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Thermal conductivity and stability of multilayered thermal barrier coatings under high temperature annealing conditions

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Abstract

Pyrochlore oxides have most of the relevant attributes for use as next generation thermal barrier coatings (TBCs) such as phase stability, low sintering kinetics and low thermal conductivity. One of the issues with the pyrochlore oxides is their lower toughness and therefore higher erosion rate compared to the current state of the art TBC material, yttria (6–8 wt.%) stabilized zirconia (YSZ). In this work, sintering characteristics were investigated for novel multilayered coating consisted of alternating layers of pyrochlore oxide viz. $Gd_2Zr_2O_7$ and t' low k (rare earth oxide doped YSZ). Thermal gradient and isothermal high temperature (1316 °C) annealing conditions were used to investigate sintering and cracking in these coatings. The results are then compared with that of relevant monolayered coatings and a baseline YSZ coating.

Keywords: TBC; YSZ; Pyrochlore oxides; Thermal conductivity; Sintering

1. Introduction

The current thermal barrier coating (TBC) material, 6–8 wt% yttria stabilized zirconia (herein referred to as Std. YSZ), exhibits the necessary attributes to maintain the turbine engine metal components' temperature at required level. These properties include relatively low thermal conductivity, high thermal expansion coefficient and high erosion resistance. Std. YSZ is also in thermochemical equilibrium with the thermally grown oxide (TGO) at the bond coat/Std. YSZ interface and exhibits the metastable t' phase which provides high toughness. However, Std. YSZ is inadequate for the higher temperatures necessary for enhanced efficiency of gas turbine engines. This is due to an elevated temperature induced thermal instability, increased sintering rates and inferior thermal conductivity.

For TBC applications beyond 1200 °C, pyrochlore oxides of the rare earth zirconates are promising substitutes for Std. YSZ.[1–8] Specifically, gadolinium zirconate (GZO–$Gd_2Zr_2O_7$) has been studied by several authors due to its high thermal stability ceiling, low thermal conductivity, relatively large coefficient of thermal expansion and reduced propensity for sintering.[2–6] Drawbacks of GZO and other rare earth zirconates are the very low toughness and thereby very poor erosion performance of the cubic structure as well as the instability with the TGO.[1,7] It has been suggested that the latter can be circumvented by first depositing a Std. YSZ interface layer before GZO deposition, thus preventing diffusion of the Gd into the TGO layer.[1]

Doping ZrO_2 with trivalent rare earth oxides such as Gd_2O_3 and Yb_2O_3 has been shown to create immobile defect clusters within the structure.[9] These defect clusters serve to reduce thermal conductivity and provide sintering resistance, while increasing toughness and phase stability.[10] Below approximately 6 mol% of total dopant, YSZ maintains the t' structure (t' low k) and thus higher toughness, while above 6 mol%, the cubic structure (cubic low k) is stable.[11] This is important, as increasing the dopant concentration is favorable in terms of reducing thermal conductivity but will compromise toughness and therefore erosion resistance. There appears to be a need to

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develop technologies to impart toughness to materials such as GZO and cubic low *k* for higher temperature TBC applications.

In an attempt to increase erosion resistance with respect to GZO while maintaining its lower thermal conductivity and increased sintering resistance with respect to Std. YSZ, the present authors have initiated a systematic study to evaluate the potential of multilayered TBC architectures consisting of alternate layers of *t′* low *k* and GZO.[12] It was hypothesized that multiple interfaces of the multilayered structure will provide higher toughness and enhanced scattering of heat carriers thereby decreasing erosion rate (increasing erosion resistance) and thermal conductivity, respectively. It was further hypothesized that such multilayered design with adequate microstructure will provide elevated temperature thermal conductivity close to that of GZO while providing better erosion resistance than GZO. The erosion rate of the multilayered TBCs has been compared with that of the monolayered GZO TBC.[12] Al_2O_3 particles (50 μm) were used as erodent and the erosion rate was determined by measuring the weight loss of TBC as a function of mass of the erodent fed. It was found that the erosion rate of GZO is an order of magnitude higher than Std. YSZ which can be reduced by 57% when utilizing a nano-multilayered structure.[12] The earlier work[12] has shown that multiple interfaces of the multilayered structure can provide higher toughness and enhanced scattering of heat carriers thereby drastically decreasing erosion rate with respect to GZO while maintaining a low thermal conductivity close to that of GZO.

The present work involves manipulation of the multilayered coating microstructure and design to further reduce thermal conductivity. Also, in the present work sintering characteristics of the multilayered coatings under thermal gradient as well as isothermal conditions were examined. For comparison purpose similar characteristics of monolayered coatings were also examined.

2. Experimental procedure

2.54 cm diameter (Pt, Ni) Al bond coated (Howmet) Rene N5 (Sophisticated Alloys, Butler PA) buttons were used as substrate materials. For high temperature isothermal heat treatment work, 2.54 cm × 2.54 cm polycrystalline Al_2O_3 substrates (Coors Tek, 99.5% pure) were also utilized. The substrates were grit blasted and ultrasonically cleaned for 20 min in solutions of acetone and methanol with a DI water rinse and nitrogen dry after each clean. The substrates were then tack welded to a 5.08 cm diameter mandrel using 304 stainless steel strips. Next, the mandrel was mounted in an industrial prototype Sciaky electron beam-physical vapor deposition (EB-PVD) unit capable of using six EB-guns and three independent ingot feeders.[12] EB-PVD was used to fabricate TBCs of various architectures as presented in Table 1. Only one side of the substrate was coated.

Monolayers of Std. YSZ (Matrix 1), *t′* low *k* (Matrix 2) and GZO (Matrix 3) were fabricated as a baseline for comparisons with the multilayered coatings. The multilayered TBC structures (Matrices, 4, 5 and 6) were fabricated by depositing alternate layers of *t′* low *k* and GZO. For **the nanolayered samples from** Matrix 4 and 5, the necessary ingots were co-evaporated and a vapor shield was used to prevent intermixing of the vapor clouds. Rotation through each vapor cloud therefore provided a coating with alternating layers of *t′* low *k* and GZO at individual layer thicknesses of ∼200 nm. In **the modified nanolayer from** Matrix 5, the deposition rate was increased, compared to Matrix 4, to introduce more porosity in each layer. In the thick layer from Matrix 6, the electron beam was alternated between two ingots, thus only a single ingot was evaporated at a time. This also yielded layered coatings with individual layer thicknesses on the order of ∼25 μm. The overall nominal thickness of all the monolayered and multilayered coatings was about ∼200–300 μm. Prior to the deposition of monolayered GZO, a thin (25 μm) layer of Std. YSZ was deposited on top of the bond coat to maintain thermochemical stability between GZO and TGO. In the case of multilayered TBCs, *t′* low *k* was the first layer (25 micron) deposited on top of the bond coat. In addition to Rene N5, the multilayer coatings from Matrix 6 were also deposited onto bare Al_2O_3 substrates. Further details of the coating deposition procedure are described elsewhere.[12]

Thermal conductivity of the as-fabricated TBCs was measured by the steady-state heat flux technique at NASA Glenn Research Center. Pass through heat flux and the measured temperature gradients through the ceramic coating system were used in conjunction with a one dimensional heat transfer model to calculate the thermal conductivity.[13] Briefly, the TBC surface temperature was maintained at 1316 °C for 20 h through a constant heat flux from a 3.0 KW CO_2 laser while backside air cooling was used to maintain the desired specimen temperature. Thus the thermal conductivity tests involved thermal gradient conditions. Surface and backside temperatures were measured via optical pyrometers while a laser reflectometer measured the reflection loss at the surface. A laser delivered heat flux was calibrated using a sample of known thermal conductivity and by subtracting the laser reflection loss at the surface from the known heat flux, the pass through heat flux can be determined. The pass-through heat flux was further verified experimentally. The TBC/metal interface temperature was obtained using the known thermal conductivity of Rene N5 metal substrate. The overall thermal conductivity as functions of coating thickness, temperature and testing time was determined from the heat fluxes and the corresponding temperature gradients across the ceramic coating. Details of the thermal conductivity measurement procedure are given elsewhere.[13,14]

X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques were used to characterize the phase and microstructure while box furnaces were used to carry out the high temperature anneals.

3. Results and discussions

Thermal conductivity results of all the fabricated TBC systems from Table 1 are shown in Fig. 1. The monolayered Std. YSZ exhibited the highest initial or “as deposited” thermal conductivity of ∼1.45 W/m K, along with the highest “sintered” thermal conductivity of 2.2 W/m K after a full 20 h of high heat flux testing at 1316 °C. The increase in thermal conductivity of