TOWARDS DURABLE THERMAL BARRIER COATINGS WITH NOVEL MICROSTRUCTURES DEPOSITED BY SOLUTION-PRECURSOR PLASMA SPRAY


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Abstract—The feasibility of a new processing method—solution precursor plasma spray (SPPS)—for the deposition of ZrO₂-based thermal barrier coatings (TBCs) with novel structures has been demonstrated. These desirable structures in the new TBCs appear to be responsible for their improved thermal cycling life relative to conventional plasma-sprayed TBCs. Preliminary results from experiments aimed at understanding the SPPS deposition mechanisms suggest that nanometer-scale particles form in the plasma flame, followed by their deposition by sintering onto the substrate in the intense heat of the plasma flame. The SPPS method, which offers some unique advantages over the conventional plasma-spray process, is generic in nature and can be potentially used to deposit a wide variety of ceramic coatings for diverse applications. © 2001 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

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1. INTRODUCTION

Thermal barrier coatings (TBCs) have been extensively used for the thermal protection of internally-cooled, hot-section components in gas turbine engines for jet aircraft and power generators (see reviews [1–3]). A typical TBC system consists of a thin oxidation-resistant metallic bond coat (50–125 µm) sandwiched between the high-temperature superalloy component and a thick (125–500 µm) Y₂O₃-stabilized ZrO₂ (YSZ; containing 7–8 wt% Y₂O₃) ceramic top-coat which is exposed to hot gases [4]. YSZ is the ceramic of choice, primarily because it has a thermal expansion coefficient (~10⁻⁵/°C [5]) closer to that of the superalloy, and it has a very low high-temperature thermal conductivity (2.5 W/m K at 1000°C for a dense polycrystalline ceramic [6]). The YSZ top-coat is deposited by either electron-beam physical-vapor deposition [7] or plasma-spray deposition using powder feedstock [8]. Both these methods result in coatings with defective microstructures that help alleviate stresses arising from the thermo-mechanical mismatch between the metal and the ceramic (strain tolerance), and further reduce the thermal conductivity of the YSZ top-coat. The latter can result in a temperature drop of up to 200°C across the top-coat. The electron-beam method gives columnar microstructures with defects such as cracks and grain boundaries running normal to the ceramic/metal interface. These microstructures have superior strain tolerance but do not reduce the high-temperature thermal conductivity appreciably (~2.0 W/m K [9]). In contrast, the plasma-spray method results in layered and porous microstructures, with “splat” boundaries/cracks running parallel to the ceramic/metal interface. These defects, while effective in reducing the high-temperature thermal conductivity (0.8–1.7 W/m K [10, 11]), leave the top-coat relatively less strain-tolerant and are a source of weakness that ultimately result in the TBC delamination and/or spallation.

In this study we demonstrate the feasibility of a new processing method—solution precursor plasma spray (SPPS)—for the deposition of YSZ-based TBCs with novel micro/nanostructures and improved...
performance. Note that although the SPPS method has been described before [12, 13], those researchers [12] were unable to obtain high-quality coatings of usable thicknesses and controlled structures. Also, the properties of the resulting coatings were not reported. In the SPPS method a liquid-precursor feedstock is used instead of the conventional powder feedstock. (See [14] for a description of the conventional plasma-spray process.) Here we show that porous TBCs deposited using the SPPS method do not appear to contain the strength-limiting “splat” boundaries/cracks which are omnipresent in state-of-the-art, commercial TBCs deposited using the conventional plasma spray process. However, the new SPPS-deposited TBCs contain evenly spaced cracks running normal to the ceramic/metal interface, which are beneficial in providing improved strain tolerance [15]. In addition, the high-temperature thermal conductivity of the new TBCs was found to be comparable to conventional plasma-sprayed TBCs. Preliminary thermo-mechanical tests (cyclic) show that the thermal cycling lives of these SPPS-deposited TBCs are better relative to conventional TBCs.

It is believed that the aforementioned unique microstructural features in the SPPS-deposited TBCs have the potential for improving the durabilities significantly. Furthermore, the use of solution-precursor feedstock in the plasma-spray deposition offers several potential advantages over the conventional method, such as: circumvention of the costly powder-feedstock preparation step, better control over the chemistry of the deposit and the ability to deposit compositionally-graded coatings with ease, the ability to deposit coatings that are inherently nanostructured (nanometer-scale grain sizes), and processing versatility.

2. EXPERIMENTAL PROCEDURE

2.1. Processing

Figure 1 is a schematic illustration of the new SPPS deposition method, where an atomizer nozzle injects the solution precursor into the plasma flame. The precursor used here was an aqueous solution containing zirconium and yttrium salts, to result in a solid solution of 93 wt% ZrO₂ and 7 wt% Y₂O₃ (7YSZ) in the coating. All coatings reported here were deposited under nominally identical experimental conditions (plasma-spray parameters, solution-precursor flow rate and pressure, and torch-substrate distance). Coatings of thickness ~250 µm were deposited on bondcoated (~125 µm) single-crystal superalloy substrates (~25 mm diameter, ~3 mm thickness) obtained commercially; only one circular face of each substrate was coated. The direct current (DC) plasma torch used here was of the Metco GP type, which was attached to a six-axis robotic arm at the thermal spray facility at the University of Connecticut. The plasma power used was 35–45 kW. Ar and H₂ were used as the primary and the secondary plasma gases, respectively, whereas N₂ was used as the atomizing gas. The substrate was held stationary without external heating or cooling, while the plasma torch was scanned across the substrate by the robotic arm; multiple passes were used to build up the coatings. The substrate was CMSX-4 and the bond coat had the following composition (wt%): 51.5% Ni, 20% Co, 20% Cr, 8% Al, and 0.5% Y.

Conventional plasma-sprayed-deposited TBCs (~250 µm thick, 7YSZ) on bond-coated superalloy substrates (substrates identical to those above) were obtained from a commercial source. These TBCs were used as reference for the evaluation of thermal cycling life of the new SPPS-deposited TBCs. Coatings were also deposited on steel substrates for micro-structural characterization. Thicker (~1 mm) coatings were deposited on steel substrates, which were later removed from the substrates and were used for thermal conductivity and density measurements.

In an effort to understand the basic SPPS process, single-droplet deposits were thermophoretically extracted and characterized. The sample extraction was accomplished by inserting a glass-slide substrate (microscope slide) in the path of the plasma flame for a very short duration (100 ms) using a mechanical arm, where the substrate is oriented parallel to the centerline of the plasma flame. Owing to the vast temperature difference, the particles in the plasma flame are strongly attracted to the relatively colder substrate by thermophoretic forces [16].

2.2. Characterization

The TBC microstructures were observed using a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Two types of SEM specimens were used: (i) polished cross sections (1 µm finish) of the entire TBCs on substrates, and (ii) fractured cross sections of TBCs previously removed from substrates. The polishing was performed using routine metallographic techniques. These specimens (unetched) were sputter-coated with gold before observing in the SEM (ESEM 2020, Philips Electron Optics, The Netherlands). The fractured specimens were removed from metal substrates because they had to be thermally etched (at 1100°C...
for 1 h) in order to delineate grain boundaries. These specimens (uncoated) were observed in a high-resolution SEM (DSM 982, Zeiss DSM, Germany) equipped with a field-emission source.

Plan-view TEM specimens were prepared by first removing loosely bonded 7YSZ coatings (~250 µm thickness) from the substrate. Disks, 3 mm in diameter, were core-drilled from these coatings, and subsequently polished to ~100 µm thickness. The centers of these disks were then dimpled to a thickness of ~40 µm. The dimpled disks were subsequently ion-beam milled (PIPS and DuoMill, Gatan Corp., Pleasanton, CA) to perforation. Additional TEM specimens were also prepared by lightly crushing the coating, and dispersing the resulting particles onto carbon-coated TEM copper grids. The thermophoretically-extracted single-droplet samples were lightly scraped from the glass slide and were dispersed onto separate carbon-coated TEM copper grids. All types of TEM specimens (uncoated) were then observed in a conventional TEM (EM420, Philips Electron Optics, The Netherlands) operated at 120 keV.

As-sprayed TBCs were characterized using X-ray diffraction (Cu Kα radiation; D5005, Bruker AXS, Germany). The resulting diffractograms were analyzed to identify the phases present in the 7YSZ, and to determine the grain size using the Warren–Averbach method [17] with LaB6 internal standard.

The thermal diffusivity (α) was measured on a free-standing SPPS-deposited TBC specimen (9×9×1 mm) using the laser-flash method (Holometrix Micromet, Thermashot 2200) [18] as a function of specimen temperature. The specimen was previously coated with very thin layers of gold and carbon to prevent direct transmission of the laser beam and to enhance absorption/emission in the specimen, respectively. All the measurements were performed in Ar atmosphere. The accuracy of the thermal diffusivity measurements was within ±5%. The specific heat (c), as a function of temperature, was measured using differential scanning calorimetry (DSC-2, Perkin Elmer, Wilmington, DE) with alumina as the reference material. The thermal conductivity k is then given by k = ρcα, where ρ is the Archimedes immersion density.

2.3. Thermal cycling

The thermal cycling experiments were performed in a specially designed, automated furnace. This bottom-loading box furnace was preheated to a temperature of 1121°C. The following steps constitute one thermal cycle: (i) the furnace is opened by lowering the floor of the furnace (using an elevator) and the samples are placed on the floor. The samples are leaned against a refractory holder such that the TBC-coated circular face, which is almost normal to the floor, does not make contact with the refractory holder. (ii) The floor is raised and the furnace is closed; the time is set to zero. (iii) After 50 min, the floor is lowered and the samples are conventionally cooled using a fan for 10 min. Steps (ii) and (iii) are repeated. Each red-hot sample was observed visually during the cooling cycle. The occurrence of spallation, where the TBC falls off the metal substrate, is easy to discern. Delamination, where a portion of the TBC is detached but is still hanging onto the substrate, results in a distinct change in contrast: the attached area appears dark whereas the detached area appears bright. A sample was considered to have failed when the TBC failure area (spallation plus delamination) reached ~50% of the total TBC area. Note that in this test both the substrate and the coating are at the same temperature in the furnace. In an actual TBC application, the substrate is at a relatively lower temperature due to internal cooling, resulting in a thermal gradient across the TBC and relatively longer thermal cyclic lives.

3. RESULTS

Figure 2(a) shows the microstructure of a typical SPPS-deposited TBC in cross section, with several features of note. The coating is porous, with pores as large as ~10 µm. The immersion-density (Archimedes method) of a free-standing coating was measured to be 4762 Mg/m3, corresponding to 16.4% porosity (assuming a theoretical density of 5698 Mg/m3 [6]), which is typical of commercial plasma-sprayed TBCs. The X-ray diffraction analysis confirmed that these TBCs are primarily composed of tetragonal phase ZrO2. The most important feature in
these coatings [Fig. 2(a)] is the absence of horizontal, strength-degrading “splat” boundaries/cracks. As mentioned earlier, these are always present in conventional plasma-sprayed TBCs, and are typically several hundreds of microns long, as seen in Fig. 2(b). Also note the vertical cracks in Fig. 2(a), which were found to be spaced 100–300 µm across the entire coating (in cross section).

Figure 3(a) is a SEM micrograph of a cross-section fracture surface of a SPPS-deposited TBC, once again showing a complete lack of “splat” boundaries/cracks. Note the 3-D interpenetrating nature of the structure and the porosity. The loosely connected structure by “necks” is evident in the higher magnification SEM micrograph in Fig. 3(b). Also evident in Fig. 3(b) are submicron-scale features within the aggregates revealed by thermal etching. (SEM studies of specimens before and after thermal etching revealed that the etching only helped delineate the grain structure, without altering the fracture surface.) Although these features could not be resolved more clearly in the SEM, X-ray diffraction characterization suggests that these aggregates are polycrystalline in nature, and are composed of nanometer-scale grains. Significant X-ray line broadening was observed, the analysis of which resulted in an overall grain-size estimate of ~30 nm. The TEM studies further confirm these results, as described below.

Figure 4(a) is a dark-field TEM image of a “rounded” aggregate (~600 nm) showing its polycrystalline nature, with an average grain size of the order of 30 nm (crushed coating). Figure 4(b) is a bright-field TEM image of a region within the SPPS-deposited TBC (ion-beam-milled coating) showing uniformly distributed polycrystalline grains with an average size of the order of 20 nm. TEM studies also confirmed the tetragonal nature of the ZrO₂ phase in the SPPS-deposited TBCs; the presence of some amorphous phase, however, cannot be ruled out. Both SEM and TEM studies of the SPPS-deposited TBCs revealed no evidence of conventional “splats”—the primary deposition mechanism in powder-feedstock plasma-spray deposition [14].

Figure 5 shows the thermal conductivity of the SPPS-deposited coating as a function of temperature. Within experimental error, the thermal conductivity is independent of the temperature, and is about 1.3 W/m K. This compares with the reported values in the range 0.8–1.7 W/m K for conventional plasma-sprayed TBCs [10, 11].

Figure 6 compares the thermal cycling life of SPPS-deposited TBCs and commercially obtained conventional plasma-sprayed TBCs, which only differ
in their microstructures. Note the superior thermal cycling life of the SPPS-deposited TBC. It is acknowledged that these results are preliminary and that the number of specimens tested were few. However, considering the fact that these new coatings are not optimized and that the commercial TBCs have been in development for over three decades, these results are encouraging, with the potential for significant improvements in the durability of SPPS-deposited TBCs.

4. DISCUSSION

The failure of conventional plasma-sprayed TBCs under thermal cycling is an extremely complex process, involving an interplay between several phenomena, some of which are listed below (see e.g. [19–23]): (i) thermo-mechanical stress buildup, (ii) oxidation of the bond coat and the formation and growth of a thermally grown oxide (α-Al₂O₃) at the undulating interface† between the bond coat and the TBC, (iii) cyclic creep of the bond coat, (iv) depletion of Al in the bond coat leading to the formation of brittle oxides other than α-Al₂O₃, (v) sintering of the porous TBC and the attendant deterioration of strain tolerance and thermal resistivity, (vi) degradation of the metal/ceramic interface toughness, and (vii) delamination and spallation along “splat” boundaries/cracks.

In this context, the unique microstructures of the new SPPS-deposited TBCs offer two key advantages over the conventional plasma-sprayed TBCs. First, the absence of “splat” boundaries/cracks eliminates long, uninterrupted defects, which are otherwise relatively easy to propagate resulting in TBC failure [21–23]. Second, the presence of the evenly spaced cracks running normal to the ceramic/metal interface improve the strain tolerance of the SPPS-deposited TBC. Although failure mechanisms in both conventional and SPPS-deposited TBCs appear to be similar [21], a combination of the above desirable attributes appears to result in a delay in TBC failure. Note that the nanostructured nature of the SPPS-deposited TBCs does not appear to play a role in this regard. Therefore, the ubiquitous microstructural coarsening in these TBCs during high-temperature service is not likely to contribute towards performance degradation. The nanostructured nature of SPPS-deposited ceramic coatings, however, may be a desirable attribute in some other low-temperature applications such as wear-resistant coatings.

Although the SPPS method holds great promise for the deposition of a new generation of TBCs, the deposition mechanisms that result in these unique microstructures/nanostructures are not understood at this time. In this context, the results from the TEM characterization of the thermophoretically-extracted single-droplet deposits provide some clues. These deposits were found to occur in three main types of particle morphologies, as shown in Figs 7(a)–(c). Figure 7(a) shows a relatively large polycrystalline particle (~600 nm) which contains grains of sizes 50–100 nm. Figure 7(b) shows a network of much smaller particles (sizes 10–20 nm), which appears to be loosely bonded together. Figure 7(c) shows a combination of the two types of morphologies, where the

† The surface of the bond coat is roughened before the plasma-spray deposition of the YSZ for mechanically keying. However, these undulations also result in out-of-plane thermo-mechanical stresses arising from the thermal expansion mismatch and the oxide growth/accommodation.
Fig. 7. TEM bright field images of 7YSZ particles obtained from single-droplet deposition experiments. Three different types of particle morphologies were obtained: (a) relatively large polycrystalline particles, (b) aggregate of relatively smaller particles, and (c) a combination of (a) and (b) where the particle aggregates surround the larger particles.

larger particles are surrounded by the small-particle network.

There appears to be a close correspondence between the observed particle morphologies in the single-droplet experiments and features in the SPPS-deposited TBCs. The aggregates of YSZ grains seen in Figs 3(b) and 4(a) compare with the morphology observed in Fig. 7(a). The other type of particle morphology observed in Fig. 7(b) is similar to the fine nano-scale features which appear to cement the TBC together, as seen in Fig. 4(b).

These observations suggest that YSZ particles form during the SPPS process, in a manner similar to the flame pyrolysis process [24]. However, since the plasma flame temperatures (∼10^4 K) and velocities (10^2 m/s) are significantly higher than combustion flames, the kinetics of particle formation are likely to be considerably faster, resulting in particles in the nanometer size range. Also, due to the higher temperatures some of these particles appear to be sintered [Figs 4(a) and 7(a)] on their way to the substrate. The SEM micrographs of the fracture surface of a SPPS-deposited TBC in Figs 3(A) and (b) are reminiscent of partially sintered ceramics [5], which suggests that the intense heat of the plasma assists in the sintering of these different types of particles onto the substrate as they arrive. Continuous arrival and sintering of the subsequent particles onto the coating is likely to result in the coating buildup. It is possible that this process may be further assisted by vapor condensation, something akin to chemical vapor deposition. The intense heat of the plasma is also likely to result in the beneficial cracks running normal to the ceramic/metal interface [Fig. 2(a)] as a result of thermal shock [15].

Once again, no evidence of “splats” was observed in the SPPS-deposited coatings. This suggests that the conventional plasma-spray process of powder particle melting and rapid resolidification of the molten droplets (typically several tens of microns in diameter) into “splats” (a few microns thick, several hundreds of microns in diameter) on the substrate [14] does not play a role in the SPPS-deposition process. However, melting and resolidification of nano-scale particles during SPPS deposition cannot be ruled out. These processes at the nano scale are likely to be surface-tension dominated and may not result in “splats”.

As mentioned earlier, the SPPS-deposition methods offer several advantages over the conventional plasma-spray process and may have a broad appeal, beyond the deposition of the thermal barrier and structural coatings. There is a critical need for porous, nanostructured coatings in several other applications, for example biomedical materials for prostheses [25] and catalyst supports [26]. Thus, the SPPS process may be suited for the deposition of a wide variety of ceramic coatings for diverse applications.

5. SUMMARY

The new SPPS method can be used to deposit YSZ-based TBCs with novel structures and improved performance. These new TBCs have the following features: (i) absence of “splat” boundaries/cracks, (ii) evenly spaced vertical cracks, (iii) porous microstructures with nanometer-sized grains, (iv) low thermal conductivity, and (v) improved thermal cycling lives. It appears that the deposition mechanism consists of the following events in the plasma flame: (i) synthesis of nanoparticles from liquid precursor, (ii) deposition of the particles on the substrate, and (iii) partial sintering of the coating in the intense heat of the plasma.

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