J Mater Sci (2007) 42:9491–9494
DOI 10.1007/s10853-007-2048-1

LETTER

Laser nanostructuring of EB-PVD thermal barrier coatings for ultra-low thermal conductivity

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Received: 16 July 2007 / Accepted: 23 July 2007 / Published online: 20 August 2007

In recent years, there are serious efforts to reduce thermal conductivity of thermal barrier coatings (TBC) in order to (i) improve the TBC durability, reduce the metal temperature, and retard the thermally-induced failure; (ii) improve engine efficiency by allowing it to operate at higher temperatures; and (iii) allow designers to reduce the TBC thickness and thereby decrease the significant centrifugal load that the mass of the TBCs imposes on the rotating turbine engine components [1, 2]. Nanoparticle structuring of TBC has the potential to offer ultra-low thermal conductivity in addition to providing other desirable properties such as low density, high thermal expansion, high strength, and high toughness. Hence, in this study, an array of thermally stable, uniform nanoparticles, and nanoporous structures (<100 nm) in electron beam-deposited TBC coatings were synthesized by the use of femtosecond laser irradiation followed by a dip in nanostabilizing-slurry. In addition, the effect of nanostructure on thermal conductivity was evaluated.

TBCs, universally made of yttria-stabilized zirconia YSZ (ZrO_2–7 wt% Y_2O_3) with a thickness of 100–500 μm, are used for over 50 years in gas-turbine engines of aircraft propulsion, marine propulsion, and power generation to increase engine operating temperatures and reduce cooling requirements [2, 3]. YSZ has the lowest thermal conductivity (2.3 W/m K at 1,273 K for a fully dense material) of all ceramics at elevated temperatures because of its high concentration of point defects (oxygen vacancies and substitutional solute atoms), which scatter heat-conducting phonons [4]. Low thermal conductivity of TBCs coupled with internal air-cooling enabled major reductions in the surface temperature (100–300 °C), thereby improving engine efficiency and performance [5].

Thermal conductivity of intrinsic YSZ can be reduced by engineering the microstructure, controlling the porosity, and adding rare-earth oxides. The microstructure is essentially determined by the coating processes, which include: (i) air-plasma-spray (APS) deposition and (ii) electron beam physical-vapor deposition (EB-PVD). APS coating exhibits "splat" grain morphology with inter-"splat" boundaries and cracks and porosity parallel to the metal/ceramic interface that are responsible for reducing thermal conductivity from 2.3 W/m K for a fully dense material to a more typical 0.8–1.7 W/m K [6]. However, the undulating nature of the metal/ceramic interface produces out-of-plane stresses responsible for in-service failure. EB-PVD coatings consist of equiaxed grains at and near the metal/ceramic interface, columnar YSZ grains growing out of the equiaxed-grain region to the top-coat surface, nanometer-scale porosity within the columnar grains and channels separating the columnar grains. Porosity and cracks assist in reducing the thermal conductivity (1.5–2 W/m K [7]), but to a lesser extent than APS TBCs, because the channels run parallel to the direction of heat flow.

In order to maximize YSZ's performance, low thermal conductivity, high thermal expansion, increased strength, and toughness are required for which nanoparticle structure is ideally suited. Nanoparticles exhibit unique mechanical and physical properties as a result of their large surface area-to-volume ratios; large fraction of atoms residing at the interfaces; phonon scattering; extremely fine grain, phase, and domain sizes; changes in the electronic structure (density of states, band gap, energy levels etc.); and mean

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free path being smaller than the size of nanoparticles. The highly controlled hierarchical architectures of nanoparticles have already proven to substantially improve the performance, lifespan, and reliability of devices and parts in the fields of microelectronics, MEMS, information storage, and tribology [8, 9].

YSZ is intrinsically an electronic insulator and hence heat is transported only by lattice vibrations (phonons) and radiation (photons) where the latter becomes dominant at high temperatures. Being a molecular solid, YSZ consists of optical and acoustic phonons of a spectrum of frequencies. The fundamental equation for phonon conductivity is:

$$\kappa = \frac{1}{3} C v l$$

where C is specific heat per unit volume, v is speed, and l is mean free path. C and l are functions of the frequency while v is constant (according to Debye theory). Different imperfections scatter with different frequency dependence. Point defects such as solute cations and oxygen vacancies reduce the contribution of the high-frequency spectrum by scattering phonons as the fourth power of frequency [10]. Extended imperfections such as grain boundaries and voids scatter phonons at low frequencies. Interaction between phonons can contribute to scattering although this phenomenon is independent of frequency. All these phonon conductivity reductions can be enhanced by *decreasing the average grain size*. In contrast to phonon conduction, radiation heat transfer is little influenced by point defects and grain boundaries. The near-field radiation, due to a layer of cooler gas at around 1,200 °C in the engine environment, acts as a component of the thermal conductivity, which is dependent on the thickness of layer of cooler gas and refractive index of the coating. The radiative component of the thermal conductivity is comparable to the phonon conductivity at high-temperatures. Radiative heat transfer can be reduced not only by porosity content but also by doping YSZ with other rare earths like Neodymia, Gadolinia, and Lanthana [11, 12]. Such dopant additions introduce vacancies as well as strain centers into the lattice, reducing also phonon conductivity.

In order to achieve thermal conductivity of <0.5 W/m K, nanometer sized grains and point defects are required for phonon conductivity while pores or dopants are needed to reduce the radiative component. Pores may be preferable to dopants, since they present a larger contrast in the index of refraction, provided they can be introduced in the right size. For example, recent innovations in YSZ are creating nanoporous microstructures [11] and doping it with multicomponent rare-earth oxides [12] to promote reduction in thermal conductivity. Theory predicts that thermal conductivity of YSZ can be reduced by about 60% for 40–60 nm diameter nanoparticles [10].

In the present work, superalloy samples with a nominal size of 25 mm by 25 mm with a bond coat (NiCrAlY) thickness of 75 μm and top coat (YSZ) thickness of 100 μm were acquired from coating manufacturers. A 100-fs pulsed Ti:sapphire laser based on the chirped pulse amplification (CPA) technique was then used to ablate the coating at very low energy fluence. Femtosecond pulsed laser was chosen over nanosecond pulsed laser for ablation due to reduced thermal effects that in turn prevent the formation of non-periodic microstructures, recast layers, aggregates, compact islands, large particles by coalescence, and non-uniformity among particles. The 6-mm diameter laser beam with Gaussian energy distribution was circularly polarized, expanded to twice using an up collimator, and steered by a 45° mirror onto a lens onto the sample that was mounted on the *x*–*y*–*z* positioning table. A direct-writing method in raster configuration (preprogrammed CAD pattern) was employed to perform high volume throughput. A helium assist gas was used during the ablation. Experiments were performed at laser energy fluencies in the range of 0.2–0.4 J/cm^2, which are well below the single-shot, thermal damage threshold of 0.5 J/cm^2. Following laser ablation, a nanoparticle-stabilizing treatment which consists of dipping the sample in base slurry of pH 9 and 5 mol.% fumed silica in an open reactor system at 350 K for about 10 h [13] was utilized to reduce sinterability of these nanoparticles during the high-temperature exposure. The silicate is negatively charged under basic conditions and has strong bonding power toward the zirconia surface leading to reduced growth [13]. For thermal conductivity measurements, a steady-state technique developed by NIST that uses a laser for heating the coating and an infrared microscope for measuring temperature differences was employed [14]. Details of this technique may be referred to NIST's publication [14]. The primary advantage of thermal microscopy method is its capability to measure thermal conductivity of very thin (20–100 μm) TBCs within 10% accuracy.

Figure 1 shows the nanoparticles that were generated in large areas by rapid rastering method. Uniform spherical nanoparticles (<100 nm) are formed and packed closely (Fig. 2). There is no evidence of typical thermal damages like cracks, heat-affected-zones, columns, and recast layers. However, once the fluence reached 0.5 J/cm^2, the YSZ surfaces underwent thermal degradation accompanied by the appearance of micron and sub-micron sized particles. Time-of-flight mass spectrometer measurements indicated a strong emission of electrons followed by explosive emission of positive ions and clusters, suggesting Coulomb explosion as the mechanism of nanostructuring.

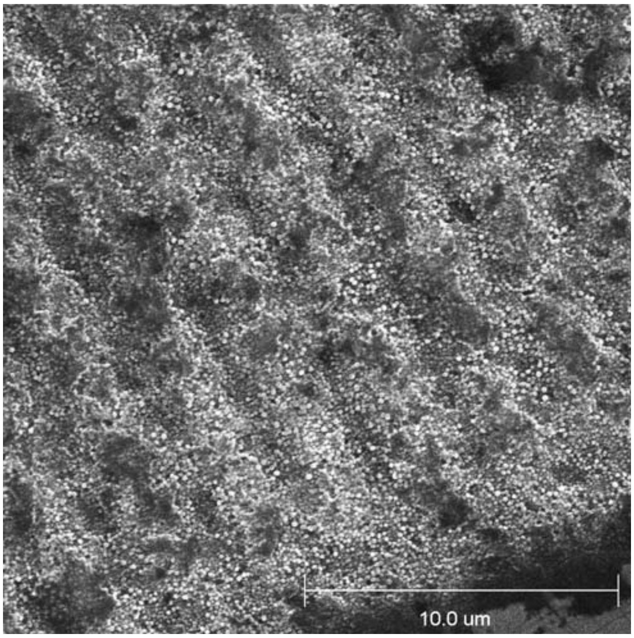


Fig. 1 SEM micrograph showing the nanoparticle (50–100 nm) in ultrafast laser scanned EB-PVD YSZ coatings

Consequently, the region explodes, leaving nanopores distributed homogeneously over the surface. Coulomb explosion has been proven to be a mechanism for direct nanostructuring of semiconductor or insulator surfaces in ion-beam sputtering using highly charged ions at low impact energies through experiments and molecular dynamics simulations [15, 16]. In many respects, these results are similar to those observed in femtosecond pulsed laser ablation [17].

Auger electron spectroscopy (AES) and X-ray diffraction (XRD) analyses revealed that the chemical composition of nanoparticles was identical to that of original YSZ. Nanoindentation tests revealed a hardness of 20–22 GPa, an increase of 40% over the EB-PVD coatings. Figure 3 shows the dramatic effect of nanostructuring on thermal conductivity that is attributed to the generation of numerous phonon and photon scattering sites.

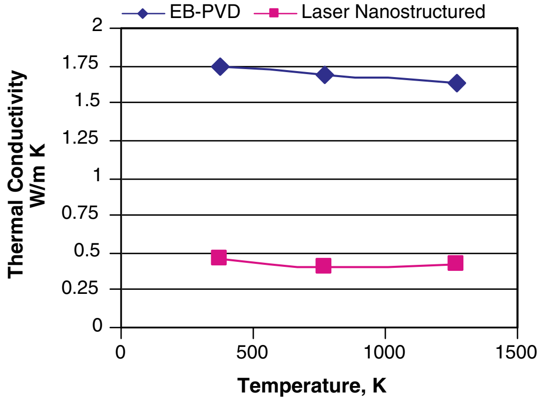
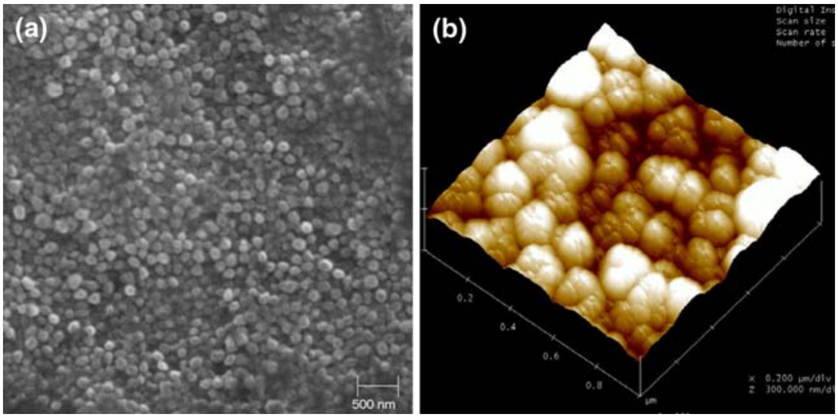


Fig. 3 Average thermal conductivity of as-received EB-PVD and laser treated EB-PVD 7YSZ coatings

The methodology described here is in sharp contrast to the traditional laser ablation methods [18, 19] where nanoparticles and clusters are synthesized under mostly vacuum conditions and then either collected in a container or loosely deposited on a substrate. In addition to making the nanoparticles susceptible to contamination, the traditional laser ablation is characterized by the formation of micron-sized particles and various other species, making it very inefficient. Furthermore, the issues such as reactivity, storage, agglomeration, and segregation are not resolved. Recently there is an exploration of investigations on TBC nanocoatings [20–22]. Inframat, Inc. has developed a process designated as solution plasma spray (SPS) that produces nanocoatings of YSZ [20]. The SPS consists of atomization of a precursor solution of zirconium and yttrium through a hot plasma flame. SPS coatings exhibited higher thermal cycling durability (an increase of 40%) over APS and EB-PVD coatings due to a unique microstructure that consisted of nanometer pores, through-thickness cracks, and the absence of coarse, brittle "splat"

Fig. 2 Micrographs showing nanoparticles in laser treated EB-PVD YSZ coating (**a**) SEM (**b**) AFM



boundaries. Applied Thin Films, Inc. has developed a new disordered TBC material based on layered perovskite compositions ($BaNd_2Ti_3O_{10}$) that offers low thermal conductivity (0.7 W/m K above 1,573 K) combined with excellent strain tolerance and thermal expansion match with substrates [21]. Finally a European patent demonstrates that nano-features including intersplat columns, mixed oxide particles, and secondary columnar grains are essential to improve the high-temperature performance of TBC coatings [22].

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