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Plasma-sprayed $La_2Ce_2O_7$ thermal barrier coatings against calcium–magnesium–alumina–silicate penetration

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Abstract

As one of promising thermal barrier coating (TBC) candidates, $La_2Ce_2O_7$ (LC) has attracted increasing attention because of its low thermal conductivity and potential capability to be operated above 1250 °C. In this paper, the microstructure evolution and mechanical properties of the plasma-sprayed LC TBC with calcium–magnesium–alumina–silicate (CMAS) glassy deposits at 1250 °C were investigated. Due to chemical reaction between the CMAS deposits and LC coating, a dense sealing layer, mainly composed of $Ca_2(La_xCe_{1-x})_8(SiO_4)_6O_{6-4x}$ and CeO_2, was formed on the coating after heat-treatment at 1250 °C and effectively prevented CMAS from further penetration. The interaction layer had the micro-hardness of ~10–12 GPa, relatively harder than the LC coating.

Keywords: $La_2Ce_2O_7$ (LC); Yttria stabilized zirconia (YSZ); Thermal barrier coatings (TBCs); Calcium–magnesium–alumina–silicate (CMAS); Microstructure

1. Introduction

Thermal barrier coatings (TBCs) are applied onto hot-components of turbine engines to protect the components, which have a complex multi-layered structure: a metallic bond coat (MCrAlY, M = Ni, Co or both) for oxidation/corrosion resistance and a ceramic topcoat of yttria stabilized zirconia (YSZ) for thermal protection.[1,2] Extensive efforts have been made to understand the failure mechanisms of TBCs subjected to mechanical and thermal loads in the past decades.[3–6] One of the failure mechanisms is that fine sand particles ingested by the engine deposit on the coating surface as molten calcium–magnesium–alumina–silicate (CMAS) glass penetrate into YSZ and result in loss of strain tolerance and premature failure of TBCs. The CMAS attack of TBCs is becoming a critical issue in the development of advanced gas turbine engines due to the increased operating temperatures higher than the melting point of most silicate deposits (~1200 °C).[7–12]

Numerous attempts have been made to prevent the damage to TBCs from molten CMAS deposits. A protective layer can be prepared on the coating surface, which actually works as an impermeable/sacrificial layer to inhibit liquid CMAS from infiltrating into or reacting with YSZ coating at elevated temperature. Pd, Pt, SiC, SiO_2, Ta_2O_5, $MgAlO_4$, Al_2O_3, MgO, CaO and their mixtures are considered as potential candidates for the protective layer.[13,14] Rai et al.[13] have fabricated a Pd film on the YSZ TBC by magnetron sputtering. However, the Pd film was not able to completely stop the penetration of CMAS because it replicated the columnar structure of the underlying TBC. By further EB glazing processing, a dense Pd protective film was obtained, which can physically prevent from CMAS infiltration. A dense crack-free alumina overlay for TBCs was synthesized by Mohan et al.[14] using electrophoretic deposition (EPD) technique. The overlay can also effectively suppress the infiltration of CMAS by chemically interacting with CMAS deposits at high temperature. However, it seems that this approach has some imperfections due to thermal expansion mismatch between the alumina layer and the YSZ coating, which is detrimental to TBC durability during thermal cycling.

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Besides, some modified TBCs with alternative compositions have been also investigated. Aygun et al.[15,16] have fabricated TBCs of YSZ containing 20 mol% Al_2O_3 and 5 mol% TiO_2 by solution precursor plasma spray (SPPS). The TBC served as a reservoir of Al and Ti and effectively arrested penetration of CMAS front. However, YSZ TBC cannot be used for long term application above 1200 °C due to the phase transformation and accelerated sintering of zirconia.[17,18]

Recently, rare-earth zirconates have attracted increasing attention due to their outstanding merits such as low thermal conductivity and excellent phase stability.[19,20] Krämer et al.[21] have reported that columnar $Gd_2Zr_2O_7$ TBC can largely suppress CMAS infiltration even in the absence of a thermal gradient across the coating, which is attributed to the formation of a sealing layer made of crystalline $Ca_2Gd_8(SiO_4)_6O_2$ phase as a result of high-temperature chemical interaction between the $Gd_2Zr_2O_7$ coating and CMAS deposits. Moreover, the resistance to penetration of molten CMAS deposits is relatively insensitive to the TBC microstructure (APS or EB-PVD).[22] Besides, $La_2Zr_2O_7$ also shows a good resistance to CMAS attack.[23,24]

$La_2Ce_2O_7$ (LC) possesses lower thermal conductivity, better phase stability and larger thermal expansion coefficient than YSZ.[25,26] Plasma-sprayed LC/YSZ double ceramic layer TBC exhibited lifetime of more than 2000 cycles when the TBC surface was heated by gas flame to ~1250 °C.[26] Due to these merits, LC is considered as one of promising TBC candidates for applications at temperatures above 1250 °C. However, there is little knowledge about the microstructure and performances of the LC TBC when it is exposed to CMAS glassy deposits. In this paper, the microstructure, thermal interaction and mechanical properties of the plasma-sprayed LC TBC under simulated CMAS conditions were investigated, and the associated mechanism for the LC TBC against CMAS penetration was discussed. For comparison, the microstructure evolution of the YSZ TBC exposed to CMAS glassy deposits was also studied.

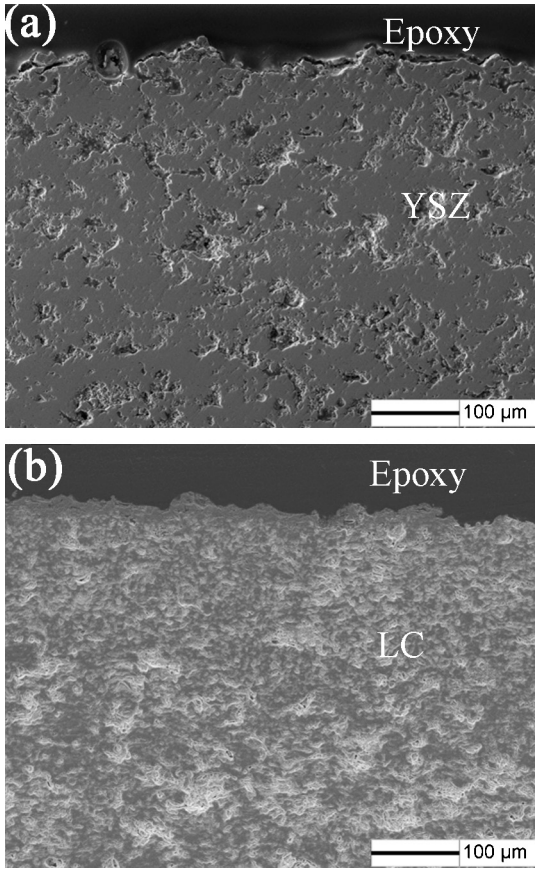

Fig. 1. Cross-sectional SEM images of plasma-sprayed YSZ (a) and $La_2Ce_2O_7$ (b) coatings.

Table 1
Chemical composition of the CMAS deposited on the free-standing coating samples (in mol.%).

CaO	MgO	$AlO_{1.5}$	SiO_2
24.1	19.2	17.2	39.5

2. Experimental procedure

2.1. TBCs preparation

The LC coating was sprayed on Ni-based superalloy substrate by atmospheric plasma spraying (APS) using a 7 M plasma gun (Sulzer Metco). $La_2Ce_{2.5}O_8$ powders produced by dried spraying technology, the chemical composition of which was optimized in our previous work,[26] were chosen for producing the $La_2Ce_2O_7$ coating with stoichiomertric composition. For comparison, 8YSZ coatings were also produced by the APS unit. The processing parameters for spraying LC and YSZ coatings were also chosen based on our previous work.[27] The LC and YSZ coatings thickness were both ~1 mm. Free-standing coating specimens were produced by removing the coatings from the substrates in hydrochloric acid.

2.2. CMAS deposition

A laboratory synthesized CMAS with chemical composition of $22CaO–19MgO–14AlO_{1.5}–45SiO_2$ in mole percent was used in this study. The chemical composition of CMAS was determined based on that of the deposits on vane blades in aircraft engines after hundreds hours of flight service. CaO, MgO, Al_2O_3 and SiO_2 powders were suspended in deionized water and fully mixed by planetary ball milling (QM-3SP4) for 24 h at a speed of 400 rpm. These CMAS powders were dried in an oven at 120 °C for 8 h and then deposited onto the LC and YSZ coating samples by plasma spraying at a concentration of 30 mg/cm^2. After spraying, the composition of the CMAS deposits showed a little variation, as shown in Table 1. The content of Si decreased, possibly due to the loss of SiO_2 during spraying. The LC and YSZ coating samples with CMAS deposits were heat-treated in air furnace at 1250 °C for 3 h, 12 h, 40 h and 100 h, respectively. The temperature was chosen based on an experiment in which the YSZ samples with the CMAS deposits were heated in the furnace at increasing temperatures above 1200 °C till the melting of the CMAS was detected.