Process-Structure-Property Relations for the Erosion Durability of Plasma Spray – Physical Vapor Deposition (PS-PVD) Thermal Barrier Coatings

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Abstract

New thermal barrier coating (TBC) materials and microstructures are under development to increase gas turbine operating temperatures beyond the ~1200°C threshold of standard 7 wt. % yttria stabilized zirconia (7YSZ). To deposit these advanced coatings, a new thermal spray deposition technique is used: Plasma Spray – Physical Vapor Deposition (PS-PVD). PS-PVD is capable of depositing from the vapor phase to yield strain tolerant columnar microstructures similar to Electron Beam – Physical Vapor Deposition (EB-PVD) or, alternatively, the traditional splat-like lamellar microstructure common to Air Plasma Spray (APS). This study investigates the process-structure relationships and resulting erosion response for plasma gas flow, amperage, and feed rate. It was found that in the selected design space, porosity and surface roughness vary

from ~12-26% and ~5-10 μm , respectively. Erosion behavior is discussed and the mechanism is identified to be heavily dependent upon the intercolumnar spacing. The lowest erosion rates are similar to EB-PVD, while the highest erosion rates were closer to APS. This is attributed to the hybrid nature of the PS-PVD process and provides an opportunity to tailor coatings with a wide range of properties, and thus performance.

1.0 Introduction

Thermal barrier coatings (TBCs) are utilized in gas turbines to protect the engine components from the high temperatures and oxidizing environment generated by the combustion process. As engine conditions have changed, TBCs have evolved from a simple protective outer layer to a specially designed multifunctional coating system where bond coats are tailored to substrates and topcoats are deposited for a given application environment (low thermal conductivity, low erosion, calcium-magnesium-alumino-silicate (CMAS) resistance, etc.). The TBC system is comprised of four parts: the nickel-based superalloy engine component or substrate, a metallic 'bond coat', the thermally grown oxide scale ($\alpha\text{-Al}_2\text{O}_3$) which forms on the bond coat, and finally, the ceramic topcoat. In this study, we have focused on the insulating topcoat, traditionally composed of 7 wt. % yttria stabilized zirconia (7YSZ). In the t' phase, 7YSZ exhibits a low bulk thermal conductivity ($\sim 2.5 \text{ W/m}\cdot\text{K}$ [1,2]) and sintering rate while possessing a relatively high fracture toughness ($2\text{-}4 \text{ MPa}\cdot\text{m}^{1/2}$) due to its ferroelastic behavior [3]. Unfortunately, it suffers from phase instability when experiencing temperatures above $\sim 1200^\circ\text{C}$ for prolonged periods [4] so replacement materials are needed for increased turbine inlet temperatures. Above this temperature, the material undergoes an equilibrium transition from the metastable t' phase to the equilibrium cubic and tetragonal phases, the latter of which

undergoes a martensitic transformation to the much larger (~5%) monoclinic phase upon cooling, often resulting in spallation [5]. Additionally, above this temperature ingested dust, sand, fly ash, and volcanic ash, generally referred to as CMAS, can melt and infiltrate the TBC resulting in chemical attack and loss of strain tolerance [6–10]. Due to the aforementioned issues, new materials are under development which exhibit lower thermal conductivities, higher thermal stability, and improved CMAS resistance. This includes the rare earth (RE) pyrochlore zirconates ($\text{RE}_2\text{Zr}_2\text{O}_7$) [1,2,11–14] which exhibit very low bulk thermal conductivities (~1.2 W/m*K) [2,11], high thermal stability limits ($\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore phase is stable to ~2300°C), and a significantly improved resistance to CMAS degradation [15,16] when compared to 7YSZ. However, the pyrochlore zirconates, along with many other new TBC materials, possess a low fracture toughness ($1 \text{ MPa}\cdot\text{m}^{1/2}$) [17] which results in poor durability both in terms of thermal cyclic life and erosion resistance [12]. This poor durability can be a limiting factor for utilization of these coating materials and thus for the improvement of gas turbine engine efficiencies.

One method of improving coating durability is through microstructural modification. For instance, the characteristic columnar microstructure of Electron Beam – Physical Vapor Deposition (EB-PVD) typically offers an order of magnitude improvement in erosion durability compared to a standard lamellar Air Plasma Spray (APS) coating [18]. Recent work has investigated methods to improve the durability of APS coatings via dense vertical cracking and deposition from small particle suspensions or precursor solutions [19,20]. The common factor in each of these methods is the formation of a vertically oriented porosity that inhibits lateral cracking and promotes strain tolerance, yielding erosion rates approaching EB-PVD. Additionally, composite structures have been shown to increase the erosion durability of cubic phase EB-PVD [12] and APS [21] coatings. This study investigates the process-structure-

property relations in a new hybrid process, Plasma Spray – Physical Vapor Deposition (PS-PVD). This process is very similar to standard APS or Low Pressure Plasma Spray (LPPS) methods, with the primary difference being that the pressure during deposition is in the range of 1×10^2 Pa compared to 1×10^6 Pa for APS and 8×10^4 Pa for LPPS. This facilitates vaporization of the molten particles [19,22–24]. Tailoring the degree of vaporization enables deposition of splat-like lamellar morphologies at high feed rates to pseudo-columnar morphologies at (generally) low feed rates and high powers [23]. This study investigates the interplay of processing parameters with coating microstructures and the subsequent effects on erosion durability with discussion on the erosion mechanism itself.

2.0 Experimental Procedure

MDC-153L PtAl bond coated (Alcoa Howmet – Whitehall, MI) Rene N5 (Sophisticated Alloys – Butler, PA) and $\text{Co}_{36.28}\text{-Ni}_{32.09}\text{-Cr}_{21.98}\text{-Al}_{9.02}\text{-Y}_{0.63}$ coated Mar-M-247 (Sophisticated Alloys – Butler, PA) 2.54 cm diameter x 0.32 cm thick discs were used as substrates. Prior to deposition, the discs were given a mild furnace treatment (705°C, 1 hour), abrasive blasted with fine alumina media and ultrasonically cleaned in acetone, ethanol and DI water for 20 minutes each. The top coat material used in this study was a t' Low-k composition (AE10054VF – ZrO_2 : 1.7 Y_2O_3 -1 Gd_2O_3 -1 Yb_2O_3 at. %) which was supplied by Oerlikon Metco – Westbury, NY. The d_{10} , d_{50} , and d_{90} particle sizes were 4.7 μm , 12.5 μm , and 20.2 μm , respectively. The top coats were deposited at NASA Glenn Research Laboratory using a Metco custom built PS-PVD rig. TBC powders were injected into the plasma torch with carrier gas flow rates of 10-12 normal liters per minute (NLPM) at feed rates (FR) of ~2-11 g/min at a spray distance of ~1.7-2.2 meters. Plasma gas flow (GF) through the torch was 80-120 NLPM resulting in pressures

ranging from ~0.8-1.12 Torr. An Ar/He plasma gas mixture ratio of 1:2 was fixed for all depositions in this study. These gas conditions have been shown to create high enthalpy plasmas with the very high temperatures suitable for PS-PVD [25]. Current (A) ranged from 1600-1800 A, yielding powers in the range of 70-90 kW. Substrate temperatures ranged from ~900-1020°C, as measured by two 'K' type thermocouples affixed to the front side of the mounting plate. The coatings were deposited as a function of gas flow (80, 100, and 120 NLPM), amperage (1600, 1700 and 1800 A), and powder feed rate (2.6, 6.6 and 10.5 g/min). When exploring each of the processing variables, one variable was changed while the other the intermediate conditions were used and held constant for the other two variables were held constant at their intermediate values. Therefore, only seven depositions were needed to investigate each of the relationships as the intermediate condition (100 NLPM, 1700 A, and 6.60 g/min feed rate) could be used across all three sets of experiments. Additional conditions were deposited to explore extreme conditions in order to bound behavior, with two conditions exhibiting particularly low and high erosion rates. These conditions were 88 NLPM, 1641 A, 4.2 g/min and 112 NLPM, 1641 A, 9.0 g/min (labeled C1 in and C2, respectively in Table 1)

Coating cross sectional microstructure and surface morphology was characterized via SEM (FEI Quanta 200 ESEM, Hillsboro, OR) and optical profilometry (Zygo NewView – Middlefield, CT) was used to measure surface roughness (Root Mean Square - RMS). During profilometry, a 50X/0.5X magnification was used with a 4x4 stitch (25% overlap) for a total field of view of 0.91 x 0.69 mm. Three locations were imaged for each sample, which were averaged to obtain the reported roughness value. Image analysis (GIMP v2.8.14) was performed on the coating cross sections to determine porosity by thresholding the grey level of high contrast backscattered electron (BSE) images into black and white images to determine percent porosity.

The cross sections used for image analysis were cropped to a minimum area of 75 μm thick by removing the highest area of the bond coat and the lowest area of the coating surface, therefore preventing bias due to surface porosity and the dense bond coat. During thresholding, ‘blurring’ of the edges of the intercolumnar particles as well as the columns can overestimate porosity. In order to minimize this bias, each image was thresholded at two levels and averaged over five image locations for each sample to estimate the porosity with the standard deviations reported.

Room temperature erosion was performed on the TBCs at Penn State University and has been described in detail previously [12,13,26]. Briefly, Al_2O_3 media with a mean particle size of 50 μm was used as the erodent and accelerated to a velocity of 100 m/s through a 38.1 cm long by 1.27 cm diameter stainless steel tube at a feed rate of 2 g/min via a vibratory feeder. The source to substrate distance was 22.9 cm ~~and an~~ at an impingement angle of 90° while the specimen surface was masked with a 1.27 cm diameter opening to produce an erosion scare of well-defined geometry. Specimen mass was measured prior to erosion and after every five grams of erodent fed using a scale with precision of 0.01 mg. Steady state erosion rates were determined by plotting the coating mass loss vs. mass erodent exposure after each five gram dose for a total of 50 grams of erodent and fitting a linear trend through the last five data points. Initial rates were calculated from the weight loss after the first five gram dose of erodent. It is important to note that most tests show a relatively high erosion rate initially that slowly decreases to a steady state value after several exposures. This steady state value is the number which is most characteristic of the TBC. Though these tests were performed at room temperature, high temperature erosion testing is also becoming more common [27] and will be considered for future work.

3.0 Results

3.1 Coating Morphology

All of the PS-PVD coatings exhibited a pseudo-columnar morphology, as observed in Figure 1. Column widths are on the order of 20-40 μm which is significantly larger than the 5-10 μm typically observed for EB-PVD coatings. The columns themselves are not fully dense and exhibit a chevron-like nucleation and growth morphology with porosity between the chevrons, similar to the feather morphology of EB-PVD columns. Intracolumnar porosity is present, as often observed in EB-PVD coatings. The diagonal nature of chevron-like nucleation and growth combine with the intracolumnar porosity would likely reduce the thermal conductivity of these coatings. The intercolumnar gaps appear to contain dense particles, many of which are less than 5 μm which suggests incomplete vaporization of molten feedstock material as the feedstock d_{50} was 12.5 μm . Figure 2 shows a cross section of powder which has been mounted in epoxy where there are larger particles with diameters of approximately 50 μm which may be difficult to fully vaporize after melting. The surface morphology was relatively uniform and is shown in Figure 3a with what has been described as a ‘cauliflower-like’ appearance. Figure 3b is a greyscale representation of the optical profilometry data which shows the surface morphology has been accurately captured by the optical profilometer and thus the resulting surface roughness values accurately characterize the surface. The ‘cauliflower-like’ surface morphology of the PS-PVD contrast to the splat-like appearance of an APS coating (Figure 3c) and the highly oriented and textured surface of an EB-PVD coating (Figure 3d). The rotation through the vapor plume combined with the elevated substrate temperature in EB-PVD results in a textured morphology where the tips of the columns appear as pyramid or A-frames, characteristic of a (200) growth texture. In the PS-PVD process, the vapor impinges uniformly

and perpendicular to the sample surfaces and results in a fiber-like texture which results in no observed preferred orientation in standard θ -2 θ scans. The lack of texture in the PS-PVD coatings results in cylindrical columns which are not as faceted as EB-PVD columns. Further evidence of the radially uniform growth can be observed in some of the micrographs, where columns appear to abruptly stop growing or seem to suddenly appear above porous regions (red circle in Figure 1). This is due to columns that are nucleating and branching into/out of the plane of the cross section.

3.2 Erosion Rates

An exemplary mass loss vs. mass erodent exposure plot is provided for the intermediate condition (100 NLPM, 1700 A, 6.6 g/min) as well as typical APS and EB-PVD samples in Figure 4. The coatings are characterized by a high initial erosion rate (0.9 g/kg in this case) which decreases until reaching a steady state erosion rate (0.112 g/kg in this case). All of the PS-PVD coatings investigated in this study exhibited this behavior. In addition, the typical EB-PVD and APS samples composed of t' Low-k are also provided in the graph for reference. The standard deviations in the sample weight result in error bars that are smaller than the data points in the coating mass loss vs. mass erodent exposure plots. In terms of standard deviations, the 100 NLPM, 1700 A, 6.6 g/min conditions were repeated several times (6) through the deposition matrix and the average erosion rate for these conditions was 0.111 ± 0.005 g/kg suggesting a good reproducibility and a standard deviation of less than 5%.

The room temperature erosion rate is shown as a function of gas flow (GF), amperage (A) and feed rate (FR) in ~~Figures 4~~ Figures 5a-c, respectively. Table 1 provides the structural data for each of the conditions as well as traditional EB-PVD and APS coatings for reference. As shown in ~~Figure 4~~ Figure 5a, as gas flow increased, the erosion rate increased from a low of 0.07

g/kg to a high of 0.13 g/kg. The deposition rate increased with gas flow while the porosity decreased. Increasing gas flows from 80 to 100 NLPM caused a 7% higher power and thus higher deposition rates. The surface roughness was relatively uniform across the gas flow conditions signifying similar growth behavior which suggests adatom mobility remains comparable. This is plausible as deposition rate increases with gas flow, thus reducing adatom mobility, and substrate temperature increases with gas flow, (100 °C for our conditions) thus increasing adatom mobility.

For increasing amperages, a decrease was observed in the erosion rate as shown in **Figure 4-Figure 5b**. In this case, the erosion rate started at 0.13 g/kg and decreased to 0.09 g/kg. Again, the deposition rate increased with amperage while the porosity values were relatively close (within standard deviations). The increased current causes a substantial 17% increase in power and thus the degree of vaporization which nearly doubles the deposition rate. This is a more drastic change in the vaporization, and thus a more significant impact on the deposition rate than when increasing gas flows. The large difference in deposition rate and plasma conditions results in the surface roughness showing a decreasing trend with amperage with a total change from 7.99 ± 0.43 to 5.55 ± 0.18 μm .

In **Figure 4-Figure 5c**, the erosion rate did not show a clear linear relationship with the feed rate; the erosion rates are relatively high at low feed rates then reach a minimum at intermediate feed rates and begin to slightly increase at higher feed rates. It should be noted that the thickness of the high and low feed rate conditions yielded slightly thicker coatings (136 and 149 μm , respectively) than the intermediate feed rate (107 μm) which could affect the results. It is currently believed from observations of thicker coatings of similar conditions that the morphology does not significantly change with thickness beyond ~ 75 μm , however this will be

confirmed in future studies. It is plausible that a non-linear relationship may exist between feed rate and erosion rate due to changes in deposition modes with feed rate, which is a phenomena that has been shown by Mauer *et al.* [23]. From the SEM images in Figure 1, the morphology appears to be primarily in the cluster/vapor/particle regime, however, the fraction of each of those constituents may change enough to cause non-linear erosion behavior as a function of feed rate. As expected, the deposition rate increased significantly with feed rate. Porosity decreased initially and showed minimal changes from intermediate to high feed rate conditions while surface roughness showed a similar trend to the erosion with an initial decrease to a minimum and then a slight increase. Additional conditions were investigated to understand the effects of depositing at combinations of low and high values of processing conditions. The two most extreme erosion rates from conditions C1 and C2 have been included in this study to enable a deeper understanding of the erosion mechanism by having a larger breadth of the erosion response. C1 (88 NLPM, 1641 Amps, 4.2 g/min) exhibited a very low erosion rate of 0.068 g/kg and C2 (112 NLPM, 1641 Amps, 9.0 g/min) exhibited a relatively high erosion rate of 0.5 g/kg.

4.0 Discussion

4.1 Process-Structure-Property Relations

Several clear relationships between the processing variables and the room temperature erosion rates (property) have been discussed, however, the structural linkage to form process-structure-property relationships is not always as clear. For example, with EB-PVD the deposition rate is often linked to the structure where higher deposition rates yield smaller and more fractionated columns. In this work, the deposition rate does not appear to correlate with the erosion rate which indicates a complex relationship between deposition rate and microstructure

that is likely tied to slight changes in deposition mode. To better understand the relationship between erosion and microstructural changes, the coatings were quantitatively assessed in terms of surface roughness. In the case of amperage and feed rate, the surface roughness appears to correlate with erosion rate where lower erosion rates occur for lower surface roughness values and vice versa. Intuitively, a larger surface roughness should yield a higher erosion rate, as there are more asperities which can be quickly worn down. This is especially true in columnar coatings, where a larger surface roughness indicates higher amounts of surface porosity and thus reduced mechanical stability. Likewise, a coating with a lower surface roughness presents fewer asperities and an increased apparent density, and therefore a more robust mechanical response. The relationship between surface roughness and erosion rate breaks down in the case of gas flow, where the surface roughness remained relatively stable while the erosion rates increased. This is likely a result of the surface not necessarily characterizing the bulk of the coating, where the steady state measurement is taken.

In ~~Figure 5~~ Figure 6, the surface roughness is plotted against the initial erosion rate (the slope of mass loss/kg fed after the first increment). The initial erosion rates are much higher than the steady state rates and correlate very well to the surface roughness. The linear fit confirms the relationship between surface roughness and erosion, and the magnitude of the initial erosion rates confirms the understanding that the roughness (and therefore porosity) at the surface causes increases in the erosion rate with respect to steady state. In addition, the same behavior is observed for the EB-PVD coating where the initial rate (calculated to be 0.24 g/kg) is roughly 3X higher than the steady state rate. This difference is less than the 9X change for the PS-PVD coating, which makes sense given the lower surface roughness of EB-PVD (2-4 μm) compared to PS-PVD (6.9 μm for this sample). On the other hand, the APS sample only has a minor

change from its initial erosion rate (calculated to be 1.485 g/kg) since the coating fails in a different manner. The fact that steady state erosion rates as a function of gas flow do not trend with surface roughness may therefore suggest a change in microstructure between the bulk of the coating where the steady state measurement is taken, and the surface of the coating where the initial measurement is made.

The porosity measurements minimized incorporation of surface porosity and so were expected to be a good representation of the bulk of the coating yet there were no obvious trends between measured porosity and erosion rate. This is surprising, as porosity clearly affects mechanical properties and therefore should affect the erosion rate. In the case of columnar coatings this relationship is not always the case as the column size can change while the porosity can remain unchanged and vice-versa. For example, column width can be reduced by half while intercolumnar porosity remains constant due to a concomitant change in intercolumnar spacing. Column width is an important factor in the erosion of EB-PVD coatings as increasing column width was simulated to cause increases in erosion rates [28]. To the authors' knowledge the literature presents no effective way to measure these column characteristics and therefore, as a first attempt, the average PS-PVD column width was measured manually using SEM images at a location 75 μm from the substrate. Unfortunately, it was found to be very difficult with standard deviations that effectively encompassed most of the results, as seen in the last column of Table 1. Though we cannot compare the column widths at each of the conditions, we can still derive useful information from these results. The overall 15-20 μm column widths in PS-PVD are significantly larger than those in EB-PVD which are typically 4-10 μm . Additionally, the magnitude of the variability indicates non uniformity of the coating morphology where a large standard deviation in column size results in a non-uniform mechanical response due to variations

in local stresses and column stiffness and bending. Another factor which could have an effect is the magnitude and changes in intra-columnar porosity; i.e. porosity which is contained within the columns. It should be noted that high resolution ($<1\ \mu\text{m}$ voxel) X-ray computed tomography could potentially enable much more quantitative microstructural characterization and help alleviate many of the challenges mentioned. Mechanical property measurements should correlate to the erosion response and enable a stronger linkage to the processing variables, however, good indentation data has been difficult to acquire for these microstructures. Preliminary measurements of the modulus of these coatings via dynamic mechanical analysis at NASA Glenn have yielded in-plane moduli values of 26-30 GPa, in line with that of EB-PVD at 28 GPa from Johnson *et al.* [29]. This suggests the coatings will have good thermal cyclic lives. Characterization of the mechanical properties and thermal cyclic lives of these coatings will be the subject of a future publication.

4.2 Erosion Mechanism

To understand the erosion mechanism for PS-PVD it is first helpful to examine what is known for EB-PVD and APS erosion as these mechanisms have been heavily covered in the literature [18,28,30–34] while erosion of PS-PVD has seen minimal investigation [20,35]. The velocities and particle sizes used in this study fit into the Mode I regime as described by Wellman *et al.* [30] where lateral cracking is the primary damage mechanism. In APS coatings, the large flaw population of splat boundaries, microcracks, and pores all serve as stress concentrators. During particle impact, these stress concentrators enable formation and propagation of lateral cracks. Successive impacts eventually cause crack linkage, which enables removal of regions of material comparable to the splat size of the sprayed coating. Figure 6 Figure 7a shows an SEM image of an APS coating after experiencing erosion where large

amounts of flaws and cracking are present. The arrows indicate regions of large cracks and possible avenues of crack linkage. When comparing these features to the scale bar, it is evident that large (50-100 μm) regions can be removed leading to relatively high erosion rates. In general, the EB-PVD columnar microstructure has a lower flaw concentration than the APS coating. However, the feathery pores at the column edges can act as stress concentrators which can then initiate cracking from particle impact. The important difference is the depth and size of the cracks in EB-PVD coatings which results in a much smaller damaged volume and lower material removal rate. Depending on impact velocity (and therefore energy) the impacting particles can cause large plastic deformations and significant bending in the columns, or significantly less deformation which results in minor densification near the surface. The latter is more descriptive of the erosion process observed in 100 m/s lab testing, and in this case, the cracking typically occurs just underneath this dense region, evidenced by the arrows shown in **Figure 6** **Figure 7b**. When cracks link up across several columns, the material is easily removed. However, in this densified region, relative flaw size is much smaller than APS ($\sim 5\mu\text{m}$ vs. $20+\mu\text{m}$). Additionally, EB-PVD coatings possess a lower flaw population than APS coatings, so it takes more successive impacts (time) to link the cracks than in the heavily flawed APS coatings. This leads to smaller volumes of material being removed, and a slower rate. The result is that APS coatings typically exhibit a 10x higher erosion rate compared to the same material deposited via EB-PVD.

In the PS-PVD coatings deposited in this study, the microstructures are similar to EB-PVD yet the erosion mechanism differs. **Figures 7** **Figures 8a-f** show SEM micrographs of samples after being eroded. The low erosion rate sample C1 shown in **Figure 7** **Figure 8a-b** exhibits densification at the top $\sim 1-2\mu\text{m}$ of the surface, resulting in a flaw size similar to EB-

PVD. However, the significant cracking that is typically observed under this dense layer in EB-PVD was not observed in PS-PVD. This could be due to the nature of the column widths. The column width at the surface of the sample in the PS-PVD sample shown in Figure 7 Figure 8a-b (~20-30 μm) is much larger than the EB-PVD sample (~4-10 μm) in Figure 6 Figure 7b. Thus, the energy required to form and propagate a crack through the entirety of the column is likely larger for the PS-PVD sample. Overall, the similarity in the flaw size and local failure regions results in similar erosion rates for benchmark EB-PVD (0.08 g/kg) and low erosion rate PS-PVD samples. In fact, the lowest erosion rate PS-PVD C1 (0.068 g/kg) performed slightly better than the baseline EB-PVD. It should be noted this EB-PVD sample was not optimized for the absolute lowest erosion rate as this could cause significant reduction of thermal cyclic life. For the intermediate erosion rate samples (intermediate conditions – 0.111 g/kg), there is more porosity and larger/less uniform intercolumnar porosity. The uniformity of the intercolumnar pores is important as regions with large intercolumnar gaps will be eroded at a higher rate as shown by the arrow in Figure 7 Figure 8c, resulting in an overall slightly higher erosion rate for the coating. Another note is that trans-columnar cracking was generally not observed in the low erosion rate coating, however, it was occasionally observed across the intermediate condition as shown in Figure 7 Figure 8d. Notably, the column which has cracked has a relatively small column size while the neighboring columns which have not cracked have larger column sizes. This suggests that in this type of microstructure, large columns may be favorable. This could be explained by considering an impacting particle of a given force which results in a stress wave. The wider columns would potentially spread the force over a larger area yielding a lower stress. Another explanation could be that the wider columns have a smaller aspect ratio and are stiffer which results in a smaller bending moment. For the high erosion rate sample C2 (0.5 g/kg), the

microstructure exhibits high porosity *and* regions of large intercolumnar spacing. This leads to local regions of severe erosion forming ‘divots’ in the surface, as observed in ~~Figure 7~~ **Figure 8e,f**. This phenomenon occurs due to the porous gaps having very low durability which results in a rapid erosion rate for that region. These divots then tend to form around columns and can allow individual columns to become isolated on the surface and experience the entire force of an incoming particle. An example of this type of behavior is provided in the SEM image in ~~Figure 8~~ **Figure 9** where a single isolated column is protruding from the surface (red arrow). This can lead to fracture of the columns and large material removal rates. The larger the gap, the larger the potential flaw size and in this case, the flaw size (tens of microns) is reminiscent of those seen in APS coatings. Not surprisingly, the erosion rate for the C2 coating was similar to what has been observed for APS t’ Low-k (0.78 g/kg). Though the PS-PVD microstructures all appear columnar, similar to EB-PVD, the flaw size or damaged volume of the eroded regions spans the gap from APS-like to EB-PVD-like, and therefore erosion rates vary nearly an order of magnitude.

5.0 Conclusion

This study investigated process-structure relationships and the resulting erosion rates for PS-PVD thermal barrier coatings composed of a rare earth doped t’ Low-k zirconia material. The resulting coatings were all t’ phase and exhibited a pseudo-columnar microstructure, similar to EB-PVD deposited coatings. The hybrid nature of the deposition technique is exhibited by the erosion rates which span nearly an order of magnitude range using the same feedstock with the highest rate still superior to a standard APS coating and the lowest rate marginally better than an EB-PVD coating. It is clear that more work must be done focusing on developing methods

which accurately measure microstructural features with the precision necessary for quantitative process-structure relationships. This is particularly the case for determining coating porosity and column widths/intercolumnar spacing. One method that does show promise is the application of optical profilometry to measure the surface roughness. It was found that surface roughness strongly correlates to initial erosion rates for all conditions explored, however for steady state erosion the surface roughness did not correlate for all conditions.

The erosion mechanism has been identified and has similarities with both EB-PVD and APS. For low erosion rate coatings, a densification and lateral cracking mechanism was observed, similar to EB-PVD coatings, with the exception that column sizes are significantly larger in PS-PVD and thus can be more resistant to fracture. For the high erosion rate coatings, intercolumnar gaps and pores serve as the primary flaws and are quickly eroded away; therefore coatings with larger gaps and pores have higher erosion rates and large pieces of material removed, similar to APS. Although the coatings all exhibited a vapor deposited pseudo-columnar structure, the erosion behavior was related to the flaw size which varies from EB-PVD-like to APS-like, depending on the size of the intercolumnar gaps and pores. The ability to span this large region enables this process to deposit coatings tailored for particular applications which may not be possible in a standard EB-PVD or APS process.

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Table 1: Processing conditions and resulting coating structures observed in this study as a function of plasma gas flow, amperage, and feed rate (patterns in bold). The same intermediate processing conditions are used for each trend, yielding a total of seven unique deposition conditions. For comparison, two additional deposition conditions were included, C1 and C2, along with typical APS and EB-PVD values. * Typical values for rotated components

Plasma Gas Flow	Amperage	Feed Rate	Power (kW)	Deposition Rate ($\mu\text{m}/\text{min}$)	Porosity	Surface Roughness ($\mu\text{m} - \text{RMS}$)	Thickness (μm)	Column Width (μm)
80 NLPM	1700 A	6.60 g/min	80.3	6.2	25.9 $\pm$ 3.6	6.91 $\pm$ 0.08	122	19.7 $\pm$ 5.3
100 NLPM	1700 A	6.60 g/min	83.2	6.9	15.3 $\pm$ 3.0	7.08 $\pm$ 0.17	107	14.4 $\pm$ 5.1
120 NLPM	1700 A	6.60 g/min	86.5	8.7	15.9 $\pm$ 2.5	7.01 $\pm$ 0.07	102	15.0 $\pm$ 4.8
100 NLPM	1600 A	6.60 g/min	76.9	5.2	17.1 $\pm$ 3.7	7.99 $\pm$ 0.43	136	20.0 $\pm$ 7.7
100 NLPM	1800 A	6.60 g/min	90.1	9.8	18.0 $\pm$ 3.4	5.55 $\pm$ 0.18	98	15.7 $\pm$ 4.3
100 NLPM	1700 A	2.63 g/min	82.4	2.3	19.4 $\pm$ 2.7	9.51 $\pm$ 0.29	149	18.5 $\pm$ 5.5
100 NLPM	1700 A	10.6 g/min	83.8	8.4	16.7 $\pm$ 2.7	8.42 $\pm$ 0.18	136	16.3 $\pm$ 4.4
88 NLPM (C1)	1641	4.2 g/min	77.2	3.66	18.2 $\pm$ 2.5	6.73 $\pm$ 0.37	149	15.2 $\pm$ 4.1
112 NLPM (C2)	1641	9.0 g/min	81.2	6.48	14.5 $\pm$ 3.5	10.06 $\pm$ 0.34	153	15.1 $\pm$ 5.0
EB-PVD	N/A	$\sim$ 0.5 g/min	N/A	2-4*	5-15	2 - 4	200	$\sim$ 4-10
APS	450	>100 g/min	45	>100	10-20	10 - 20	400	N/A

Figure 1: Cross sectional SEM micrograph of the PS-PVD coatings as a function of (a-b) gas flow – 80, 100, and 120 NLPM, respectively, (c-d) amperage – 1600, 1700, and 1800 A, respectively, and (e-f) feed rate – 2.63, 6.60 and 10.6 g/min, with (x) as the (100 NLPM, 1700 A, 6.6 g/min) intermediate condition used in each trend. The red circle shows a column which has branched into/out of the plane of the cross section due to the radial growth.

Figure 2: Cross sectional SEM of mounted powder showing a region with larger particles which may not fully vaporize in the plasma and are responsible for the intercolumnar particles.

Figure 3: (a) SEM surface micrograph and (b) optical profilometer 2D greyscale projection of the 100 NLPM, 1700 A, 6.6 g/min intermediate PS-PVD condition, both at the same magnification. The optical profilometry accurately captures the surface features. A surface SEM image of (c) an APS coating and (d) an EB-PVD coating are also given for reference.

Figure 4: Erosion plot for a PS-PVD coating deposited under the 100 NLPM, 1700 A, 6.6 g/min feed rate intermediate conditions, along with a standard EB-PVD and APS for reference. All PS-PVD coatings in this study exhibited a similar trend of an high initial erosion rate (0.9 g/kg for this condition) which decreases to reach a steady state rate (0.112 g/kg for this condition).

Figure 5: Erosion rate in g/kg as a function of (a) gas flow, (b) amperage, and (c) feed rate. Gas flow and amperage show clear linear trends while feed rate appears to show a minima.

Figure 6: Plot of initial erosion rate (g/kg) vs. surface roughness (μm) for the samples from this study. The initial erosion rate appears to correlate well with the surface roughness. This is most likely due to higher roughness surfaces yielding more surface area to impact and enabling break off events of areas that protrude from the surface.

Figure 7: Post erosion SEM micrographs of t' Low-k coatings deposited via (a) APS and (b) EB-PVD. The APS coatings erode as splat boundaries and microcracks link up – arrows in (a) – to enable removal of large pieces of material. The EB-PVD coatings erode as cracks form in the columns and propagate and link through multiple columns, enabling removal of material. This often occurs under a dense region, evident in arrows shown in (b).

Figure 8: Post erosion SEM micrographs of coatings from (a,b) condition C1, (c,d) intermediate condition (100 NLPM, 1700 A, 6.6 g/min), and (e,f) condition C2. The smooth surface C1 exhibits minimal surface densification (2 μm) and low erosion rates. This transitions into a rough surface for the high erosion rate coating C2. Highly porous regions are quickly eroded – arrows in (c) and (e/f) – leaving divots in the surface, further enhancing erosion.

Figure 9: Post erosion SEM micrographs of the coating from C2. The right side of the micrograph shows a column which has been severely eroded on both sides and is isolated on the surface. Incoming particles could easily snap this column, resulting in a large erosion rate.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table1

	Plasma Gas Flow	Amperage	Feed Rate	Power (kW)	Deposition Rate (μm/min)	Porosity	Surface Roughness (μm – RMS)	Thickness (μm)	Column Width (μm)
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