Surface & Coatings Technology 268 (2015) 298–302

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Evolution of microstructural and mechanical properties of lanthanum zirconate thermal barrier coatings at high temperature

G. Di Girolamo [a,*], F. Marra [b], M. Schioppa [c], C. Blasi [c], G. Pulci [b], T. Valente [b]

[a] ENEA, Materials Technology Unit, Casaccia Research Centre, Rome, Italy
[b] Dept. of Chemical Engineering, Materials, Environment, Sapienza University of Rome, INSTM Reference Laboratory for Engineering of Surface Treatments, Rome, Italy
[c] ENEA, Materials Technology Unit, Brindisi Research Centre, Brindisi, Italy

ARTICLE INFO

Available online 30 July 2014

Keywords:
Plasma spraying
Coatings
Lanthanum zirconate
Young's modulus
Heat capacity

ABSTRACT

Ceramic thermal barrier coatings (TBCs) are advanced systems for more efficient turbine engines. In this work, thick lanthanum zirconate TBCs were fabricated by Air Plasma Spraying (APS). The coatings showed a lamellar microstructure containing splat boundaries, pores and microcracks. After thermal exposure at 1200 and 1350 °C the partial sintering of the porous microstructure occurred.
High-temperature evolution of the mechanical properties was investigated by arranging specific bending tests up to 1500 °C using SiC testing assembly which allowed to calculate the strain by means of curvature measurement. The mechanical properties improved with increasing the testing temperature, due to the inelastic deformation and stress relaxation which counteracted the sintering effects.
The elastic modulus increased after thermal aging, but decreased for the aged coatings tested at higher temperature.
The thermal expansion coefficient of as-sprayed coatings slightly increased after thermal aging, while a reduction of specific heat capacity was noticed.

1. Introduction

Ceramic thermal barrier coatings (TBCs) are employed to protect Ni-based superalloy hot section parts of turbine engines in order to increase their durability, by reducing the temperature on the metal surface and the attack promoted by oxygen, molten salts and dust [1–3]. In addition, they are able to improve the turbine efficiency as well as to reduce the fuel consumption and the emissions.

Plasma spraying is a well-established technology for fabrication of porous TBCs. In such process powder particles are injected in high-energy plasma jet. The molten particles are propelled toward a substrate, where they impinge and quench, promoting the build-up of a lamellar microstructure.

A typical TBC is composed of a metal bond coat and a ceramic top coat. The bond coat provides adhesion and oxidation resistance. In turn, ceramic materials are suitable to reduce the heat transfer to the underlying metal and to improve the temperature capability and the resistance to corrosive and erosive agents. TBCs candidates include materials with low thermal conductivity, relatively high thermal expansion coefficient (CTE) and high thermal stability [4–7]. Partially yttria stabilized zirconia (YSZ) is often industrially used, due to the long-term knowledge about its high-temperature performance. However, above 1200 °C YSZ TBCs are affected by accelerated sintering and phase transition. The former reduces the strain tolerance and increases the thermal conductivity, thus negatively affecting the thermal cycling lifetime. In turn, the decomposition of tetragonal zirconia with the formation of monoclinic phase is usually accompanied by volume change and extended cracking.

The constant demand for more efficient engines focused the attention of TBC designers on alternative compositions based on rare-earth zirconates with better resistance in high temperature environments [8–10]. Among them, lanthanum zirconate (LZ) exhibits low thermal conductivity (0.7–0.8 against 0.8–1.2 $Wm^{-1}\ K^{-1}$ for YSZ) and low ionic conductivity which is expected to reduce the oxygen propagation and the oxidation of the metallic surface, one of the main factors affecting the durability of TBC systems [11–13].

Many aspects of this material have to be still investigated. Moreover, the reports about high-temperature mechanical properties of ceramic TBCs and their evolution after high-temperature exposure are not frequent.

In this work, we studied the mechanical properties of as-sprayed and heat treated lanthanum zirconate coatings by arranging four-point bending tests at various temperatures.

The evolution of coating microstructure was analyzed by scanning electron microscopy (SEM). The thermal properties of as-sprayed and annealed coatings, such as CTE and heat capacity, were also investigated.

* Corresponding author.
E-mail address: giovanni.digirolamo@enea.it (G. Di Girolamo).

http://dx.doi.org/10.1016/j.surfcoat.2014.07.067
0257-8972/

2. Material and methods

2.1. Processing

An APS system equipped with F4-MB plasma torch (Sulzer Metco, Wolhen, Switzerland) with 6 mm internal diameter nozzle was employed for TBC deposition. Stainless steel plates were sand blasted using alumina abrasive powder to improve the mechanical interlocking between coating and substrate, then placed on a rotating sample holder and coated with 2 mm thick coatings using lanthanum zirconate powder feedstock ($La_2Zr_2O_7$, 43 wt.% ZrO_2–57 wt.% La_2O_3, Trans-Tech Inc, Adamstown, MD, 37–149 μm) and the following process parameters: current 600 [A], substrate tangential speed 2083 [mm s^{-1}], Ar flow rate 35 [slpm], H_2 flow rate 8 [slpm], spraying distance 100 [mm], powder feed rate 34 [g min^{-1}].

Some samples were isothermally treated in air at 1200 and 1350 °C for 50 h, in order to investigate the evolution of their microstructural and mechanical properties. For each annealing temperature the samples were then tested at both the room and heat treatment temperature.

2.2. Microstructural analysis and high-temperature bending tests

The phase composition was investigated using an X-ray Powder Diffractometer (PW 1880, Philips, Almelo, The Netherlands) operating with CuK_α radiation, at 40 kV and 40 mA. The Θ–2Θ scan was performed between 20 and 90° by step width of 0.02° and 5 s per step.

The cross sections of TBCs were cold mounted in vacuum in polymer and polished. They were analyzed by SEM (Philips XL40, FEI B.V., Eindhoven, The Netherlands). The micrographs were then processed by image analysis software (Image J, U.S. National Institutes of Health, Bethesda, MD, USA) to calculate the porosity level of as-sprayed and annealed coatings.

Some coatings were mechanically stripped from their substrates. The samples, measuring after machining 45 × 4 × 1.8 mm^3, were polished and tested by four-point bending tests at various temperatures, *i.e.* room temperature (RT), 600, 1200, 1350 and 1500 °C, according to ASTM C1161 (RT) and C1211 (high temperature). The aged coatings were tested at RT and at the same temperature of the previous thermal aging. Free-standing coatings were tested to avoid the effects promoted by the underlying substrate. The SiC testing assembly was inside a furnace (Maytec GmbH, Singen, Germany) able to reach 1500 °C, and connected to a Zwick-Roell Z2.5 universal testing machine (Zwick GmbH, Ulm, Germany) measuring the sample load. A properly designed displacement transducer, pushing against to the tension face of the sample using three alumina rods, was able to measure the sample curvature and afterwards the deformation. The test assembly is reported in [14]. Finally, the stress–deformation curves, the elastic constants and the mechanical properties were assessed.

2.3. Thermal characterization

The thermal expansion of as-sprayed and annealed LZ coatings was measured with a high-temperature dilatometer (Model 402E/7, Netzsch-Gerätebau GmbH, Germany) up to 1500 °C. For thermal expansion measurements LZ coatings were cut in the shape of bars (28 × 4 × 2 mm^3) and heated in air at 5 °C/min. A certified alumina sample was used for instrument calibration. The measurement was carried out using a sample load of 0.2 N. No bending of samples was assessed after the test.

Specific heat measurements were performed up to 1250 °C using a simultaneous thermal analyzer (Model STA 429, Netzsch-Geratebäu GmbH, Selb, Germany), equipped with a sample holder for differential scanning calorimetry (DSC). The measurements were performed in static air on 4 × 4 × 2 mm^3 sized specimens. The sample weight was approximately 150 mg. Three consecutive measurement cycles were considered to calculate an average value: the heating rate was 20 °C/min. The specific heat curves of as-prepared and thermally aged samples were calculated following the procedure described in [6].

3. Results and discussion

3.1. Coating microstructure

As shown in Fig. 1 the powder feedstock is composed of single pyrochlore cubic $La_2Zr_2O_7$ phase, while in the as-sprayed coating the formation of a defective fluorite phase can be noticed and addressed to locally varying stoichiometry. This was caused by potential loss of lanthanum during plasma spraying and quenching of the molten splats at the substrate. Otherwise, the sprayed particles which were already solidified during flight were deposited as pyrochlore [15]. This is confirmed by the missing peaks, *i.e.* the peaks indexed as (311), (331), (511) and (531) in the related XRD patterns. The broadening of the other peaks suggests small crystallite size and crystal disorder. After thermal aging at 1200 and 1350 °C the crystallites grew and the fluorite phase transformed to ordered pyrochlore phase, without the formation of zirconia secondary phases.

Fig. 2 shows the cross section of the as-sprayed coating exhibiting a splat-like microstructure composed of overlapped lamellae, separated by splat boundaries and embedded in a network of microcracks and voids. The thickness of the lamellae varies from 1 to 5 μm.

The splat boundaries typically affect the thermal conductivity, while the vertical microcracks enhance the high-temperature strain tolerance. The former derived from the weak bonding between the deposited splats, depending on their solidification rate at the substrate. The latter propagated from the splat boundary as a consequence of stress relaxation. Finally, the globular pores derived from imperfect filling during coating build-up.

Fig. 3 shows the cross section of the coating annealed at 1350 °C for 50 h. The thermal treatment produced the partial sintering of the porous microstructure. Sintering necks are formed at splat boundary, improving the interlamellar bonding, whereas the closure of microcracks and pores also occurs. The fine microcracks disappear, while the large pores are influenced by densification at lesser extent.

The porosity of the as-sprayed coating was of about 15%. This value decreased to 11% for the coating exposed at 1200 °C for 50 h and down to 8% for the coating exposed at 1350 °C. After thermal aging the coating exhibited better cohesion and relatively high porosity [16], that involving good resistance to high-temperature exposure in terms of heat insulation and compliance [17,18]. As known the main

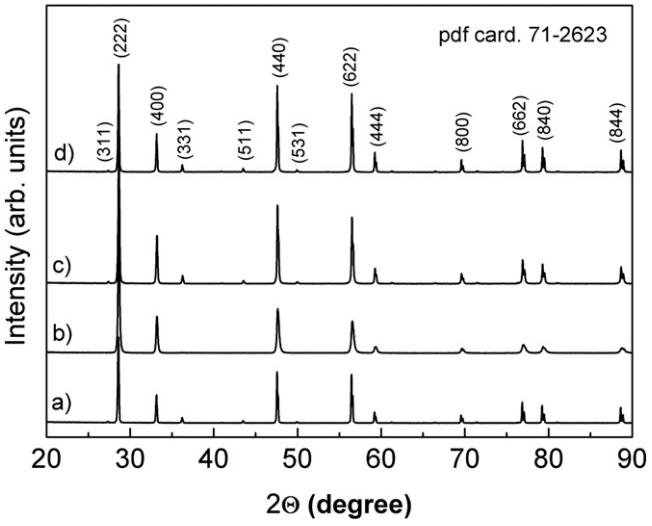

Fig. 1. XRD patterns of lanthanum zirconate (a) powder, (b) as-sprayed coating, (c) coating treated at 1200 °C and (d) coating treated at 1350 °C.