

CALCIUM-MAGNESIUM-ALUMINO-SILICATE INDUCED DEGRADATION OF $\text{La}_2(\text{Zr}_{0.7}\text{Ce}_{0.3})_2\text{O}_7/\text{YSZ}$ DOUBLE-CERAMIC-LAYER THERMAL BARRIER COATINGS PREPARED BY ELECTRON BEAM-PHYSICAL VAPOR DEPOSITION

Xin Zhou, Wuhan University of Technology, China

zhouxin1@whut.edu.cn

Chao Wang, Shanghai Electric Gas Turbine Co.,Ltd., China

Xuyang Xie, Shanghai Electric Gas Turbine Co.,Ltd., China

Hongqi Zhang, Shanghai Electric Gas Turbine Co.,Ltd., China

Xueqiang Cao, Wuhan University of Technology, China

Limin He, Beijing Institute of Aeronautical Materials, China

Shujuan Dong, Wuhan University of Technology, China

Key Words: Thermal barrier coatings; CMAS; $\text{La}_2(\text{Zr}_{0.7}\text{Ce}_{0.3})_2\text{O}_7$; double-ceramic-layer; EB-PVD.

During last decades, much effort has been made to develop new alternative thermal barrier coating (TBC) to traditional YSZ for applications above 1250°C. $\text{La}_2(\text{Zr}_{0.7}\text{Ce}_{0.3})_2\text{O}_7$ (LZ7C3) is deemed as a very promising TBC candidate for advanced gas turbine because of its extremely low thermal conductivity, high sintering resistance and phase stability from room temperature to 1600°C. Thermal cycling with a gas burner showed that the LZ7C3/YSZ double-ceramic-layer (DCL) coatings prepared by electron beam-physical vapor deposition (EB-PVD) or atmospheric plasma spraying had a much longer lifetime than that of YSZ coating at 1250±50°C. The use of the new TBC can allow higher gas temperatures, resulting in further improved thermal efficiency and engine performance. However, at these high operating temperatures, TBCs become susceptible to attack by calcium-magnesium-alumino-silicate (CMAS, relative to the main chemical components Ca, Mg, Al and Si) deposits resulting from the ingestion of siliceous minerals (dust, sand, volcanic ash, runway debris) with the intake air. CMAS becomes molten at temperatures above 1200°C and then rapidly penetrates the TBCs by capillary force, resulting in the loss of strain tolerance and premature failure of the coatings. In this paper, CMAS induced degradation of LZ7C3/YSZ DCL coatings prepared by EB-PVD method were investigated. Hot corrosion tests were performed at 1250°C at durations varying from 0.5 h to 24 h. It is observed that the infiltration of CMAS in the intercolumnar gaps was largely suppressed in the case of EB-PVD LZ7C3 coating. The penetration depth rarely exceeded 40 μm below the original surface even after 24 h exposure at 1250°C. This was ascribed to rapid dissolution of the LZ7C3 and essentially concurrent formation of a sealing layer made of crystalline apatite and fluorite phases, which is consistent with the observation on $\text{Gd}_2\text{Zr}_2\text{O}_7$. However, large vertical cracks would form in the EB-PVD LZ7C3 coating during thermal cycling as a result of re-crystallization, sintering and thermal expansion mismatch between ceramic coating and substrate. These vertical cracks can also act as channels to CMAS melt infiltration. Since the kinetics of the "dissolve-precipitation" reaction was slower than the infiltration rate of CMAS in the vertical crack, the majority of vertical cracks were not sealed. As a result, CMAS flowed down to the LZ7C3/YSZ interface along the vertical cracks, and then easily penetrated the YSZ buffer layer by capillary force. Chemical interaction also occurred in the YSZ buffer layer. What's more, the YSZ layer in the DCL coating even underwent a severer CMAS attack than the single YSZ coating. After 4 h CMAS exposure, the YSZ layer of the LZ7C3/YSZ bilayer coating was totally dissolved by molten CMAS followed by precipitation of a large number of globular ZrO_2 particles, while the single YSZ coating just suffered a slight degradation in the same experimental conditions and still kept its columnar structure. The probable reason was that the CMAS melt in the YSZ layer of the DCL coating had a higher CaO/SiO₂ ratio than the original CMAS composition due to the formation of apatite phase when CMAS reacted with the upper LZ7C3 layer. The initial Si: Ca ratio (Si: Ca≈1.4) in CMAS melt is less than the corresponding apatite (Si: Ca≈3), leading to progressive CaO enrichment during apatite crystallization. For this reason, it is suggested that the effectiveness of the CMAS mitigation strategy for YSZ TBCs by adopting a so-called CMAS-resistant top layer needs to be assessed in the context of more realistic conditions. If the formation of large vertical cracks in TBCs was not avoided, this CMAS mitigation approach may not as effective as expected.