temperature, giving rise to the improvement of the thrust-to-weight ratio and fuel efficiency of the aerospace engines [2]. State-of-the-art TBCs consist of a NiPtAl diffusion or NiCrAlY overlay bond coat (BC) as the oxidation resistant layer and a ceramic topcoat as the heat resistant layer. Up to now, the most studied and commercially used ceramic top coat is based on 6–8 wt.% yttria stabilized zirconia (YSZ) which shows superior thermophysical and mechanical properties such as low thermal conductivity, high thermal expansion coefficient and high fracture toughness. However, the maximum operation temperature of YSZ is limited to 1473 K for long-term application. At higher temperatures, YSZ coating suffers serious sintering and martensitic phase transformation accompanied by a 4–6% volume expansion, which tend to lead to early spallation failure of TBC [3–5].

In the next generation of advanced engines, further increases in thrust-to-weight ratio will require even higher gas temperature [6]. To meet the development of advanced gas turbine engines, great efforts have been made to identify new alternative TBC materials to YSZ for applications above 1473 K. Several ceramic materials such as multicomponent oxide-doped ZrO$_2$ [7], garnet (Y$_3$Al$_2$Fe$_5$–xO$_{12}$) [8], pyrochlores (Re$_2$Zr$_2$O$_7$, Re=La, Nd, Sm and Gd) [9–13], perovskites (SrZrO$_3$, BaZrO$_3$) [3,9], fluorite-type Re$_2$Ce$_2$O$_7$ (Re=La and Nd) [14], and magnetoplumbite-type LaMgAl$_{11}$O$_{19}$ [15,16] have been evaluated as TBC materials. Among the numerous oxides that have been explored as alternate thermal barrier materials, the rare earth zirconates especially La$_2$Zr$_2$O$_7$ (LZ) have received great attention. Compared with YSZ, LZ has lower thermal
data have been fitted to a parabolic TGO growth law: $(x - x_0)^2 = k_t t$, where $x_0$ is the "as-deposited" TGO thickness, $x$ is the thickness after accumulating a time $t$ at 1373 K [38]. To reduce the scatter in the data, TGO thicknesses have been measured at a minimum of three locations for TBCs. As shown in Fig. 8, the DCL coating has a lower TGO growth rate (0.0667 μm²/h) than YSZ whose parabolic rate constant is 0.0958 μm²/h, which can be explained by the lower oxygen diffusivity of LZ7C3. A lower TGO growth rate would be one of the reasons for the longer thermal shock life of the DCL TBCs.

3.4. Interdiffusion of LZ7C3/YSZ DCL TBCs during thermal shock testing

EDS map scanning analysis of the DCL coating after 6734 cycles are shown in Fig. 9. As expected, TGO is rich in Al and O as the content of Al and O are very high at the interface of the ceramic coats and bond coat, confirming that bond coat has been deeply oxidized during long-term thermal exposure. The distribution of the corresponding elements proves that there is no obvious diffusion of La, Ce and Zr from one layer into the other one by taking into account the testing error. However, a bit of Y element has diffused into the LZ7C3 top layer after 6734 cycles, which is evident in Fig. 9. This phenomenon suggests a faster diffusion coefficient of yttrium out of the tetragonal phase than that of La out of the mix phase of pyrochlore and fluorite. The outward diffusion of yttrium is not desirable in the DCL TBC systems as it may cause a phase transformation of YSZ layer from $t$-ZrO$_2$ to $m$-ZrO$_2$ when the Y concentration is reduced beneath a critical level. In addition, the diffusion of Y may be responsible for the partial sintering at the bottom of the LZ7C3 columns as shown in Fig. 7f. Opposite to the current finding, in Sm$_2$Zr$_2$O$_7$/YSZ DCL TBCs [38] or Gd$_2$Zr$_2$O$_7$/YSZ DCL TBCs [23] prepared by EB–PVD method, Sm (or Gd) has been found to diffuse into the 7YSZ in a limited thickness region while no yttrium outward diffusion into the pyrochlores. Identification of the reasons for this opposite behavior is the topic of ongoing research.

As shown in Fig. 9, it is surprising to find that the alloying element of Cr in bond coat has partially diffused out and even extends to the LZ7C3 layer. The outward diffusion of Cr is also confirmed by the high magnification SEM image of the sample surface after 6734 cycles and corresponding EDS result as shown in Fig. 6d and f. It can be seen that small grains containing mainly in La, Cr, O elements are formed on the surface of sample after a long-term exposure. This phenomenon is also consistent with the XRD results in Section 3.2 where LaCrO$_3$ is detected on the coating surface after 6734 cycles, indicating that Cr has outward diffused to the sample surface. However, no obvious Cr diffusion can be observed in single YSZ coating after 6052 cycles from the EDS elements mapping analysis showed in Fig. 10. Since these two coatings were deposited on the same bond coat/substrate structure and underwent the same thermal shocking conditions, the diffusion of Cr from bond coat to ceramic coat can be attributed to the presence of LZ7C3 top layer in the DCL TBCs. In the case of single YSZ coating, Cr should diffuse from bond coat to YSZ because of the present of a Cr concentration gradient. However, since the diffusion coefficient is extremely low, the content of Cr in YSZ coating is under the detection range even after a long-time thermal cycling. In the case of LZ7C3/YSZ DCL coating, a chemical reaction between CeO$_2$ and Cr will take place as soon as Cr diffuses into LZ7C3 layer, which will break the local diffusion balance. As a result, Cr could migrate continuously from bond coat into LZ7C3 layer though the column grain boundaries. The migrating Cr atoms are eventually absorbed by the formation of LaCrO$_3$ as having been substantiated by XRD (Fig. 3). Evidently these reactions remove Cr from YSZ columnar grain boundaries at a much faster rate than does the process of diffusion into the YSZ grains. The accumulation of Cr in LZ7C3 layer which is detected in the EDS map scanning analysis is therefore obtained in accessible time (~561 h) and temperature (1373 K). The crystal structure of LaCrO$_3$ below 513 K and above 553 K is orthorhombic- and rhombohedral-distorted perovskite structure, respectively. During the thermal exposure, it undergoes a phase transformation from orthorhombic to rhombohedral structure, which might introduce a discrete volume change. That could be one of the reasons for the initiation of microcracks within the ceramic coatings as shown in Fig. 7. In addition, the abundant Cr diffusion is undesirable for the selective oxidation of the bond coat when it is reduced beneath a certain level, which may lead to a less stable TGO layer. What’s more, a strong outward diffusion of Cr from BC would be the main reason for the emergence and enlargement of the micropores in the DCL TBCs as shown in Fig. 7. It has been reported in our previous paper and by other studies that LZ7C3 sinters less than YSZ when parallel columns are considered. However, opposite findings are obtained in present work. After thermal cycling, LZ7C3 top layer is more compact than YSZ layer in the DCL TBCs as shown in Fig. 7j. This abnormal phenomenon would be attributed to the abundant Cr cation migrating in. In order to understand clearly the influence of Cr diffusion on the durability of the DCL TBCs and alleviate its adverse effects, more fundamental work is required in the future. Therefore, the phase transformation of LZ7C3, the abnormal oxidation of bond coat, and the outward diffusion of Y and Cr alloying element into LZ7C3 coating would be the primary factors for the spallation of LZ7C3/YSZ thermal barrier coating.

4. Conclusions

LZ7C3/YSZ double-ceramic-layer TBCs were deposited by EB–PVD and their thermal shock behavior was systematically investigated. The findings can be summarized as follows:

1. A fluorite to pyrochlore ordering takes place for LZ7C3 coating during thermal shock test as detected by X-ray diffraction and Raman spectra. It seems that this phase change may affect the durability of the DCL TBCs.
2. The LZ7C3 layer spills from the YSZ surface after certain thermal cycles and the cracks occur not only at the interface between the LZ7C3 and YSZ layer, but also inside the LZ7C3 coating. Apparently, the occurrence of microcracks could be partially attributed to the phase transformation and the reduction–oxidation of cerium oxide of LZ7C3.
3. After cycling, some diffusion of Y from YSZ to LZ7C3 layer is observed. This Y diffusion is detrimental to the phase stability of YSZ. Additionally, an obvious outward diffusion of Cr from bond coat into LZ7C3 layer takes place due to the chemical reaction of LZ7C3 and Cr.

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