Surface & Coatings Technology 286 (2016) 119–128

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Gadolinium zirconate/YSZ thermal barrier coatings: Mixed-mode interfacial fracture toughness and sintering behavior

Martin Frommherz [a,*], Alfred Scholz [a], Matthias Oechsner [a], Emine Bakan [b], Robert Vaßen [b]

[a] *Fachgebiet und Institut für Werkstoffkunde, Technische Universität Darmstadt, Grafenstraße 2, 64283 Darmstadt, Germany*
[b] *Institut für Energie- und Klimaforschung, IEK-1, Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Straße, 52425 Jülich, Germany*

ARTICLE INFO

Article history:
Received 10 September 2015
Revised 10 November 2015
Accepted in revised form 6 December 2015
Available online 10 December 2015

Keywords:
Double-layer thermal barrier coatings
Gadolinium zirconate
Mixed mode interfacial fracture toughness
Delamination behavior
Sintering behavior

ABSTRACT

In this work, the delamination toughness and the sintering behavior of modern double-layer thermal barrier coatings of type gadolinium zirconate (GZO)/yttrium-stabilized zirconia (YSZ) are investigated in detail. These properties mainly determine the strain tolerance and thus the performance of thermal barrier coatings (TBCs). The delamination toughness was determined using a modified four-point bending setup. It is shown that the delamination behavior differs significantly from conventional monolayer coatings and is highly dependent on the specific microstructure of the GZO layer. The stiffness and sintering behavior of freestanding GZO layers were determined using impulse excitation, a test method sensitive to the global stiffness of the ceramic coating. The increase in stiffness is thereby correlated to microstructural changes, explicitly the healing of micro-cracks and the sintering of inter-lamellar cracks and unmolten particles. The results reveal that the specific spray structure of GZO has a great influence on the sinter stability which results in a characteristic temperature dependency. In this case the GZO coatings have an advantage in comparison to conventional YSZ coatings at temperatures above 1300 °C.

1. Introduction

For over 30 years, TBCs have been a key technology to allow increase of the hot gas inlet temperature to achieve higher energy efficiency. With the application of TBCs the cooling effort as well as the metal temperature of turbine components can be reduced which leads to a further increase in efficiency and component lifetime [1–4]. Usually plasma-sprayed TBCs consist of a ceramic top coat and a metallic bond coat layer which provides a sufficient bonding and oxidation-resistance of the metallic substrate [2]. Yttrium-stabilized zirconia (YSZ) is well established as the standard top coat material due to its superior property profile, e.g. low thermal conductivity, relatively high coefficient of thermal expansion and good thermo-cyclic performance [5,6]. Unfortunately, the application of YSZ is limited to a surface temperature range of about 1200 °C for long-term application due to phase transformations and increased sintering of YSZ which will lead to a degradation of the layer system [7–9].

Gadolinium zirconate with a pyrochlore crystal structure is one candidate for an alternative TBC material with a higher temperature capability. GZO has no volumetric phase transformation like YSZ and it undergoes an order–disorder transition first at approx. 1530 °C–1550 °C, transforming from a defect fluorite structure (Fm3m) to a pyrochlore structure (Fd3m) [10–12]. Its coefficient of thermal expansion (10.5×10^{-6}/K) is comparable to YSZ [13,14] which is favorable to avoid additional thermal stresses in the coating. Due to the lower thermal conductivity [13,15] the metal temperature can be reduced effectively to slow down bond coat oxidation which is one possible failure mechanism of the coating [16]. Moreover it was shown in [17] that pyrochlore oxides exhibit a higher sinter stability, which is one main requirement for higher surface temperatures since coating failure may be further affected by an increase in stiffness of the TBC which causes higher thermal stresses [18]. Unfortunately, pyrochlore oxides suffer from a lower intrinsic fracture toughness than YSZ [17,19,20] and GZO is prone to react at high temperatures and long annealing times with the thermally grown oxide (TGO) at the bond coat interface forming perovskite structures [21]. One solution is a double-layer system, combining an upper layer of GZO and a bottom layer of YSZ, where the YSZ layer provides a sufficient toughness against TGO growth induced stresses and inhibits a possible reaction between the GZO and the TGO [22]. It was shown in Refs. [23,24] that a significant improvement in cycle lifetime could be achieved with the double-layer concept in a burner rig test. It is stated that a tailored microstructure of the GZO layer, this means a high cumulative porosity (~20%) with a large amount of globular pores and inter-lamellar cracks and low amounts of unmolten particles, are favorable to achieve high a high cycle lifetime [24].

For a lifetime assessment, there is a fundamental need for a quantitative description of the relevant damage and the characterization of the layer properties which can change significantly with time and

---

[*] Corresponding author.

http://dx.doi.org/10.1016/j.surfcoat.2015.12.012
0257-8972/

temperature [16,18,25,26]. From a mechanical aspect stiffness and toughness are two fundamental properties which mainly determine the strain tolerance and thus the durability of TBCs under thermo-mechanical loading [26,27].

These properties are determined by the specific spray structure of coatings deposited by atmospheric plasma spray (APS), especially by the high density of crack-shaped defects which form during the spray process [28–31]. In general the defects can be distinguished by cracks perpendicular to the lamellar structure, so-called segmentation or intra-splat cracks, and those parallel to the lamellar structure, so-called inter-lamellar cracks. Moreover, the spray structure consists of globular pores, micro-porosity and additional defects such as unmolten particles. APS coatings have a pronounced anisotropic behavior due to the lamellar spray structure, thus in-plane and out-of-plane properties are of relevance [32].

1.1. Fracture mechanics properties

APS–YSZ coatings show a quite complex fracture behavior due to the specific microstructure. During crack propagation, the cracks preferentially follow the preexisting network of defects, such as intra-splat and inter-lamellar cracks [33,34]. Toughening mechanisms such as crack bridging and crack branching occur. Moreover the contact interaction of the crack seam during crack propagation leads to higher dissipation energy. These mechanisms result in a pronounced R-curve of APS–YSZ coatings [33–35]. Thurn et al. [35] determined the energy release rate G_c for segmentation in bending experiments, where the energy release rate was in the range of 20 N/m to 60 N/m for crack length below 100 μm, and between 150 N/m and 230 N/m for crack length between 300 μm and 400 μm. WOL (Wedge Opening Loading) tests reveal a characteristic R-curve behavior of delamination cracks and a steady state value of about 150 N/m for crack length above approx. 300 μm [33,34]. It was shown by Malzbender and Steinbrech [34] that limited stable growth of intra splat cracks occurs before a macroscopic crack growth can be detected. These crack mechanism which involve shear effects between the splats (splat sliding) and crack closure start from quite low toughness values of about ~3–26 N/m.

Delamination studies conducted with a modified four-point bending setup determined an energy release rate for APS–YSZ coatings in the as-sprayed condition in the range between 100 N/m and 200 N/m [25] and 150 N/m [36], which is in the same magnitude of order as the WOL test results. The toughness is dependent on the interface roughness between the metallic bond coat and the ceramic coating and in addition on the thermal heat treatment. Coatings with higher interface roughness have greater resistance to delamination. Annealing can lead to a successive decrease in G_c [25]. In comparison to that, the results of Yamazaki et al. [36] show an increase in G_c at medium annealing times, where the crack path shifted from the interface into the ceramic coating. The increase in G_c was correlated to an increase of fracture toughness due to sintering of micro-cracks.

It must to be pointed out that the toughness of TBCs is dependent on mixed-mode conditions during crack propagation [37,38]. The mixed-mode is thus characterized by the phase angle Ψ, with $\pm 90°$ for pure mode II and 0° for pure mode I loading [39]. In general, the energy release rate increases with increasing mixed-mode conditions. It is supposed that the additional mode II results in a higher dissipated energy because of contact interactions of the crack seams or a bigger plastic zone in front of the crack tip respectively [40]. In the case of interface cracks, the elastic mismatch of the materials induces a mode II component; thus mixed-mode conditions are present at the interface crack tip. As the toughness respectively the energy release rate is dependent on the crack length scale, the crack path (in-plane or out-of-plane), the microstructure and the mixed-mode conditions, a wide range of toughness values exists in the literature [32–37,41–43].

It is evident that pyrochlore oxides have generally a lower intrinsic fracture toughness in comparison to stabilized zirconia [17,19,20]. SEVNB tests conducted by Choi et al. [20] on hot pressed pyrochlore oxides ($La_2Zr_2O_7$, $Nd_2Zr_2O_7$, $Gd_2Zr_2O_7$, $La_2Hf_2O_7$) show that the fracture toughness of the bulk material is quite low with a value of about 1 MPa $m^{1/2}$. Vassen et al. [19] determined the fracture toughness of hot pressed $La_2Zr_2O_7$ by an indentation technique to 1.1 MPa $m^{1/2}$. Only limited data on the fracture behavior and fracture mechanics properties of APS-coatings made of pyrochlore oxides coatings is available in the literature. Dwivedi et al. measured the fracture toughness in the out-of plane direction of freestanding GZO coatings using a double torsion technique presented in Ref. [44]. The freestanding GZO coatings have a quite lower toughness, in the range of 50%–70% of APS–YSZ coatings. In the case of the YSZ coatings, annealing led to a significant increase in fracture toughness by a factor of approx. two, whereas only a little increase was observed for the GZO coatings. Bast et al. [17] determined the delamination toughness of monolayer APS-coatings made of pyrochlore oxide material using a modified four-point bending setup. The results show that the investigated pyrochlore coatings have significant lower interface toughness values of about 5%–20% of APS–YSZ coatings. There exist no data in literature on the in-plane fracture mechanic properties of GZO and double-layer coatings based on GZO/YSZ respectively. Since the resistance to delamination is one main parameter affecting the lifetime, it is therefore of interest to assess the in-plane properties and especially the delamination toughness.

1.2. Stress–strain behavior

In addition to the fracture toughness, the stiffness is another fundamental property which determines the strain tolerance of the ceramic coating [26,27]. An increase in stiffness can lead to a degradation of the TBC system, since greater stiffness induces higher stresses during thermal cycling [27]. It is notable that the stiffness of APS coatings is highly dependent on the loading direction (in-plane, out-of-plane, tensile, compressive), the stress and strain level and residual stresses in the layer system [31,45–47]. It was shown by several authors [45–47] that TBCs show a nonlinear dependence of the stiffness on the strain due to opening and closure of micro-cracks, pores and internal sliding. The stiffness increases with increasing compressive strain, whereas it is decreasing with increasing tensile strain [47]. Arai et al. showed that splat sliding plays an important role in the inelastic behavior of APS–TBCs [48]. It is notable that the stiffness determined by dynamic measurements (sound velocity or resonance frequency) is quite higher than the stiffness determined by quasi-static tests. Eldridge et al. [46] stated that in the dynamic tests the effect of internal sliding is absent because the strain changes are not sufficient enough to overcome static friction. As a result higher stiffness values are observed. Nevertheless dynamic measurements can be used to investigate the effect of sintering on the stiffness of thermal barrier coatings [49].

Moreover, the stiffness is sensitive to the test volume: methods sensitive to the local stiffness will show a larger scatter as the stiffness is dependent on the local defect density; methods sensitive to global stiffness represent the behavior of the spray structure itself [28,29].

For APS–YSZ coatings, a significant increase in stiffness is observed above 1000 °C [28,49–53]. The increase in relative stiffness is highly dependent on temperature and varies between 1 and 2 at 1000 °C and 3–5 at 1400 °C for annealing times of 100 h [31]. The increase in stiffness is thereby correlated to healing of micro-cracks and sintering of inter-lamellar cracks. Up to now, the sintering behavior of GZO has not been investigated in detail; few results are available [44]. Sintering test on powder compacts conducted by Bast et al. [17] show that pyrochlore oxides have a lower sinter activity than yttrium stabilized zirconia.

In this study, two fundamental properties, the in-plane stiffness and the delamination toughness which determine the strain tolerance and thus the performance of TBCs were investigated in detail to get a further understanding of GZO as a TBC material and the behavior of double-layer TBCs of type GZO/YSZ. The main goal is to assess the in-plane properties, which are supposed to be damage relevant.