Surface & Coatings Technology 275 (2015) 75–83

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Heat transfer through nanoscale multilayered thermal barrier coatings at elevated temperatures

D. Josell [a,*], J.E. Bonevich [a], T.M. Nguyen [a], R.N. Johnson [b]

[a] Materials Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States
[b] Pacific Northwest National Laboratory, Richland, WA 99354, United States

ARTICLE INFO

Article history:
Received 11 December 2014
Revised 18 May 2015
Accepted in revised form 19 May 2015
Available online 23 May 2015

Keywords:
Thermal barrier coating
Heat transfer
Interfacial thermal resistance
Interfacial thermal conductance
Multilayer
Alumina
Zirconia
7YSZ

ABSTRACT

Heat transfer through thermal barrier coatings (TBCs) composed of alternating nanometer thick layers of aluminum oxide and 7% yttria stabilized zirconia (7YSZ) was studied by pulsed heating at temperatures in the range 1275 K to 1375 K. The thermal diffusivity of the TBCs, deposited on thin metal foils by electron beam evaporation and coated with an opaque, submicrometer metal capping layer, was studied by applying a sub-μs duration heating pulse from a Q-switched laser to the substrate and then monitoring the temperature rise on the opposing, metal-capped surface of the TBC. The recorded temperature transients were modeled using properties of the constituent materials in order to obtain an upper bound of the thermal resistance associated with the interfaces between layers. The results thus provide insight into the feasibility of using interfacial thermal resistance in this material system to improve TBC performance by decreasing thermal conductivity.

Published by Elsevier B.V.

1. Introduction

1.1. Background

Thermodynamic considerations place well understood temperature-dependent limits on the possible efficiency of combustion engines. The desire for increased efficiency of airplanes and power plants thus pushes engine operation toward higher temperatures. Thermal barrier coatings (TBCs) are key to progress in this regard as they increase operating temperatures by reducing the temperatures experienced by key engine parts such as turbine blades and rotors consistent with material-related limitations.

Absent voids, interface-related photon or phonon scattering and intermixing, the introduction of a higher thermal conductivity material into a lower thermal conductivity material will yield a composite of intermediate thermal conductivity. The question of relevance to thermal barrier applications is whether the introduction of sufficient interfaces can, specifically through their impact on phonon and/or photon mediated energy transport, more than compensate for the degraded bulk thermal conductivity, thereby producing a material for TBC applications with lower effective thermal conductivity than either constituent.

There exists a substantial literature on a range of properties of multilayer TBCs ([1,2] and references therein). The broader search for advanced materials with lower thermal conductivity [3,4] includes study of thermal transport in TBCs composed of coated or layered nanoparticles [5,6] as well as homogeneous materials with controlled interface density [7,8] and multiphase [9] and multilayer TBCs [10]. In some cases, thermal conductivities are found to be below those anticipated using volume weighted properties. However, where interfaces are present, the overall transport properties of the composite material are typically provided without explicit evaluation of the impact of an interface. The elevated temperature, steady-state laser heatflux measurement approach used in some cases complicates such evaluation; these experiments can involve a temperature drop across the TBC of 200 K to 500 K [11] so that temperature dependent thermal conductivity (e.g., that of Al_2O_3 changes by 500% from 575 K to 1275 K) [12] likely overshadows interface properties. In other cases, uncontrolled internal geometry precludes such evaluation.

At lower temperatures, an interfacial thermal resistance (ITR) ρ [cm^2 K/W], also known as an interfacial thermal impedance, or its inverse, known as the Kapitza conductance, is usually used to relate heat flow across an interface by phonon conduction to the associated temperature discontinuity across the interface ([13–15] and references therein). In many cases the ITR is measured using multilayered materials specifically because such materials permit the interface density to be systematically varied. While, as with studies of TBCs, some studies focus on the overall transport properties, a large number of studies using a number of techniques have focused on evaluating ITR. Among these, room temperature thermoreflectance studies of a number of

* Corresponding author at: 100 Bureau Dr., NIST, Gaithersburg, MD 20899.
E-mail address: daniel.josell@nist.gov (D. Josell).

http://dx.doi.org/10.1016/j.surfcoat.2015.05.036
0257-8972/Published by Elsevier B.V.

metal/metal systems yielded values of 2.3×10^{-5} cm^2 K/W and below [16]. Measurements on yttria-stabilized zirconia and amorphous silicon dioxide multilayers using the 3ω method found an upper limit of 1×10^{-6} cm^2 K/W for YSZ/SiO_2 interfaces [17]. Mirage technique measurements on Ti/Al multilayers found 2.1×10^{-6} cm^2 K/W [18].

Larger values of ITR ranging from 10^{-4} cm^2 K/W to as high as 10^{-2} cm^2 K/W have been found [13–15]. These are typically for the interfaces between highly dissimilar materials at and near room temperature. However, ITR measurements using contact probes and heatsinks [19,20] are incapable of separating the contribution of the internal interface of interest from that of the specimen/heatsink interface associated with the measurement approach. Values of ITR exceeding 10^{-2} cm^2 K/W obtained using this technique are thus suspect. Indeed, even higher values have been found to be associated with the specimen/heatsink interface [21].

That said, an ITR as high as 10^{-2} cm^2 K/W can substantially reduce thermal conductivity in micrometer-scale multilayer materials while even an ITR of order 10^{-4} cm^2 K/W can do the same in nanometer-scale multilayered materials. Such values suggest multilayer TBCs hold substantial promise for improving the performance of TBCs. However, at the elevated temperatures relevant to TBC operation, pulsed heating measurements of Cu/Fe multilayers at 1200 K determined the impact of interfaces on thermal transport could be captured using an ITR no higher than the mid 10^{-5} cm^2 K/W [22]. Similar experiments on Mo/alumina multilayers yielded an upper bound ITR of 6×10^{-5} cm^2 K/W [23]. The authors are not aware of studies of ITR for oxide systems at temperatures relevant to the operation of thermal barrier coatings. This paper therefore details pulsed heating experiments conducted on alumina/7% yttria stabilized zirconia (7YSZ) multilayer thermal barrier coatings with modeling to quantify the impact of the internal interfaces on heat flow through these materials.

1.2. Interface resistance and thermal conductivity in multilayered materials

If the basic bilayer repeat unit of a multilayer material is to be superior to an equivalent thickness of homogeneous material then the thermal resistance of the two layers (equal to the ratio of layer thickness d and thermal conductivity κ) plus the thermal resistance of the two interfaces between them (2ρ) must exceed the thermal resistance of a single layer of the lower conductivity material that is as thick as the two layers combined, i.e.,

$$\frac{d_1 + d_2}{\kappa_1} < \frac{d_1}{\kappa_1} + \frac{d_2}{\kappa_2} + 2\rho. \quad [1]$$

Here κ_1 is the thermal conductivity of the lower conductivity material, κ_2 that of the higher thermal conductivity material, while d_1 and d_2 are their respective thicknesses. The effective thermal resistivity of the composite material $1/\kappa_{eff}$ is given by

$$\frac{1}{\kappa_{eff}} = (d_1 + d_2)^{-1}\left(\frac{d_1}{\kappa_1} + \frac{d_2}{\kappa_2} + 2\rho\right). \quad [2]$$

For nonzero ITR ρ, this effective thermal resistivity can be made arbitrarily large by reducing the thicknesses d_1 and d_2 to zero. While arbitrarily small layers are not possible (or likely stable), the thermal resistivity should be maximized by making the layers, especially the higher conductivity constituent, as thin as possible. Just how thin the layers must be to obtain significant improvement depends on the value of the ITR and the difference between the thermal conductivities of the two constituents.

2. Experiment details

The multilayer TBCs were deposited on metal foils from 1 cm to 2 cm across at Howmet Corporation and Pacific Northwest National Laboratory.[i] Depositions were conducted using a 10 kW electron beam evaporator deposition system in a vacuum chamber with base vacuum of 10^{-6} Torr (10^{-4} Pa) or better. Compositional modulation was accomplished using a rotating shutter that allowed only alternating exposure of the two sources. The controlled-power deposition rates were in the range 0.1 nm/s to 1 nm/s based on TBC thicknesses and deposition times. Depositions were conducted without additional oxygen, the stationary substrates maintained at temperatures between approximately 1275 K and 1350 K using quartz tube radiant heaters. A submicrometer metal capping layer was deposited on the surface of each TBC. The optically opaque top layer ensured that pyrometry measured the surface temperature alone in the event of significant radiative transport within the coating; it had negligible impact on thermal transport through the structure. Fig. 1 shows a cross-sectioned TBC imaged using a scanning electron microscope; the brighter layers are the 7YSZ. The thickness and average composition of each TBC were determined after the transport measurements were conducted. Using the number of layers in the TBC, the average thicknesses of the individual Al_2O_3 and 7YSZ layers were then determined.

The deposits exhibit a columnar growth structure. Transmission electron microscopy (TEM) was conducted using a FEI Titan operating at a voltage of 300 kV. Fig. 2a shows a region of the same TBC imaged using scanning transmission electron microscope (STEM) mode. The line indicates the location where a scan of the elemental distribution within the layers was conducted. Integration of the energy dispersive X-ray (EDX) spectrum along the line, shown in Fig. 2b, indicates the elements present in the coating. The composition of select elements along the scan (from upper left to lower right in the image) is shown in Fig. 2c. Fig. 3 shows higher magnification TEM imaging of the same specimen; the relative contrast of the layers has switched from that obtained in STEM mode so that the Al_2O_3 layers are now brighter. There is some indication of porosity in Figs. 1 and 2, particularly between the columnar grains.

TEM characterization of an Al_2O_3/7YSZ TBC with $\approx$ 5 nm layer thickness similar to that of specimens for which thermal transport was examined is shown in Fig. 4. The columnar structure and scalloping of the layers are similar to those seen with the TBC having thicker layer. The nonplanarity arises within the thickness of the deposit as well as from the underlying Nb substrate surface. Regions of decreased density are evident between the columnar grains. Fig. 4b shows no such porosity within a single grain.

In metal/metal multilayers with similarly thin layers, epitaxy of the layers within a column grain is sometimes observed [24,25]. A diffraction pattern obtained from the multiple layers within the grain pictured in Fig. 4c is inset; the probe beam, with diameter slightly larger than the grain width, was centered in the middle of the image. The brightest spots, exhibiting 2-fold symmetry, indicate a single orientation for the contributing layers. The integrity of the layering is seen in the lower and higher magnification images. It is also evident in the overlaid compositional map of the Zr distribution in Fig. 4c obtained in STEM mode; fluorescence induced by the higher energy X-rays generated in the adjacent Zr prevented acquisition of a corresponding Al map at this length scale.

Pulsed heating experiments at temperatures ranging from approximately 1250 K to 1375 K were used to measure thermal transport through the coatings. As these temperatures are similar to those associated with the TBC depositions, and test durations were shorter than the deposition times, the microstructures shown are representative of both as-deposited and post-study microstructures. The TBCs on the substrates upon which they were deposited were tested in a vacuum

[i] Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.