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Thermal cycling behavior and failure mechanism of $La_2(Zr_{0.7}Ce_{0.3})_2O_7$/$Eu^{3+}$-doped 8YSZ thermal barrier coating prepared by atmospheric plasma spraying

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ABSTRACT

Double-ceramic-layer (DCL) thermal barrier coatings (TBCs) of $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ (LZ7C3) and Eu^{3+}-doped zirconia which was partially stabilized by 8 wt% yttria (8YSZ:Eu) was prepared by atmospheric plasma spraying. Thermal cycling behaviors of DCL coating were studied. The DCL coating shows a promising performance at 1250 ± 50 °C. The DCL coating spalled bit by bit from the top ceramic layer (LZ7C3) to the inner ceramic layer (8YSZ:Eu) during thermal cycling. The similar thermal expansions of LZ7C3 and 8YSZ prolonged the thermal cycling life of the coating. The sintering effect and phase transformation of LZ7C3, formation of the thermally grown oxide (TGO), and the sintering of 8YSZ:Eu, are the primary factors for the spallation of DCL coating.

1. Introduction

Thermal barrier coatings (TBCs) have been widely used in the production of corrosion-resistant and high-temperature structural parts such as gas turbine engines, diesel engines and power generation systems to protect substrate materials against thermal corrosion and oxidation [1–4]. The state-of-the-art topcoat material typically used is yttria partially stabilized zirconia (YSZ), especially 8YSZ [5,6]. 8YSZ performs well up to about 1200 °C, but it cannot be used above 1200 °C for long-term due to sintering and phase transformation [7,8]. In order to increase the operation temperature and improve the lifetime, new TBCs structures were designed and new material were developed. The concept of multilayer is an effective way to overcome these limitations and improve the thermal cycling life of TBCs [9,10]. Based on the multilayer system, the double-ceramic-layer (DCL) coating system has been proposed. In the DCL coating, the top ceramic layer should have a low thermal conductivity and high phase stability, and it acts as a thermal insulator to protect the inner layer.

Some researchers have reported the thermal cycling failure modes of the DCL coating systems [11–16]. $La_2Zr_2O_7$/8YSZ [12] and $La_2Ce_2O_7$/8YSZ [13] dual layer coating systems have been studied, however, thermal expansion coefficient of $La_2Zr_2O_7$ (LZ) is low [17] and $La_2Ce_2O_7$ (LC) has a high sintering ability [12]. Doping CeO_2 into LZ results in $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ (LZ7C3), which has a higher sintering resistance, low thermal conduction ability and high thermal expansion coefficient (TEC). Due to the high sintering resistance of $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ (LZ7C3) [18] and superior performance of 8YSZ, it is hoped that these materials will exhibit newly layered coatings with LZ7C3 coating on the top of 8YSZ coating for good thermal protection. 8YSZ was selected as the inner ceramic layer as all the necessary properties taken into consideration especially the thermal expansion coefficient and toughness properties.

The coating is mostly prepared by air plasma spraying (APS) and electron beam-physical vapor deposition (EB-PVD) methods. Compared with the EB-PVD method, coatings prepared by APS are low thermal conductive, more repeatable and more economic [19]. However, although some work about the DCL coating of LZ7C3/8YSZ prepared by EB-PVD method has been done [15], no data on the DCL coating of LZ7C3/8YSZ prepared by APS has been reported in literatures up to date.

Phosphor has been used to measure the surface temperature dates back to the early 1950s [20]. Concepts for luminescence sensing of TBCs have been proposed by Gentleman and Clarke [21]. An approach which utilized a luminescent sublayer to indicate the

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delamination of plasma-sprayed TBCs has been developed by Eldridge [22]. Europium-doped and terbium-doped sublayers also have been used to self-indicate the location and depth of erosion in TBCs [23]. Recently, rare-earth oxides have been introduced into the ceramic to produce a sensor TBCs which could be used as a temperature indicator [24–30].

Besides the traditional characterization methods usually used in the research of TBCs, a simple non-destructive method we demonstrated before [31] was also used in our research. A Eu^{3+}-doped luminescence sublayer was used to indicate the spallation and damage degree of DCL coatings. Eu^{3+}-doped 8YSZ (8YSZ:Eu) and LZ7C3 were used as the inner ceramic layer and outer ceramic layer for the DCL coating, respectively. 8YSZ:Eu coating has an intense excitation peak at 254 nm, so UV light at 254 nm was chosen as the excitation light source. There are two intense emission peaks at 592 nm and 608 nm which respectively correspond to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ions for excitation at 254 nm. As the UV light cannot penetrate the ceramic coating, only the exposed 8YSZ:Eu layer can produce orange luminescence under UV illumination.

2. Experimental

2.1. Synthesis of LZ7C3 and 8YSZ:Eu

In the present study, rare earth oxides powders (La_2O_3, ZrO_2, CeO_2, Eu_2O_3) and 8YSZ were heat-treated at 1000 °C for 1 h in air because rare earth oxides are hygroscopic.

LZ7C3 powder was synthesized by a solid state reaction method. La_2O_3 (99.99%, Shenghua Chemicals of Hunan, China), CeO_2 (99.99%, Shenghua Chemicals of Hunan, China), ZrO_2 (Zr (Hf) $\geqslant$ 99.5%, Dongfang Chemicals of Guangdong, China) were selected as the starting materials. The three powders were mixed together in proper ratio. A deionized-water-based suspension of this mixed powder was ball-milled for 24 h using zirconia balls. The slurry was then dried and heated at 1400 °C for 12 h to obtain the final product. The as-synthesized LZ7C3 powder was ball milled together with Arabic gum, triammonium citrate and deionized water for 72 h. The obtained slurry was then spray-dried (Jiangsu Yangguang Ganzao Co., Ltd.), leading to the formation of LZ7C3 powder with free-flowing for plasma spraying. The solid state reaction method to synthesize the LZ7C3 powder for APS was shown in Fig. 1.

8YSZ:Eu (Eu^{3+}, 1 at%) was synthesized in the similar progress. Eu_2O_3 (99.99%, Shanghai Yuelong New Materials Co., Ltd., Shanghai, China) and 8YSZ (Beijing General Research Institute of Mining and Metallurgy, Beijing, China) were selected as the starting materials. The ball-milled materials mixture was heated at 1600 °C for 24 h to obtain 8YSZ:Eu.

2.2. Preparation of coating

Coatings were atmospheric plasma sprayed on the Ni-based superalloy substrate (30 mm in diameter and 3 mm in thickness) with a Ni–23.7Co–20Cr–8.7Al–0.6Y–3.5Ta (wt%) bond coat (100 μm in thickness), using the Sulzer Metco plasma-spraying unit with a F4-MB gun. The nominal composition of the superalloy is given in Table 1. Fig. 2 shows the cross-sectional microstructure of the as-sprayed DCL coating. The SEM image shows a typical successive splats-structure of APS coating. As can be seen in Fig. 2, the average thickness of LZ7C3 coatings is 60 ± 25 μm and the average thickness of 8YSZ:Eu layer is 85 ± 25 μm.

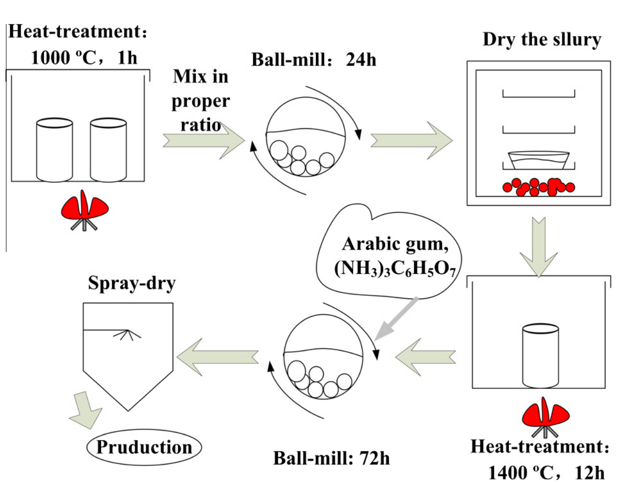

Fig. 1. The solid state reaction method to synthesize LZ7C3 powder for APS.

2.3. Thermal cycling tests

The thermal cycling tests were carried out on a burner-rig setting with a coal gas/oxygen flame. The thermal cycling was finished by heating the coating surface from room temperature to 1250 ± 50 °C for 5 min, followed by quenching to room temperature within 2 min by a cooling air jet. The cycling process repeats again and again until the coating is failure.

2.4. Characterization

The coating samples were embedded in a transparent epoxy resin, and then sectioned with a low speed diamond saw and polished with diamond pastes down to 1 μm. The surface and cross-sectional morphology were characterized by scanning electron microscopy (SEM, XL-30ESEM FEG, Mico FEI Philips) equipped with energy dispersive X-ray spectrometer (EDS).

The phase structure of powders and coatings were analyzed by X-ray diffraction (XRD) (XRD, Bruker D8 Advance) with Cu Kα radiation at a scan rate of 8°/min.

To observe luminescence from the exposed sublayer, eroded specimens were viewed under the 254 nm UV illumination provided by an UV viewing lamp (ZF-1).

3. Results and discussion

3.1. Surface photographs of the TBCs

The surface photographs of LZ7C3/8YSZ:Eu coating before and after thermal cycling are shown in Fig. 3. Even after 7370 thermal cycles, there is no large area of spallation on the coating surface.

As shown in Fig. 4, spot spallation was observed at the coating edge after 502 thermal cycles. The original spot spallation enlarged and some pine-like spallation appeared on the coating surface with thermal cycling test going on. Some of the spallation penetrated through the entire ceramic layer. The LZ7C3/8YSZ:Eu coating spalled bit by bit from the top ceramic layer (LZ7C3) to the inner ceramic layer (8YSZ:Eu) during thermal cycling.

The thermal cycling lifetime of the traditional 8YSZ TBC and other DCL coating systems with new materials are presented in Table 2 for comparison. All the results in Table 2 are from the same test methods. All the coatings are prepared by APS methods on a disk-shaped Ni-based superalloy substrate with a diameter of 30 mm. The coatings were dealt with a gas-burner test facility. The burner rig tests were carried out with a natural gas or coal gas. The substrate is cooled by the compressed air from the backside and the surface temperature is measured with a pyrometer operating at a wavelength of 8–13 μm. During thermal cycling test, the maximum temperature was reached after heating for ~20 s. After 5 min [12,32,33], the burner was automatically removed from the surface. As for LC, LC/8YSZ and 8YSZ in Ref. [14], the coating was heated for another 5 min, a little different from coatings in other references. Then, the coating was quenched to room temperate by a cooling air jet for 2 min. The cycling process repeats again and again until a visible spallation of the coating occurs. The lifetime in hours in Table 2 means the sum of time which the coating exposed to the high temperature gas flame. As shown in Table 2, LZ7C3/8YSZ:Eu dual layer coating has a much longer lifetime than that of dual layer LZ/8YSZ, LC/8YSZ coating and single layer LZ7C3, 8YSZ coating. It can be concluded that LZ7C3/8YSZ:Eu TBC showed a promising thermal cycling performance at 1250 ± 50 °C.

Table 1
Nominal composition of the Ni-based superalloy (wt%).

Ni	Co	Cr	W	Al	Ta	Mo	Ti
Bal	9.5–10.5	8.4–9.4	6.5–7.5	4.8–5.4	3.5–4.1	1.5–2.5	0.7–1.2