Surface & Coatings Technology 279 (2015) 44–52

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Thermal conductivity and erosion durability of composite two-phase air plasma sprayed thermal barrier coatings

Michael P. Schmitt [a,b], Amarendra K. Rai [c], Dongming Zhu [d], Mitchell R. Dorfman [e], Douglas E. Wolfe [a,b,f,*]

[a] *The Applied Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA*
[b] *Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA*
[c] *UES Inc., 4401 Dayton-Xenia Road, Dayton, OH 45432, USA*
[d] *NASA Glenn Research Center, 21000 Brookpark Road, Cleveland, OH 44135, USA*
[e] *Oerlikon Metco (US) Inc., 1101 Prospect Avenue, Westbury, NY 11590, USA*
[f] *Department of Engineering Science and Mechanics, The Pennsylvania State University, University Park, PA 16802, USA*

ARTICLE INFO

Article history:
Received 7 May 2015
Revised 9 July 2015
Accepted in revised form 6 August 2015
Available online 10 August 2015

Keywords:
Thermal barrier coating (TBC)
Air plasma spray
Low-k
Rare earth zirconia
Composite
Erosion

ABSTRACT

To enhance efficiency of gas turbines, new thermal barrier coatings (TBCs) must be designed which improve upon the thermal stability limit of 7 wt.% yttria stabilized zirconia (7YSZ), ~1200 °C. This tenant has led to the development of new TBC materials and microstructures capable of improved high temperature performance. This study focused on increasing the erosion durability of cubic zirconia based TBCs, traditionally less durable than the metastable t′ zirconia based TBCs. Composite TBC microstructures composed of a low thermal conductivity/high temperature stable cubic Low-k matrix phase and a durable t′ Low-k secondary phase were deposited via APS. Monolithic coatings composed of cubic Low-k and t′ Low-k were also deposited, in addition to a 7YSZ benchmark. The thermal conductivity and erosion durability were then measured and it was found that both of the Low-k materials have significantly reduced thermal conductivities, with monolithic t′ Low-k and cubic Low-k improving upon 7YSZ by ~13% and ~25%, respectively. The 40 wt.% t′ Low-k composite (40 wt.% t′ Low-k — 60 wt.% cubic Low-k) showed a ~22% reduction in thermal conductivity over 7YSZ, indicating even at high levels, the t′ Low-k secondary phase had a minimal impact on thermal conductivity in the composite coating. It was observed that a mere 20 wt.% t′ Low-k phase addition can reduce the erosion of a cubic Low-k matrix phase composite coating by over 37%. Various mixing rules were then investigated to assess this non-linear composite behavior and suggestions were made to further improve erosion durability.

1. Introduction

As the demand continues for increased turbine inlet temperatures for gas turbine engines, so does the demand on the thermal barrier coating (TBC) system used to protect the engine components. Current state of the art 7 wt.% yttria stabilized zirconia (7YSZ) based TBCs have reached their thermal stability limit of ~1200 °C. Operating at temperatures beyond 1200 °C for prolonged periods of time will cause the metastable t′ phase to decompose into equilibrium cubic and tetragonal phases, the latter of which undergoes a phase change to monoclinic upon cooling. This phase change is accompanied by a large volumetric expansion of ~5% or more which causes high stresses and eventually, spallation of the coating. Additionally, bond coat and substrate materials have nearly reached their peak operating temperatures which itself can cause spallation [1], and so to maintain bond coat/substrate temperatures, the thermal conductivity of next generation high temperature TBCs must be reduced.

The TBC literature has investigated a variety of new TBC materials [2–11] including aluminates, perovskites, rare earth (RE) modified “co-doped” zirconia and the rare earth pyrochlores, as well as microstructural design architecture advancements [12–16]. The majority of recent research has focused on the rare earth modified zirconias and rare earth pyrochlores. Co-doped YSZ utilizes multiple rare earths to stabilize the tetragonal phase. The heavier rare earths efficiently scatter phonons while certain combinations have been shown to create immobile defect clusters [7,8] which have the additional benefit of reduced sintering rates. The thermal phase stability limits of rare earth modified YSZ materials have not been evaluated to the same degree as 7YSZ, but they presumably have slightly higher temperature thresholds. This is a product of the diffusion controlled nature of the equilibrium transformation in which the defect clusters reduce diffusion and thus increase stability. However, there is no detailed published data on this matter. Rare earth pyrochlores based on zirconia have gained attention in the past few years due to their high thermal stability [3,4], calcium–magnesium–alumino–silicate resistance (CMAS) [17–19], and very

---

* Corresponding author at: The Applied Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA.
E-mail address: dew125@arl.psu.edu (D.E. Wolfe).

http://dx.doi.org/10.1016/j.surfcoat.2015.08.010
0257-8972/

low thermal conductivities [4–6]. The $RE_2Zr_2O_7$ pyrochlores possess a defect fluorite crystal structure wherein the cation site is ordered with a RE replacing the Zr on every other site. Ordered oxygen vacancies are also present on the 8a Wyckoff position. The large number of oxygen vacancies, combined with the large difference in both mass and radius between the cation species yields very low thermal conductivities. With $Gd_2Zr_2O_7$ stable in the pyrochlore phase through 1550 °C and $La_2Zr_2O_7$ stable up to 2300 °C, these materials present attractive alternatives to 7YSZ. Unfortunately, high dopant cubic Low-k and pyrochlore zirconate thermal barrier coatings suffer from high erosion rates and short thermal cyclic lives due to their inherently low fracture toughness, resulting in poor overall durability. Thermal cyclic life is important to the coating lifetime estimation, while high erosion rates preclude consideration of TBCs as prime reliant systems. To improve TBC durability, the thermal cycling behavior, erosion behavior, and other factors effecting durability such as CMAS resistance, must all be understood. The thermal cyclic durability of t′ and cubic Low-k as well as pyrochlore TBCs (with or without YSZ layers) has been extensively studied and reported in the literature [20–22] and therefore the effects of the rare earth dopants on thermal cyclic life is generally well understood. Additionally, much work has been done to understand the interaction of CMAS with high rare earth containing coatings and the resultant coating properties [17–19,23]. However, the effect of rare earth dopants on the erosion aspect of durability has not been heavily investigated in the literature. This study aims to investigate these effects.

Clearly, there is no substitute material which exhibits all the necessary properties: low thermal conductivity, high temperature stability beyond 1500 °C, and high durability. Rather than develop another class of materials, a different approach is to combine the beneficial aspects of two separate materials into one composite. With this in mind, air plasma spray (APS) composite coatings have been deposited using a low thermal conductivity/high thermal stability cubic Low-k' matrix phase (ZrO_2: $6Y_2O_3$–$2Gd_2O_3$–$2Yb_2O_3$ {mol %}) and a t′ Low-k toughening secondary phase (ZrO_2: $2Y_2O_3$–$1Gd_2O_3$–$1Yb_2O_3$ {mol%}). The erosion and thermal conductivity of these composites were then determined and compared to a 7YSZ baseline.

2. Experimental procedure

Powders were provided by Oerlikon Metco and mixed according to the weight fractions listed in Table 1. HVOF NiCoCrAlY (Oerlikon Metco — A386-2) bond coatings were sprayed onto 2.54 cm diameter by 0.32 cm thick buttons composed of Rene N5 and Mar-M-247. Rene N5 substrates were used for thermal conductivity testing as they are most reflective of the engine component and perform slightly better in the oxidative environment. Mar-M-247 were used for the remaining testing and characterization as they are lower cost substrates and have no change on the resulting TBC microstructure. Three topcoat powders were used in this study; a high thermal stability/low durability rare earth modified cubic zirconia (herein referred to as cubic Low-k), a lower thermal stability/high durability rare earth modified t′ zirconia (herein referred to as t′ Low-k), and a baseline 7 wt.% yttria stabilized zirconia (7YSZ). Coatings were deposited with each of the three single phase powders and multiphase composite coatings were deposited with the three t′ Low-k and cubic Low-k powder mixtures given in Table 1 for a total of six separate TBCs. Thin (~25 μm) layers of YSZ were sprayed prior to the deposition of the composites to prevent reaction between the Al_2O_3 TGO and higher rare earth containing cubic phase material. Though this composition may not have sufficient rare earth to react with the TGO, analogous coatings composed of pyrochlore materials would react and so a barrier layer was used to enable future comparisons of identical systems. The coatings were sprayed using a TriplexPro210 torch operating at 400 A and 45 NLPM of Ar/H_2 for a power of 45 kW. The standoff distance was 0.203 m and feed rates were 150 g/min.

Table 1
Coating compositions and structure table with resulting thickness and porosity values for the as-deposited coatings.

Matrix	Composition	Architecture	Thickness (μm)	Porosity
1	YSZ	Monolithic	286 ± 17	16% ± 2.5
2	t′ Low-k	Monolithic	382 ± 15	18% ±− 1.7
3	50 t′–50 c	Composite	304 ± 16	20% ± 1.8
4	40 t′–60 c	Composite	301 ± 17	19% ± 2.8
5	20 t′–80 c	Composite	281 ± 17	19% ± 1.4
6	Cubic Low-k	Monolithic	297 ± 16	18% ± 1.8

Coatings were characterized via scanning electron microscopy (SEM — FEI Quanta 200 ESEM) and X-ray diffraction (XRD — PANalytical Empyrean) in the as-deposited state and after heat treatment in air in a box furnace at 1100 °C for 20 h. For SEM, cross sections were mounted in epoxy and polished down to a final 45 nm colloidal silica step and subsequently gold sputtered to prevent charging. Jade 2010 software was used to perform XRD pattern analysis and whole pattern fitting. The pattern fits used JDPF 01-078-4083 for cubic Low-k and 01-070-4427 for t′ Low-k. Thermal conductivity testing was performed at NASA Glenn Research Center using their high heat flux CO_2 gas laser system [24]. Briefly, the surface of the sample was heated to a preset temperature of ~1360 °C while backside cooled to ~1000 °C to maintain a gradient through the sample. Pyrometers measured surface temperatures while a reflectometer measured reflected power (loss). The measured thermal gradient and calculated heat through the sample were used in conjunction with bond coat and substrate thermal conductivities and thickness values to determine the thermal gradient through the coating. This enabled calculation of the coating thermal conductivity. Erosion testing was performed at Penn State University using a custom erosion system, described in detail elsewhere [25]. In this case, 50 μm alumina media was accelerated to 100 m/s towards the sample surface. Erodent feed rate was 100 g/min with sample masses measured after various amounts of total erodent exposure. Steady-state erosion rates were taken to be the linear slopes observed in the coating mass loss vs. mass erodent exposure, typically the last four to five data points.

3. Results and discussion

3.1. As-deposited microstructure and phase composition

SEM micrographs of the as-deposited single phase coatings are presented in Fig. 1a–d with corresponding coating thickness and porosity values given in Table 1. Porosity is consistent through each of the coatings and is ~16–18% via image analysis (GIMP 2). The microstructures show a splat like lamellar morphology, typical of APS coatings, and with no vertical segmentation cracks. A representative higher magnification view of the t′ Low-k monolithic coating is provided in Fig. 1d which shows the significant microcracking present in these as-deposited coatings. Microcracks are beneficial in reducing the overall thermal conduction of the system and can provide strain relief during thermal cycling. However, from an erosion perspective, they can serve as stress concentrators and induce cracking and crack coalescence in the material, resulting in higher rates of erosion. It is worth noting that these microcracks are apparent in each of the three monolithic coatings.

SEM micrographs of composite coatings composed of 20, 40 and 50 (wt.%) t′ Low-k phase are shown in Fig. 2a–d. These composite coatings also show the standard lamellar microstructure exhibiting consistent porosity values similar to those of the parent single phase coatings, 16–18%. In Fig. 2a–d, the dark contrast of the t′ Low-k phase appears uniformly distributed throughout the coatings indicating good mixing and a homogeneous distribution, both vertically and laterally. Homogenous mixing is crucial to ensuring the observed behaviors are a result of the mixing ratios and not local differences in microstructure and phase due to deposition process variability. The