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Thermophysical properties of Yb_2O_3 doped $Gd_2Zr_2O_7$ and thermal cycling durability of $(Gd_{0.9}Yb_{0.1})_2Zr_2O_7$/YSZ thermal barrier coatings

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Abstract

$(Gd_{1-x}Yb_x)_2Zr_2O_7$ compounds were synthesized by solid reaction. Yb_2O_3 doped $Gd_2Zr_2O_7$ exhibited lower thermal conductivities and higher thermal expansion coefficients (TECs) than $Gd_2Zr_2O_7$. The TECs of $(Gd_{1-x}Yb_x)_2Zr_2O_7$ ceramics increased with increasing Yb_2O_3 contents. $(Gd_{0.9}Yb_{0.1})_2Zr_2O_7$ (GYbZ) ceramic exhibited the lowest thermal conductivity among all the ceramics studied, within the range of 0.8–1.1 W/mK (20–1600 °C). The Young's modulus of GYbZ bulk is 265.6 ± 11 GPa. GYbZ/YSZ double-ceramic-layer thermal barrier coatings (TBCs) were prepared by electron beam physical vapor deposition (EB-PVD). The coatings had an average life of more than 3700 cycles during flame shock test with a coating surface temperature of ∼1350 °C. Spallation failure of the TBC occurred by delamination cracking within GYbZ layer, which was a result of high temperature gradient in the GYbZ layer and low fracture toughness of GYbZ material.

Keywords: $(Gd_{1-x}Yb_x)_2Zr_2O_7$; Thermophysical properties; Electron beam physical vapor deposition (EB-PVD); Thermal barrier coatings (TBCs); Thermal cycling

1. Introduction

Gas turbines operated at high temperatures exhibit improved thermal efficiency. However, elevated temperature means harsh operating condition, which would deteriorate the performance of hot section components.[1,2] The application of thermal barrier coatings (TBCs) can result in a significant temperature decrease between hot gas and surface of the hot section components, thereby lowering the surface temperature of alloys and improving engine efficiency.[3,4] TBCs are usually produced by either electron beam physical vapor deposition (EB-PVD) or atmospheric plasma spraying (APS). A TBC system typically consists of superalloy substrate, metallic bond coat, thermally grown oxide (TGO) and ceramic topcoat. Currently, the material of choice for ceramic topcoat is 6–8 wt.% Y_2O_3 stabilized ZrO_2 (YSZ). However, the problems of phase transformation and accelerated sintering limit the use of YSZ for operating above 1200 °C for long time.[5–7] Demand for enhanced gas turbine efficiencies necessitates significant increase in combustion temperatures and operating pressures. To cope with these requirements, alternate ceramic topcoat materials are strongly required having lower thermal conductivity, higher temperature capability, and better thermal cycling performance.

Extensive attention has been focused on different rare-earth doped zirconia,[6,8] fluorite-structured materials,[9,10] perovskite-structured materials,[11,12] and rare earth zirconates.[13–15] Among these rare earth zirconates ($RE_2Zr_2O_7$, RE = rare earth elements), gadolinium zirconate ($Gd_2Zr_2O_7$, GZO) shows promising thermo-physical properties and has excellent calcium magnesium alumino-silicate (CMAS) resistance. GZO is stable from room temperature to 1550 °C,[16] and the thermal conductivity of GZO is much lower than that of YSZ.[17,18] Kramer et al.[19] have reported that CMAS infiltration in EB-PVD GZO TBC can be arrested by rapid filling of the inter-columnar gaps with crystalline productions. Drexler et al.[20] have found that an impervious crystalline reaction layer can be formed in APS GZO TBC when CMAS penetrates the top surface pores, which can prevent further penetration of CMAS. In our previous work, it has been found that compared with the substitution of Zr in GZO, doping of GZO on Gd site by other rare earth cations leads to lower thermal conductivity.[21] Liu et al.[22,23] investigated the

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

Ni	Co	Cr	Al	Ti	Mo	W	Fe
Bal.	4.5–6.0	10.0–12.0	5.3–5.9	2.3	2.9	4.8–5.5	<2.0

effects of substitution on Gd site by light rare earth elements (Sm, Nd) on the thermal conductivity of GZO, and found that the thermal conductivity increases with increasing light rare earth elements contents. Wan et al.[24] have claimed that substituting RE site with another heavier and much smaller ion in $RE_2Zr_2O_7$ can lead to much lower thermal conductivity. Among rare earth elements, Yb has the largest atomic mass and the smallest ionic radii. However, the effects of substituting Gd site with Yb in GZO on thermophysical properties have not been reported in the literatures. TBCs produced by EB-PVD exhibit improved thermal cycling lifetime, so it is necessary to investigate Yb_2O_3 doped GZO TBCs produced by EB-PVD.

In the present study, Yb_2O_3 doped $Gd_2Zr_2O_7$ ($(Gd_{1-x}Yb_x)_2Zr_2O_7$ ($x=0$, 0.1, 0.3, 0.5, 0.7)) were synthesized by solid state reaction, aiming to improve the thermophysical properties of $Gd_2Zr_2O_7$. The thermophysical properties of $((Gd_{1-x}Yb_x)_2Zr_2O_7$ ceramics, phase stability and mechanical properties of $(Gd_{0.9}Yb_{0.1})_2Zr_2O_7$ were investigated. $(Gd_{0.9}Yb_{0.1})_2Zr_2O_7$/YSZ double-ceramic-layer (DCL) TBCs were produced by EB-PVD, and its thermal cycling durability was evaluated by a flame shock facility at a coating surface temperature of $1350 \pm 30\,°C$.

2. Experimental procedure

2.1. Samples preparation

$(Gd_{1-x}Yb_x)_2Zr_2O_7$ ($x=0$, 0.1, 0.3, 0.5, 0.7) ceramics were produced by solid reaction method using Gd_2O_3, Yb_2O_3 and ZrO_2 (purity higher than 99.99%) powders as raw materials. The appropriate amounts of individual oxides were dissolved in ionized water and mechanically milled for 8 h. The obtained powders were cold pressed under a pressure of ~250 MPa with 5 min holding time. Finally, the compacts were pressureless-sintered at 1600 °C for 10 h in air.

$(Gd_{0.9}Yb_{0.1})_2Zr_2O_7$/YSZ (GYbZ/YSZ) DCL TBCs were produced by EB-PVD technique. Ni-based superalloy was used as substrate material, the chemical composition of which was listed in Table 1. The specimen has a dimension of 30 mm in diameter and 2.5 mm in thickness. Ni-21Co-24Cr-10Al-1.5Y (in wt.%) ingot was used as evaporation source for bond coat, YSZ ingot and $(Gd_{0.9}Yb_{0.1})_2Zr_2O_7$ ingot were used as evaporation sources for YSZ coating and GYbZ coating, respectively. All the ingots have a dimension of 68.5 mm in diameter and 80 mm in height. The bond coat was first deposited onto the substrate by EB-PVD, followed by vacuum heat treatment at 1000 °C for 4 h and shot peening for surface strengthening. YSZ coating was then deposited onto the bond coat, followed by deposition of GYbZ coating. During deposition, the pressure of EB-PVD working chamber was kept below 1×10^{-3} Pa, and no oxygen was introduced into the operation chamber. The average substrate temperature was adjusted to $950 \pm 25\,°C$, and the substrate was rotated at 12 rpm.

2.2. Thermal cycling test

Thermal cycling tests of GYbZ/YSZ DCL TBCs were performed in a flame shock test facility operating with propane and oxygen. The coatings were heated for 20 s to the desired surface temperature and held at the temperature for 5 min. During heating stage, the backside of the sample was cooled by compressed air to maintain a controlled temperature gradient through the sample thickness. The surface temperature and substrate temperature were measured with a pyrometer (Raytech, Model: MR1SBSF, USA, 0.75–1.1 μm, 0.95–1.1 μm) and a NiCr/NiSi thermocouple, respectively. During cooling stage, the burner went out automatically and the sample was cooled by compressed air from both sides for 40 s to room temperature. Thermal cycling was stopped when visible spallation of the coating occurred, and the number of the cycles was defined as the lifetime of the TBCs.

2.3. Characterizations

The phase structure of $(Gd_{1-x}Yb_x)_2Zr_2O_7$ ($x=0$, 0.1, 0.3, 0.5, 0.7) ceramics was characterized by X-ray diffraction (XRD, Rigaku Diffractometer, CuKα radiation). The phase stability of $(Gd_{0.9}Yb_{0.1})_2Zr_2O_7$ ceramic in the temperature range of 100–1600 °C was examined by differential scanning calorimetry (DSC, NETZSCH STA 449F3, Germany). The microstructure of GYbZ/YSZ DCL TBC was characterized by scanning electron microscope (SEM, FEI, Holland) equipped with energy dispersive spectroscopy (EDS, IE 350).

Knoop hardness (H_K) was measured by microhardness tester (HXZ-1000, China). At least 10 valid indentations were made for the sample. Young's modulus (E) was determined using the following equation:[25]

$$\frac{b'}{a'} = \frac{b}{a} - \alpha \frac{H_K}{E} \quad (1)$$

where b/a is the ratio of the short diagonal and the long diagonal of each indentation (1/7.11), b'/a' is the ratio of the short diagonal and the long diagonal of the indentation after elastic recovery. H_K and E are the Knoop hardness and Young's modulus, respectively. The constant α has a value of 0.45.

The thermal diffusivities (α) of bulk materials were measured using a laser-flash apparatus (Netzsch LFA 427) from 20 °C to 1600 °C, at an interval of 200 °C. Prior to thermal diffusivity measurements, the surfaces of the specimens were coated with a thin film of graphite for thermal absorption of laser pulses. Each sample was measured three times at the selected temperatures. The specific heat capacity (C_p) was calculated from the heat capacity values of the constituent oxides based on the Neumann–Kopp rule.[26] The density was measured by Archimedes method. The thermal conductivity (λ) was obtained using the following equation:

$$\lambda = \rho \cdot \alpha \cdot C_p \quad (2)$$