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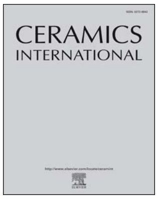

Phase stability, thermo-physical properties and thermal cycling behavior of plasma-sprayed CTZ, CTZ/YSZ thermal barrier coatings

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ABSTRACT

ZrO_2 co-stabilized by CeO_2 and TiO_2 with stable, nontransformable tetragonal phase has attracted much attention as a potential material for thermal barrier coatings (TBCs) applied at temperatures > 1200 °C. In this study, ZrO_2 co-stabilized by 15 mol% CeO_2 and 5 mol% TiO_2 (CTZ) and CTZ/YSZ (zirconia stabilized by 7.4 wt% Y_2O_3) double-ceramic-layer TBCs were respectively deposited by atmospheric plasma spraying. The microstructures, phase stability and thermo-physical properties of the CTZ coating were examined using scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric-differential scanning calorimeter (TG-DSC), laser pulses and dilatometry. Results showed that the CTZ coating with single tetragonal phase was more stable than the YSZ coating during isothermal heat-treatment at 1300 °C. The CTZ coating had a lower thermal conductivity than that of YSZ coating, decreasing from $0.89\,W\,m^{-1}\,K^{-1}$ to $0.76\,W\,m^{-1}\,K^{-1}$ with increasing temperature from room temperature to 1000 °C. The thermal expansion coefficients were in the range of $8.98 \times 10^{-6}\,K^{-1} – 9.88 \times 10^{-6}\,K^{-1}$. Samples were also thermally cycled at 1000 °C and 1100 °C. Failure of the TBCs was mainly a result of the thermal expansion mismatch between CTZ coating and superallloy substrate, the severe coating sintering and the reduction-oxidation of cerium oxide. The thermal durability of the TBCs at 1000 °C can be effectively enhanced by using a YSZ buffer layer, while the thermal cycling life of CTZ/YSZ double-ceramic-layer TBCs at 1100 °C was still unsatisfying. The thermal shock resistance of the CTZ coating should be improved; otherwise the promising properties of CTZ could not be transferred to a well-functioning coating.

1. Introduction

Thermal barrier coatings (TBCs) have been widely applied to protect the hot-section metal components of gas turbines for decades. They can significantly decrease the turbine surface temperature, thus prolonging the service life of turbine engines [1–3]. Generally, TBCs are composed of a ceramic top coat, a metallic bond coat (MCrAlY, M = Ni, and/or Co), a thermally grown oxide (TGO) layer and a superalloy substrate. The metallic bond coat has a moderate thermal expansion coefficient, which can not only alleviate the thermal stress caused by thermal expansion mismatch between top coat and substrate, but also improve the bonding strength between the ceramic top coat and substrate. The TGO layer is formed during the operation, which can effectively reduce the oxidation rate of the bond coat. The ceramic top coat provides thermal insulation for the metallic substrate. As a good ceramic top coat material, it must satisfy some important requirements: low thermal conductivity, large thermal expansion coefficient (TEC), high melting point, good phase stability, low sintering rate, and low Young's modulus. Nowadays, the state-of-the-art ceramic top coat material is zirconia stabilized with 6–8 wt% Y_2O_3 (YSZ) [4,5]. YSZ coating shows good performance at temperatures below 1200 °C. However, it exhibits a poor service lifetime for long-term applications at higher temperatures, because of the phase transformation and obvious sintering accompanied with the increase of Young's modulus [6,7]. The structure destabilization will severely limit the application of YSZ TBCs at the ambitious temperature for next generation aeroengines and industrial gas turbines. Therefore, developing new TBCs materials with even lower thermal conductivity, higher operating temperatures, better sintering resistance and phase stability are in demand for next generation aeroengines. Some new ceramic materials, such as rare earth zirconates ($Ln_2Zr_2O_7$, Ln = La to Gd), lanthanum magnesium hexaaluminate ($LaMgAl_{11}O_{19}$), perovskite-type ($SrZrO_3$) and fluorite-type

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($La_2Ce_2O_7$), have been evaluated as potential TBCs candidates to further increase the operation temperature of turbine engines [8–11]. However, most of them had a poor thermal cycling lifetime, hindered mainly by the unsatisfactory mechanical properties, especially the low fracture toughness.

On the other hand, much effort has also been paid to the ZrO_2-based system with alternative stabilizers. The phase stability can be improved by increasing the concentration of the stabilizers. However, such approach decreases the tetragonality (c/a), as well as the fracture toughness of ZrO_2. Therefore, the ZrO_2-based materials with good phase stability and high tetragonality are primary of interest. It is well known that a promoted tetragonality can be achieved by doping with an undersized cation of equal or higher oxidation state than Zr^{4+}, such as Ti^{4+}, Ta^{5+} or Nb^{5+}. Unfortunately, the formed binary solid solutions are usually transformable to monoclinic phase during the cooling process due to the immoderate distortion of the neighboring cation network [12–15]. Several ZrO_2-based ternary oxides co-doped by oversized dopants, such as Y^{3+}, Ce^{4+}, and undersized dopants, such as Ti^{4+}, Ta^{5+}, are seen as promising TBCs materials. The stable, non-transformable solid solutions with high tetragonality have been synthesized in ZrO_2-$YO_{1.5}$-TiO_2, CeO_2-TiO_2-ZrO_2 and ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ systems. In these systems, the ferroelastic toughening mechanism enhanced by the tetragonal distortion makes contribution to the increase of fracture toughness, and the phase stability is also improved by the high tetragonality [13,16–18]. Among these systems, the CeO_2-TiO_2-ZrO_2 system has a large tetragonal composition design, which will bring significant processing convenience. In addition, the CeO_2-stabilized ZrO_2 TBCs have better corrosion resistance, higher thermal expansion coefficient and lower thermal conductivity than those of YSZ TBCs [19,20]. So the ZrO_2 co-doped with CeO_2 and TiO_2 materials have attracted wide attention. Based on our basic research, ZrO_2 co-stabilized by 15 mol% CeO_2 and 5 mol% TiO_2 (CTZ) showed excellent phase stability and thermo-physical properties. Therefore, the CTZ can be explored as the candidate material for the ceramic layer in TBCs system.

Although the CTZ ceramic shows promising properties as a TBCs material, no data on the CTZ coating are reported in open literature up to now and no thermal cycling life result is available. In this work, the CTZ coating was deposited by atmospheric plasma spraying (APS). Key parameters, which were relevant to TBCs applications, including phase stability, thermal conductivity, thermal expansion behavior and thermal cycling, were investigated and discussed systematically. Since a single material may hardly satisfy all requirements for TBCs, the CTZ/YSZ double-ceramic-layer coating was also prepared and investigated in this study.

2. Experimental procedures

CTZ powders were synthesized by solid-state reaction of ZrO_2 (99.9%), CeO_2 ($\geq$ 99.99%), and TiO_2 (99%). These three powders were mixed with deionized water and ball-milled for 24 h. After drying, the powder mixtures were ball-milled for 24 h. ZrO_2 balls were used in the both milling processes. The mixed powders were sintered for 12 h at 1400 °C to obtain the final products. Considering the preferential evaporation of some components of the feedstocks in the plasma flame, the mole ratio of ZrO_2, CeO_2 and TiO_2 for CTZ synthesis was optimized to be 0.8:0.179:0.063 in order to obtain the sprayed CTZ coating with the designed stoichiometric composition.

The CTZ powders for plasma spraying were produced by the spray-drying method. The synthesized CTZ powders were mixed with gum Arabic, ammonium citrate and deionized water at a proper mass ratio, and then ball-milled with zirconia balls for 72 h and the obtained slurry suspension was spray-dried with a spray drier (SFOC-16, Shanghai-Ohkawara Dryers Co., Ltd.). The free-flowing powders with particle size between 20 μm and 125 μm were collected and used directly for plasma spraying without other treatments. The nanostructured YSZ (ZrO_2 stabilized by 7.4 wt% Y_2O_3) ceramic powders used in this experiment were obtained by a commercial channel. The characteristics of the YSZ feedstocks have been reported in authors' previous study [21]. Commercial NiCrAlY powders with a chemical composition of Ni–25.17-Cr–5.03Al–0.51Y (wt%) were chosen to prepare the bond coat of TBCs. The nickel based superalloy substrates (DZ 125) with dimensions of 30 mm × 12 mm × 2 mm were blasted with alumina sand. Then, NiCrAlY as the bond coat of ~150 μm thickness was deposited onto the superalloy substrates and then CTZ as the top coat of ~ 300 μm thickness was deposited onto the bond coat to fabricate the CTZ TBCs. To prepare the CTZ/YSZ TBCs, the YSZ coating was first deposited onto the bond coat, followed by CTZ coating , and thicknesses of the three layers (bond coat, YSZ coating and CTZ coating) in the CTZ/YSZ TBCs were almost same with each other, and equal to ~ 150 μm. To study the thermal stability and thermo-physical properties of the ceramic coatings, the spray-dried powders were also plasma-sprayed onto a graphite substrate without bond coat and subsequently burnt off from the graphite substrate to respectively obtain the free-standing CTZ coating and YSZ coating with a thickness of 1 mm. The TBCs systems were produced by APS using a Sulzer-Metco F4 plasma gun. The plasma spraying parameters were listed in Table 1.

Table 1
Plasma spray parameters of coatings.

Items	Bond coat	CTZ coating and YSZ coating
Current (A)	530	430
Power (kW)	42	30
Plasma gas Ar/H_2 (slpm)*	35/12	35/12
Carrier gas Ar (slpm)	3.2	3.2
Powder feeding rate (g/min)	17	18

* slpm: standard liter per minute.

To assess their phase stability, the free-standing CTZ coatings and YSZ coatings were respectively heat-treated with different dwell time multiplied increased from 3 h to 96 h at 1300 °C. For each exposure, the coatings were placed on a platinum foil and heated in the electric furnace at 1300 °C for specified time followed by furnace-cooling to room temperature.

The hydrothermal degradation treatment was realized in a 20 ml Teflon autoclave, and the detailed procedure was following: coatings were firstly put in the autoclave and then 10 ml deionized water was added into the autoclave. Finally, the autoclave was held at 160 °C for 24 h (the vapor pressure inside has been estimated to be the saturated vapor pressure at the corresponding temperature). The hydrothermally treated samples were dried at 100 °C for 24 h.

The thermal diffusivity measurement was carried out in an argon atmosphere using the laser flash diffusivity apparatus (Model NETZSCH LFA 457, Germany) on the free-standing coating with dimensions of 10 mm × 10 mm × 1 mm.

The linear thermal expansion coefficient (TEC) of the sample with dimensions of approximately 25 × 3 × 1 mm was determined by a high-temperature dilatometry (Model NETZSCH DIL 402 C, Germany), operating in a temperature range between ambient and 1300 °C at a heating rate of 5 °C/min in air.

The synthesized CTZ powders were first isostatically pressed at 200 MPa into pellets (approximately 10 mm in diameter and 3 mm thick), and then exposed at different temperatures (1100 °C, 1200 °C, 1300 °C, 1400 °C and 1500 °C) for 6 h to analyze the sintering resistance by measuring volume shrinkage and relative density.

The interfacial bonding strength of the CTZ/YSZ TBCs was examined by pull-off test (Mester Materials Tester, Model 5105, China) with a stretching rate of 2 mm/min based on ASTM C633-01 standard. For each experiment, three specimens were measured.

In order to evaluate the thermal durability of CTZ TBCs and CTZ/YSZ TBCs, the thermal shocking test was performed in a programmable, automated bottom-drop furnace (RL7-10-12, Wuhan, China), in which