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High Efficiency Turbine Blade Coatings

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High Efficiency Turbine Blade Coatings

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Abstract

The development of advanced thermal barrier coatings (TBCs) of yttria stabilized zirconia (YSZ) that exhibit lower thermal conductivity through better control of electron beam - physical vapor deposition (EB-PVD) processing is of prime interest to both the aerospace and power industries. This report summarizes the work performed under a two-year Lab-Directed Research and Development (LDRD) project (38664) to produce lower thermal conductivity, graded-layer thermal barrier coatings for turbine blades in an effort to increase the efficiency of high temperature gas turbines. This project was sponsored by the Nuclear Fuel Cycle Investment Area. Therefore, particular importance was given to the processing of the large blades required for industrial gas turbines proposed for use in the Brayton cycle of nuclear plants powered by high temperature gas-cooled reactors (HTGRs).

During this modest (~1 full-time equivalent (FTE)) project, the processing technology was developed to create graded TBCs by coupling ion beam-assisted deposition (IBAD) with substrate pivoting in the alumina-YSZ system. The Electron Beam - 1200 kW (EB-1200) PVD system was used to deposit a variety of TBC coatings with micron layered microstructures and reduced thermal conductivity below 1.5 W/m²·K. The use of IBAD produced fully stoichiometric coatings at a reduced substrate temperature of 600 °C and a reduced oxygen background pressure of 0.1 Pa. IBAD was also used to successfully demonstrate the transitioning of amorphous PVD-deposited alumina to the α -phase alumina required as an oxygen diffusion barrier and for good adhesion to the substrate Ni₂Al₃ bondcoat. This process replaces the time consuming thermally grown oxide formation required before the YSZ deposition. In addition to the process

technology, Direct Simulation Monte Carlo plume modeling and spectroscopic characterization of the PVD plumes were performed.

The project consisted of five tasks. These included the production of layered periodic microstructures in the coating, the Direct Simulation Monte Carlo (DSMC) modeling of particle transport in the PVD plume, functional graded layer development, the deposition of all layers to form a complete coating, and materials characterization including thermal testing. Ion beam-assisted deposition, beam sharing through advanced digital rastering, substrate pivoting, hearth calorimetry, infrared imaging, fiber optic-enabled optical emission spectroscopy and careful thermal management were used to achieve all the milestones outlined in the FY'02 LDRD proposal.

Acknowledgment

The authors thank Jim McDonald, Tom Lutz, Richard Nygren and Tina Tanaka of the Fusion Technology Department for EB-PVD operations and SEM analyses, Mark Rodriguez, Alice Kilgo and Garry Bryant of the Materials Characterization Department for x-ray diffraction and sample preparation, Samuel Graham, Jr. and Brandon Olson of the Microscale Science and Technology Department for thermal conductivity measurements, and Greg Hebner of Lasers, Optics and Remote Sensing Department for helpful discussions on optical emission spectroscopy.

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1. Introduction

This report summarizes the work performed under a two-year Lab-Directed Research and Development (LDRD) project sponsored by the Nuclear Fuel Cycle Investment Area. The EB-1200 system, a 1200 kW electron beam system located at Sandia's Plasma Materials Test Facility [1], was modified to perform industrial scale electron beam-physical vapor deposition (EB-PVD) processing as part of this effort. The project consisted of five tasks. These included the production of layered periodic microstructures in the coating, the Direct Simulation Monte Carlo (DSMC) modeling of particle transport in the PVD plume, functional graded-layer development, the *in situ* processing of all layers to form a complete coating, and complementary materials characterization including thermal testing. A total of four PVD campaigns were performed during the two year duration of this project. The first campaign was dedicated to the production of periodic microstructures. The second campaign was dedicated to dual source evaporation and ion beam-assisted deposition (IBAD). The third and fourth campaigns focused on producing graded TBCs, complete coatings and the formation of an α -phase alumina scale.

TBCs produced by EB-PVD have superior adhesion and strain compliance due to their columnar morphology, yet possess higher thermal conductivities compared to plasma-sprayed coatings. One method to lower the thermal conductivity of EB-PVD TBCs is to produce a layered microstructure. Others have investigated the use of DC and RF biasing to achieve this end [2]. This report discusses the use of substrate rotation or pivoting as well as ion beam-assisted deposition as a means to provide a layered microstructure that lowers thermal conductivity. Briefly, these graded coatings start with a 1 μm layer of pure Al_2O_3 that functions as an oxygen diffusion barrier and quickly transition to 7% yttria-stabilized zirconia (YSZ) as first described by Schultz et al. [3]. The amorphous Al_2O_3 layer is transitioned to α -phase by continuous argon ion bombardment during its deposition. The Al_2O_3 evaporation rate is reduced as the YSZ evaporation is increased with the help of digital raster-controlled electron beam time sharing. During this process, both cyclic substrate pivoting and cyclic IBAD are used to produce a layered morphology. The top 20-50 microns of coating is pure YSZ.

Since heat transfer in YSZ occurs only through phonon (lattice vibration) transport and photon (radiative) transport at high temperature, a two-pronged approach was used to lower the thermal conductivity of YSZ. First, to enhance phonon scattering, argon ion bombardment was used to produce local density variations that generate strain fields and lattice defects and effectively scatter phonons and reduce their mean free paths. A two-grid, hot cathode ion gun with collimated beam optics was used for the ion bombardment [4]. It allows for independent control of the beam energy, current density, direction and background pressure. Secondly, grain boundaries and inter-columnar porosity (air-gaps) refract radiation and reduce photon mean free paths. In this effort, both the number of grain boundaries and the inter-columnar porosity were increased to enhance photon scattering by pivoting the substrate 30° about the normal using various frequencies. Using the above techniques, it was possible to produce layered structures on a sub-micron scale without sacrificing columnar morphology.

2. Experiment

A dual source evaporation technique was utilized on the EB-1200 EB-PVD coater to perform these LDRD experiments on an industrial scale. A detailed description of the EB-1200 facility can be found elsewhere [5]. A schematic of the experimental setup appears in Figure 1. Briefly, the EB-1200 is equipped with two horizontally mounted 40 keV von Ardenne vario-anode electron beams that share a common focal point in the chamber as shown in Figure 2 [6,7]. One 600 kW gun is used to provide auxiliary heating to the stainless steel thermal cage surrounding the YSZ ingot and alumina rod sources. The thermal cage, also referred to as the “doghouse” in industrial jargon, serves several functions. It radiatively heats the substrates, enhances recycling at the walls and shields the cold vacuum vessel from the plume. The other EB-1200 gun was de-rated from its original 600 kW to 150 kW by installation of a 9-mm-diameter cathode and anode. This configuration generates a small 2-mm-diameter beam that is bent 70° by a custom vacuum compatible sector magnet onto the YSZ ingot as illustrated in Figure 3 through Figure 6. The YSZ ingots are fed through a water-cooled copper hearth shown in Figure 7. The use of horizontally mounted e-guns allows the beams to traverse under the rake that normally holds the large industrial gas turbine blades. The “through-the-rake” beam configuration commonly used for aerospace blades is not possible for coating the large industrial gas turbine (IGT) blades needed for high temperature gas-cooled reactors (HTGRs). The sector magnet, also located below the rake, then deflects the horizontal beam onto the ingot(s) for source evaporation. A 10 kHz digital rastering system provides for easy setup of the beam sharing time between the YSZ and alumina sources.

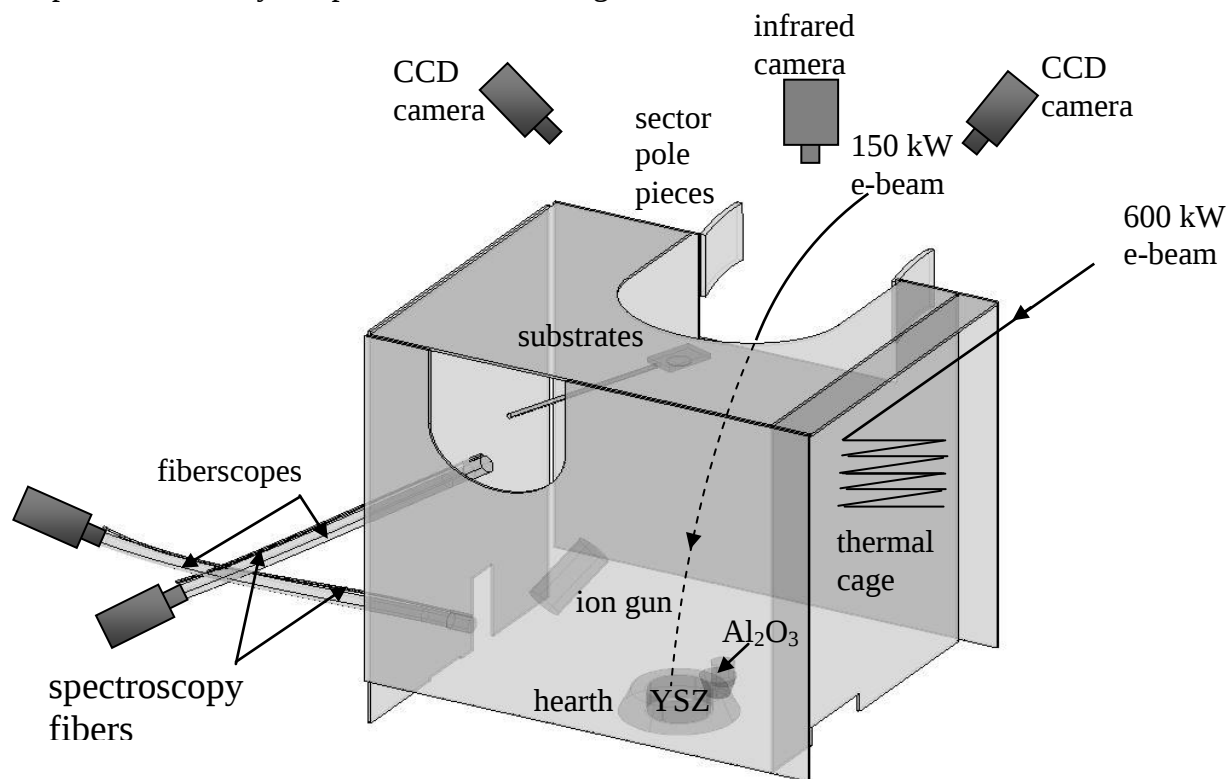


Figure 1. EB-PVD experimental setup

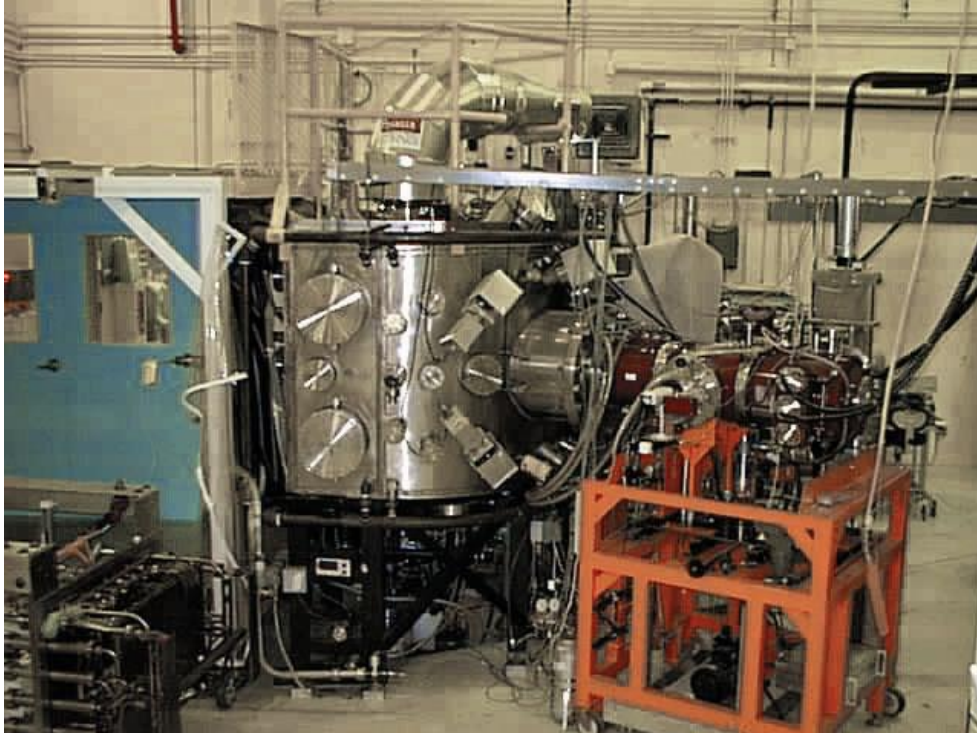


Figure 2. EB-1200 PVD Coater showing D-chamber and gun #2

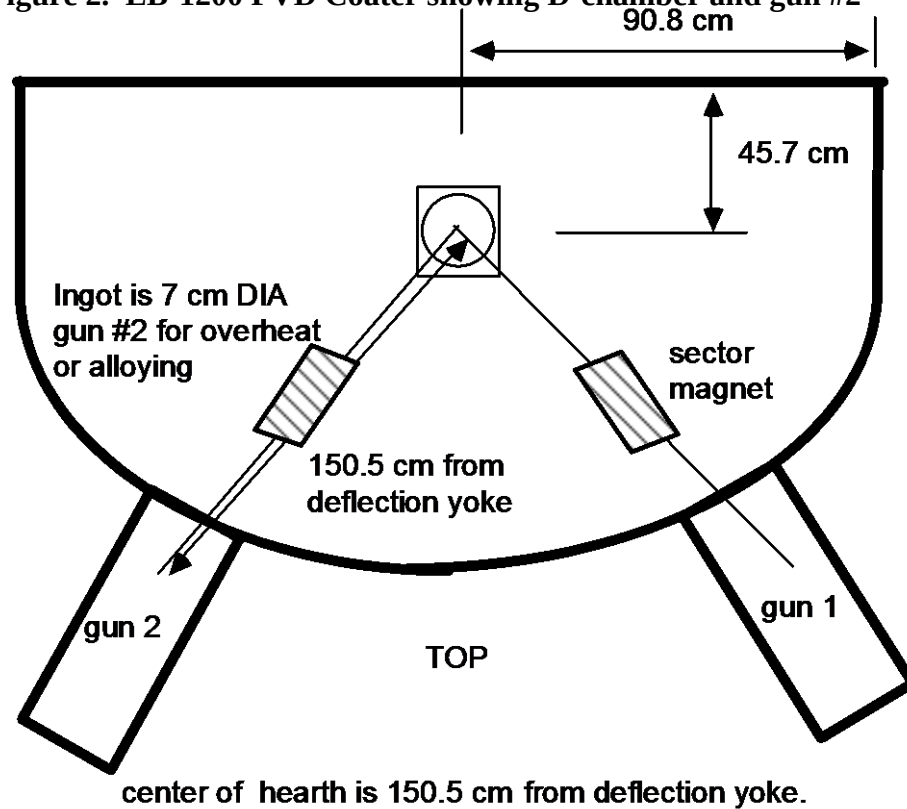


Figure 3. A single hearth and multiple guns are used in the current EB-1200 EB-PVD setup. Gun #2 can provide substrate overheat when operating with one hearth.

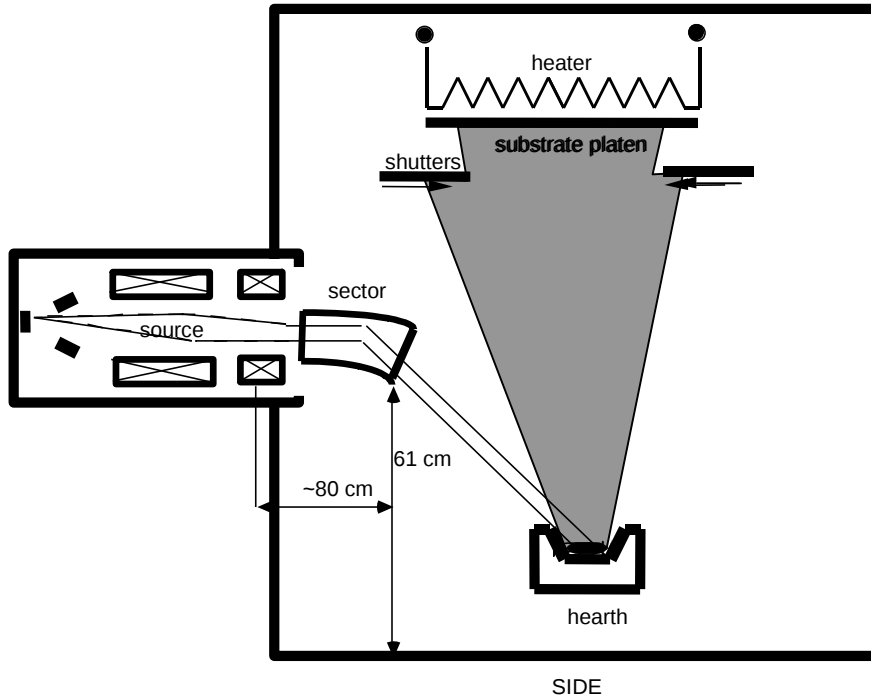


Figure 4. Concept of EB-1200 beamline equipped with an *in vacuo* sector bending magnet

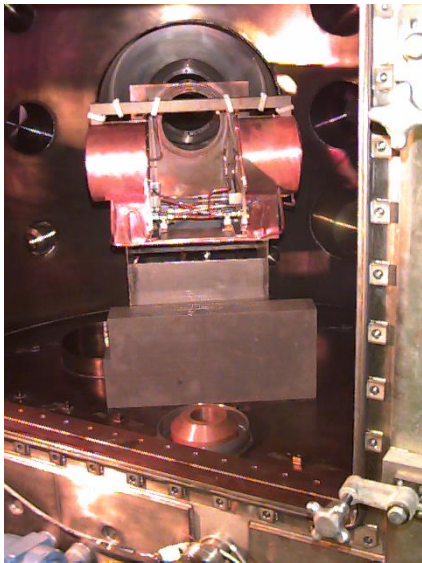


Figure 5. Sector bending magnet

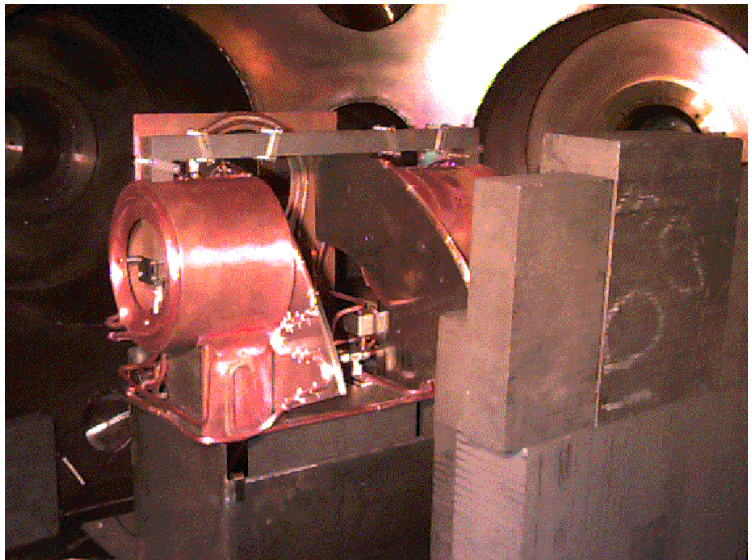


Figure 6. Bending magnet showing 70° pole pieces

The 70-mm-diameter, 20-cm-long YSZ ingots are fed by a load-locked, stepper motor controlled ingot feeder mounted under the EB-1200 chamber as shown in Figure 10. The alumina is placed in a 70-cc graphite crucible on the perimeter of the YSZ hearth. The ion beam-assisted deposition was performed with a 3-cm-diameter, collimated Kaufman ion gun installed in the thermal cage [8]. The gun supplies an Ar⁺ flux to the substrates

that are mounted on a single paddle several tens of centimeters above the vapor sources and connected to a parts manipulator. The manipulator or “stinger” provides rotation and horizontal translation into the EB-1200 chamber and is also equipped with 22 kW of quartz lamp preheat. The stinger, shown in Figure 8, is controlled by a programmable Fagor CNC controller pictured in Figure 9 [9].

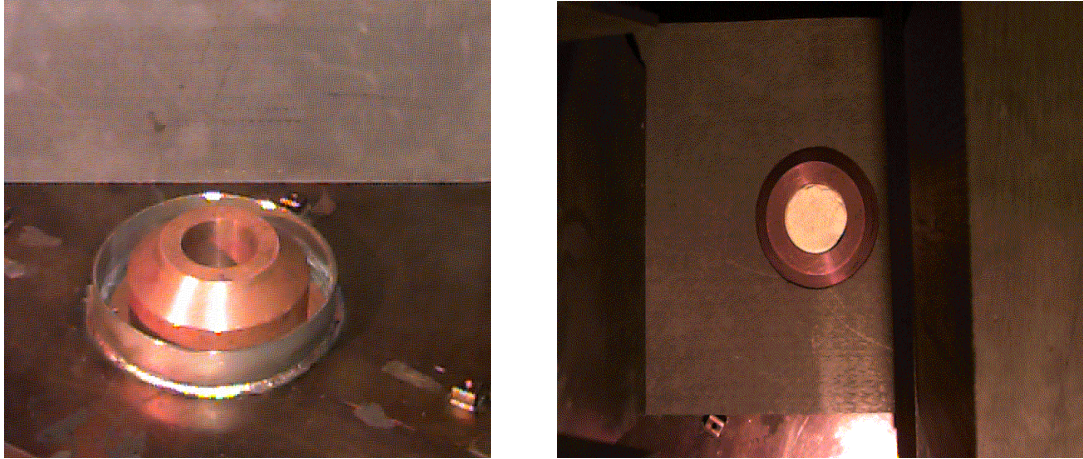


Figure 7. Water-cooled YSZ hearth (left). Hearth with loaded ingot and heat shields (right)

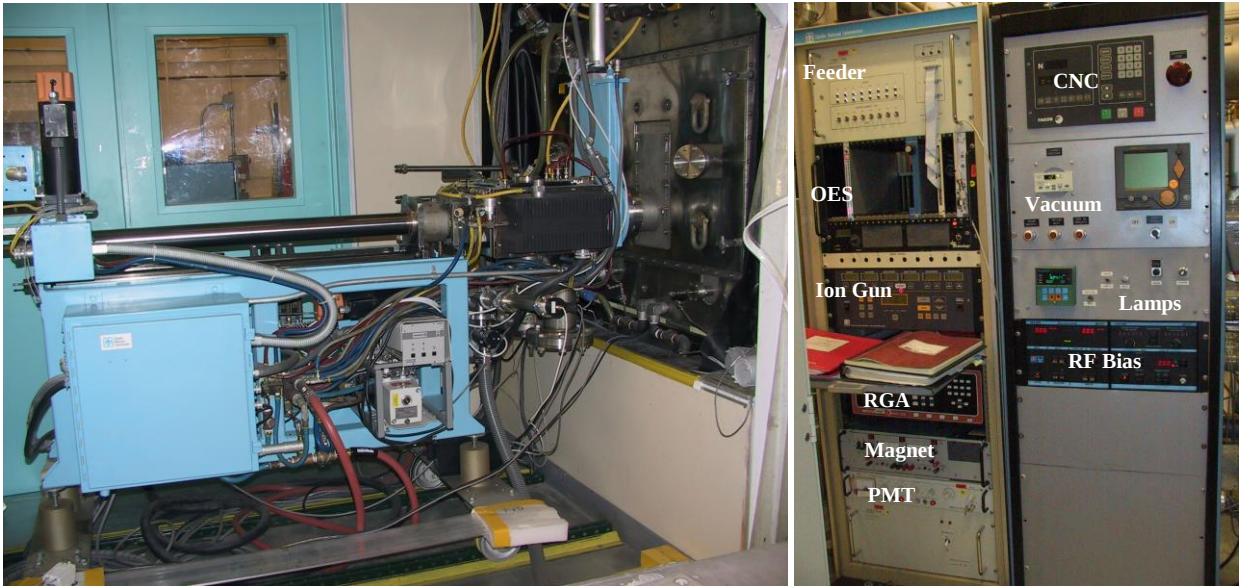


Figure 8. Stinger part manipulator

Figure 9. Stinger/PVD controls

Oxygen is injected into the process chamber at a maximum of 7.5 sccm to compensate for preferential pumping losses and retain stoichiometry in the coatings. Approximately 3.5 sccm of Ar flow is used through the ion gun. In addition, nitrogen gas is injected in the electron gun beamlines to screen out space charge. A pressure-controlled iris valve is

used on one of the two 3500 l/s cryo-pumps on the process chamber to control the pumping speed during depositions and maintain a 133 mPa background pressure.

The EB-1200 is equipped with a variety of diagnostics. These include a scanning infrared camera that views the YSZ ingot from above. Two port video cameras and two video fiberscopes are used to view the hearth level and the exposed substrates. In addition, two UV-grade fiber optic cables connected to a 0.3 m scanning monochromator interrogate the plume's optical emission just above the YSZ ingot and between the ion gun and substrate. Each substrate has a type-K thermocouple welded to the back. The thermal cage also has a type-K thermocouple to assist in the thermal management. The water-cooled hearth is equipped with a flow meter and inlet and outlet resistive temperature devices (RTDs) for real-time calorimetry as shown in Figure 11.

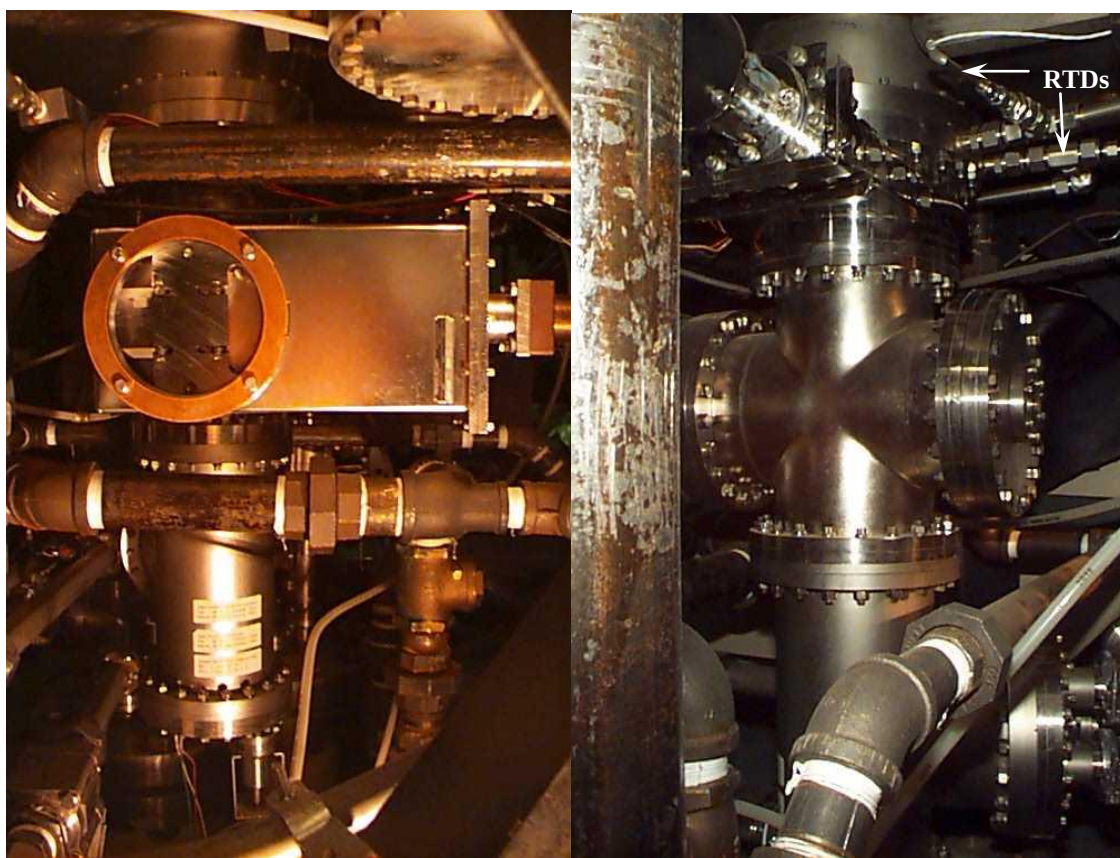


Figure 10. Ingot feeder loadlock and stepper motor drive

Figure 11. Ingot feeder viewport and isolation valve showing calorimetry RTDs on hearth

An elaborate infrared analysis package known as SandIR was developed in-house to process infrared camera images in real-time, correct for emissivity variations pixel by pixel, and plot absolute temperatures in a variety of ways. The SandIR graphical user interface (GUI) appears in Figure 12. Many analysis tools such as spots, ellipses, rectangles and lines are available to probe the image data either directly from the camera or from VHS video tape. Temporal line plots and real-time temperature profiles can be

displayed as well. SandIR is a multi-processor application that performs approximately 7 million temperature calculations per second on the 30 Hz NTSC camera frame rate. SandIR was used to determine the temperature profiles across the ingots. It was useful for pattern selection, focusing, positioning and sizing. The ingot surface cooldown rates obtained were also important for electron beam pattern switching and dwelltime determinations.

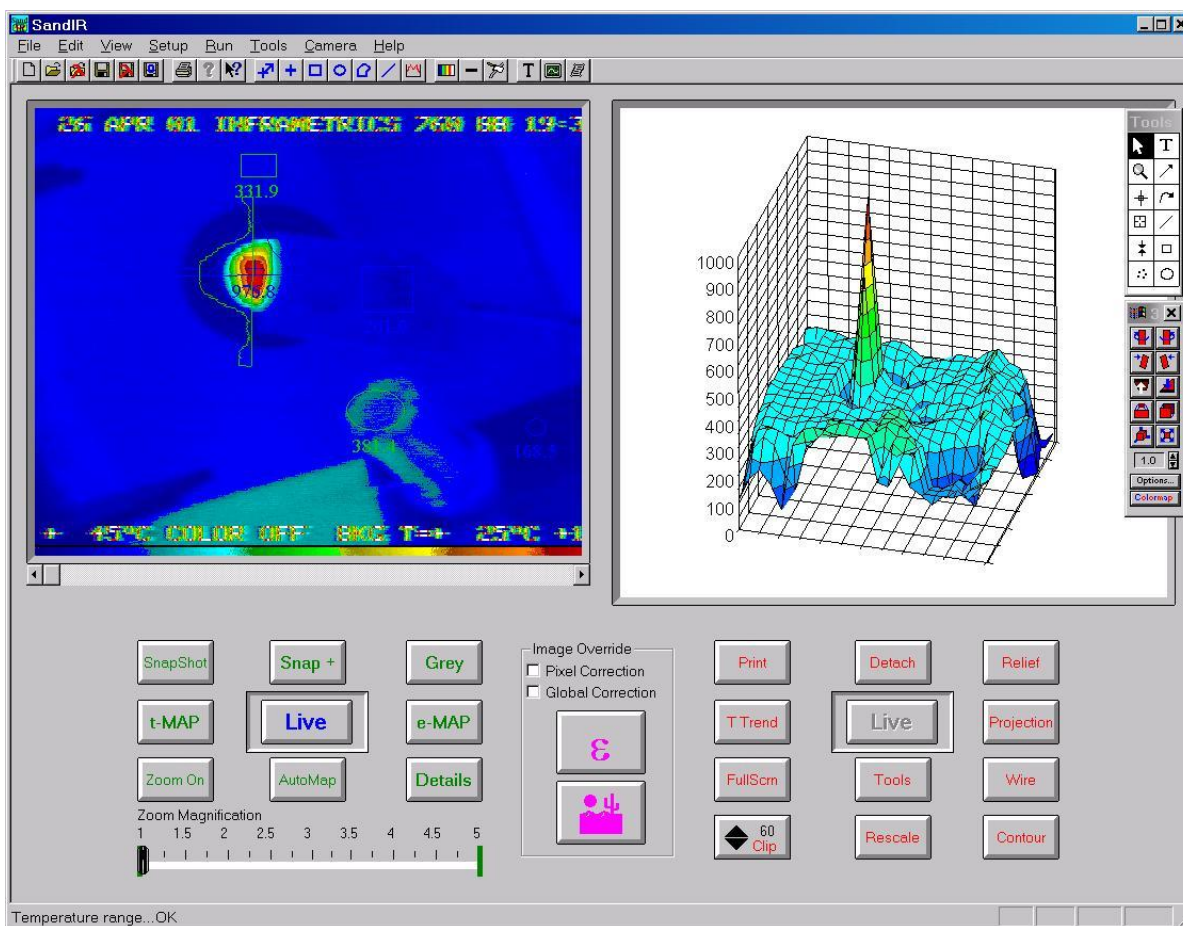


Figure 12. SandIR infrared image analysis GUI

Both EB-1200 electron guns were operated at 40 kV. Electron gun #2 was used to provide 8 to 10 kW of auxiliary heating by rastering a rectangular pattern about 10 x 10 cm² on the side of the stainless steel thermal cage. Most of the thermal cage heating, however, came from reflected electrons off the YSZ ingot. Electron gun #1 was typically operated at 25 to 40 kW to provide the source evaporation. At the start of FY'03, the 70° pole pieces on the sector bending magnet were replaced with the 30° pole pieces to minimize astigmatism in the beam spot caused by the large momentum dispersion in the beam. The shorter pole pieces required more current to bend the beam to the same required angle of deflection (70°), 0.55 A compared to 0.33 A for the longer pole pieces.

However, the shorter path length in the B-field did improve the spot focus and the pattern coverage.

The first phase of this program concentrated more on film morphology than adhesion. To save time and reduce costs, 25-mm-diameter Inconel 718 substrates were used. Ten substrates were coated in the first deposition campaign. Al was evaporated on the substrates to a depth of 50 μm using a small 270° electron beam evaporator. The Al-coated substrates were placed in the stinger, and the Al was allowed to evaporate and also partially diffuse into the Ni at 800 °C to form a thick (~ 40 μm) aluminide bondcoat. The aluminide coating acts as a diffusion barrier and improves adhesion. Typically, a few microns of pure aluminum remained on top of the Ni_2Al_3 layer. Then the substrates were allowed to cool to 600 °C and rotated in a 267 mPa (2 mTorr) oxygen background for approximately 2 minutes to nucleate an aluminum oxide scale. Next, the substrates were inserted into a pure YSZ vapor in a 267 mPa O_2 background with 5.1 sccm O_2 injection, while under 250 eV Ar ion bombardment from the Kaufman ion gun. Substrate pivoting at ± 30 degrees and 90 s cycle times were used with 30s on/30s off IBAD duty cycles. The substrate temperature was approximately 550 °C during the deposition.

The second deposition campaign investigated dual source plumes. DSMC modeling results were used to help position the alumina crucible and determine appropriate electron beam dwelltimes for each processing step. Several trials were run using various sets of dwelltimes and e-gun power levels. Reasonable agreement was obtained between overall weight gain measurements and the DSMC calculated deposition rates. The ion gun Ar^+ bombardment energy was increased to 500 eV and 19.5 mA of beam current. The O_2 feed was reduced from 5.1 to 4.0 sccm and the Ar feed was 3.15 sccm. The D-chamber pressure was 44 mPa (3.3×10^{-4} Torr) using both cryopumps. Argon sputtering of the substrates was used to remove residual oxide before the alumina deposition was initiated. Cleaning for 20 minutes with 575 eV Ar^+ bombardment was performed prior to the dual source deposition. Substrate pivoting was used with $\pm 30^\circ$ rotations and 10s cycle times to produce layering at the sub-micron level. Two Inconel 718 substrates were mounted on the backside of the paddle to determine the sticking coefficient of YSZ to stainless steel. The difference in weight gain between the direct deposited front substrates and the backside substrates which have no line of sight to the sources was used to estimate the percentage of atoms reflected from the thermal cage assuming only one reflection was possible.

This result, the wall sticking coefficient for YSZ on stainless steel, was used in the DSMC simulations to more accurately predict deposition rates from the plume. Optical emission spectroscopy was used to characterize the mixed plumes directly above the hearth. Figure 13 shows a typical scan from 500 nm to 800 nm with -900 V on the photomultiplier tube that causes saturation of intense peaks. Despite the saturation, quite a few peaks were identified. Micrographs of coatings deposited on the sides of the alumina crucible and that of the thermal cage, shown in Figure 14, clearly show the classic feathery texture of the large (non-pivoted) YSZ columns in the tetragonal phase. These columns compete for growth and become larger as the coating becomes thicker. The reduction in both void space and the number of grain interfaces raises the thermal

conductivity of the coating. These images can be contrasted with the layered morphology on the substrate coatings such as shown in Figure 15 that also contains a thermally grown oxide (TGO) layer of alumina. All were created with the same plume.

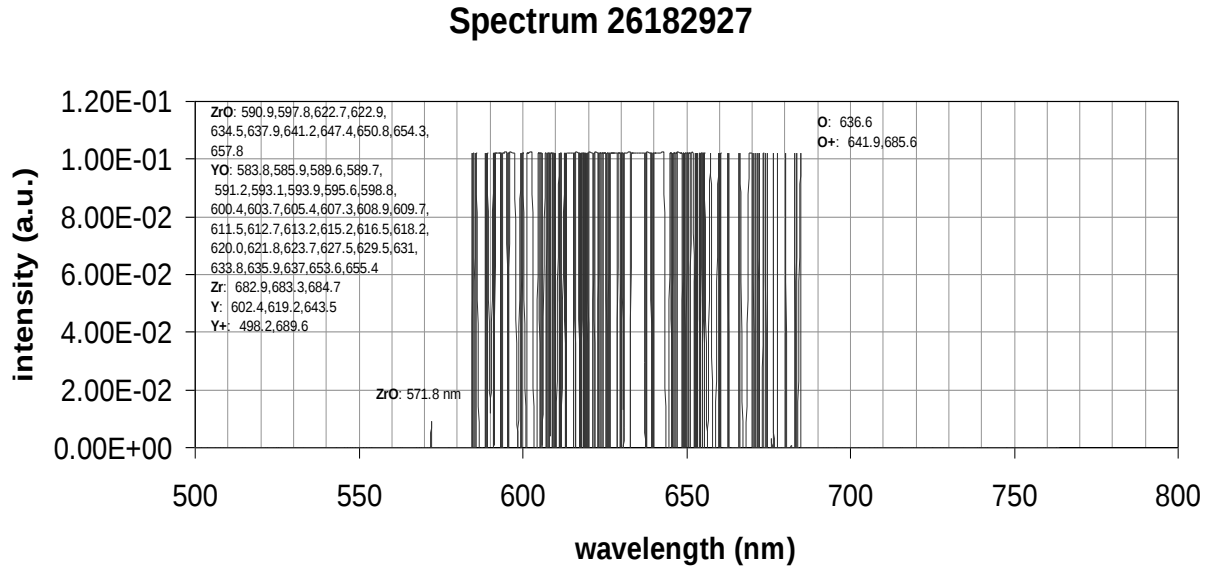


Figure 13. Saturated optical emission spectra with peaks identified

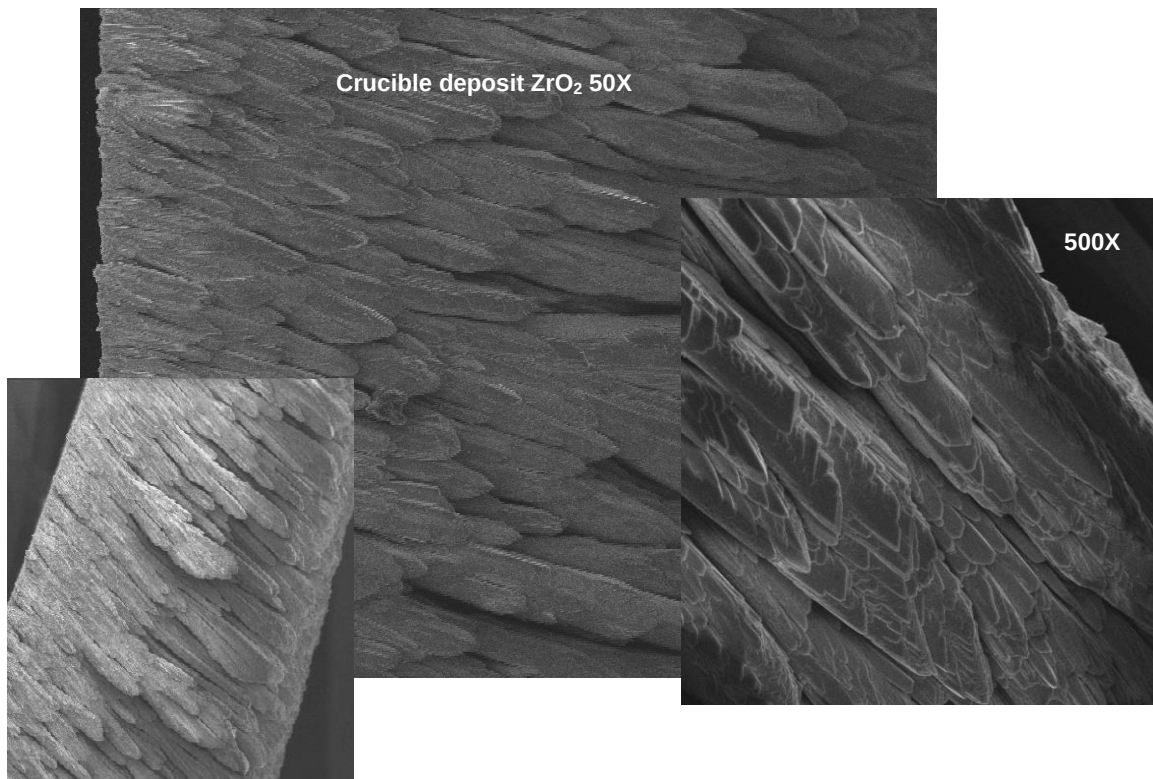


Figure 14. Typical columnar morphology of YSZ coatings deposited on crucible sidewalls (no layering)

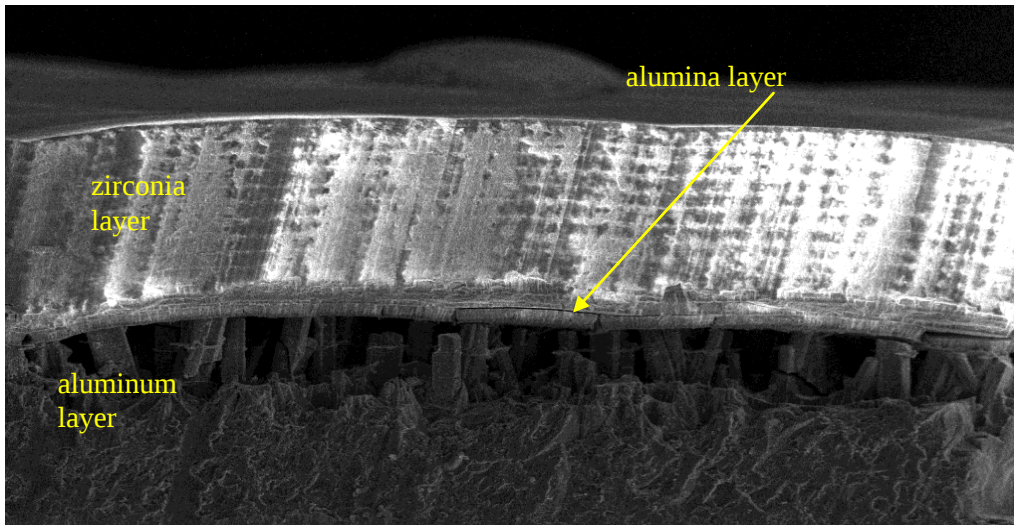


Figure 15. Multi-layer zirconia (~450 μ m) with underlying layers of alumina (~20-25 μ m) and aluminum (~400-500 μ m)

The third deposition campaign focused on graded layer development. All parts of the coating were deposited including the alumina diffusion barrier, graded layer, and pure YSZ top coat. Two Ar⁺ ion energies were investigated, 387 eV and 575 eV, for the IBAD. The D-chamber pressure was at 267 mPa (2 mTorr) with 7.5 sccm of background O₂ injection and 3.71 sccm of Ar feed through the ion gun. A cracked quartz window on the stinger interrupted the initial deposition. The windows were eliminated from the design, and the depositions continued after a lengthy delay. Substrate temperatures during the deposition were near 600 °C.

Energy dispersive x-ray (EDX) line scans across coating fracture surfaces were used to confirm that proper sequence switching was performed to produce a nearly linear gradient through the thickness starting with alumina and ending with pure YSZ. A scanning electron microscope (SEM) micrograph and EDX scan of the first mixed layer depositions appear in Figure 16 and Figure 17, respectively. These were much improved in the fourth deposition campaign discussed in section 4, under task 5.

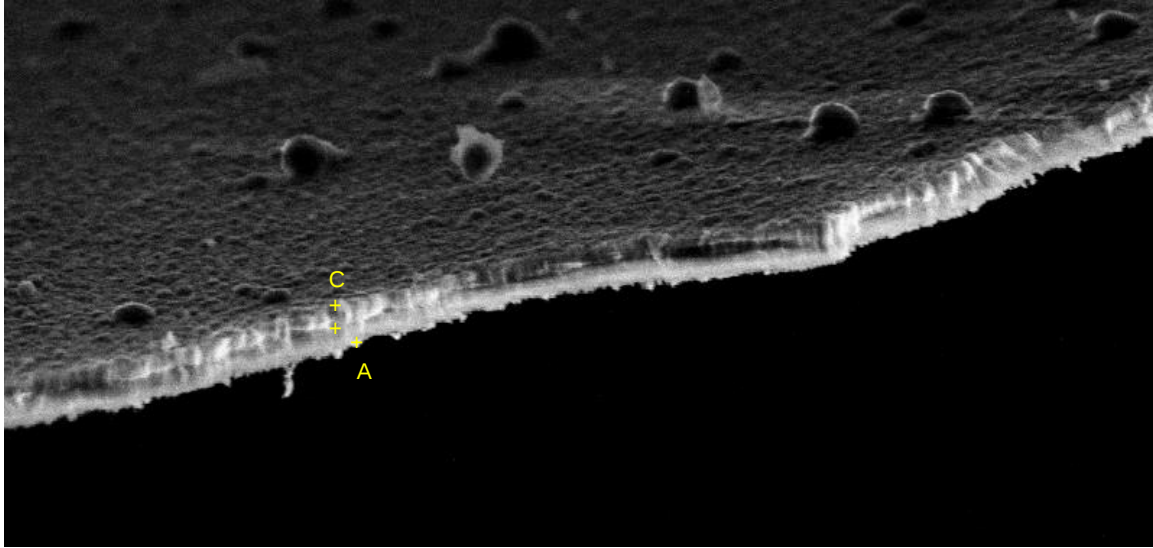


Figure 16. SEM micrograph of the first deposited mixed layer

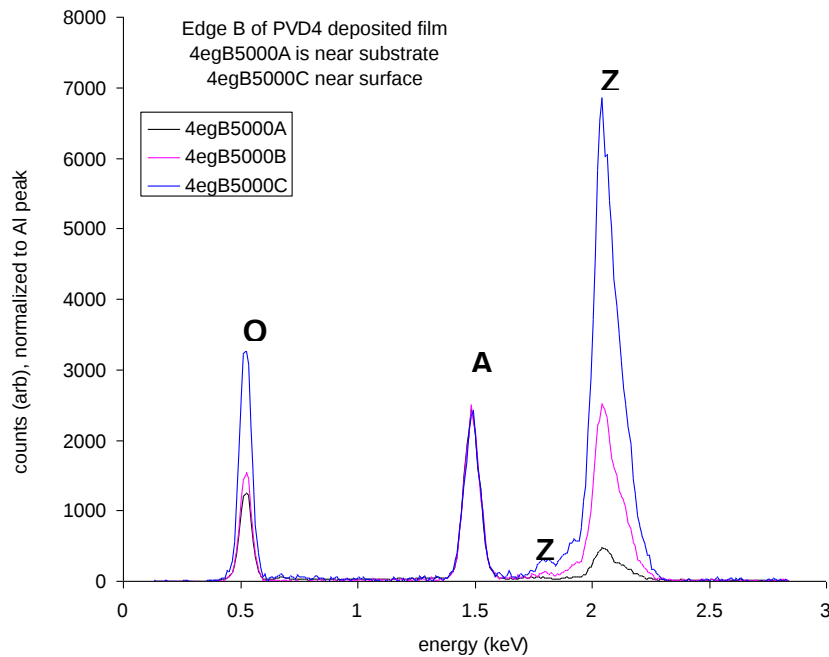


Figure 17. EDX spectra at labeled spots across the fracture surface

Unfortunately, this project ended before additional deposition runs could be performed to minimize the pure alumina layer and to minimize the depth of the gradient layer. This would ensure the lowest possible thermal conductivity for the entire coating and improve adhesion between the alumina scale and YSZ top coat. This important optimization remains to be performed. It was one of only two subtasks that were not completed in the

allotted time. It was deferred, because the direct deposition of the alumina scale and the controlled transformation of amorphous and γ -phase alumina to α -phase was identified as an important advance in the technology with high commercial value. Again, aluminum-coated substrates were subjected to a two hour heat treatment at 850 °C using the stinger. This produced a Ni_2Al_3 bondcoat approximately 40 microns deep.

The fourth deposition campaign was dedicated to producing coatings where distinct portions of the coating could be analyzed. Since YSZ is a high-Z material, x-rays cannot penetrate the top coat layer during x-ray diffraction (XRD) analysis. The estimated x-ray penetration depth on ZrO_2 is only 4 microns. Therefore, the phase and composition of the underlayers cannot be analyzed once a 50 micron layer of YSZ is applied. However, it was required to verify the transitioning of as-deposited alumina to α -phase alumina using IBAD. Clarke has demonstrated the use of a new technique, piezo-spectroscopy, to view through the topcoat and determine the alumina phase [10]. Unfortunately, we had no such in-house capability. Therefore, selected substrates were removed from the sample paddle after the completion of each processing step for SEM and XRD analyses of the coating produced during the preceding step. The following procedure was used: 1) heat treat all substrates for two hours at 850 °C, 2) remove sample #1 and 3 for XRD analyses, replace with In-718 blanks, 3) begin IBAD and perform pure alumina deposition at 900 °C, 4) remove substrates #2 and 4 for SEM and XRD analyses, replace with In-718 blanks, 5) perform Al_2O_3 /YSZ grading with cyclic IBAD and pivoting at 900 °C, 6) deposit pure YSZ top coat. Substrate #5 contained the full coating, while the blanks in 3 and 4 contained partial coatings for SEM, EDX and XRD analyses.

IBAD with a 575 eV argon ion flux at 19.5 mA was performed throughout. Substrate pivoting began with the graded layer processing in step 5. An argon flow rate of 4.11 sccm was used with 0.7 sccm of O_2 to produce a total D-chamber pressure of 36 mPa (2.7×10^{-4} Torr). The pressure increased to 56 mPa (4.2×10^{-4} Torr) during the processing. The lower pressure was used to extend the ion gun filament lifetime, which was much too short in the O_2 rich backgrounds of the second campaign. The lack of O_2 produced non-stoichiometric YSZ coatings, and the combination of O_2 deficiency and IBAD resulted in deposition of a predominantly cubic phase Zirconia coating. The thermal cage temperature reached 700 °C and the substrates reached a maximum of 755 °C during the processing. The substrate thermal history is shown in Figure 18. It was complicated by repeated failure of the computer system during the data acquisition. Unfortunately, this type of thermal history was more the norm than the exception throughout most of the project due to unexpected equipment failures, power outages, operator error, and computer glitches.

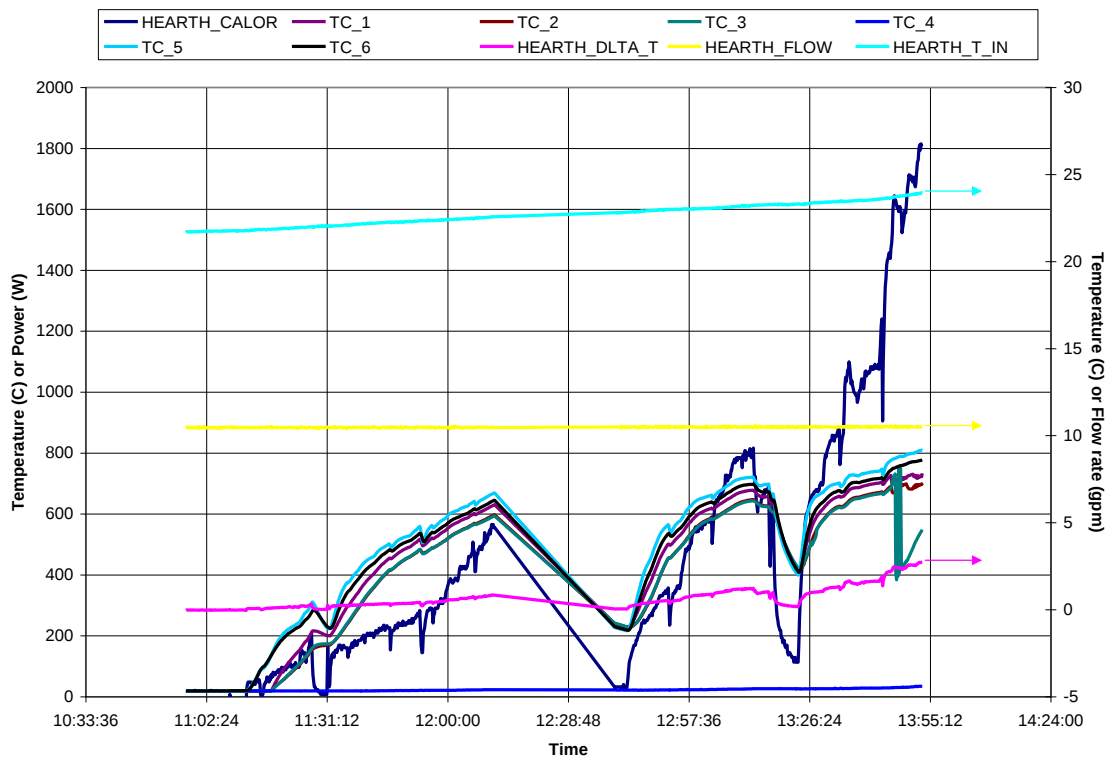


Figure 18. Substrate thermal history of deposition campaign #4

SEM micrographs, EDX line scans and XRD spectra are presented in section 5. Of most significance, the analyses confirm the existence of predominantly α -phase alumina directly above the bondcoat. Although, some cubic phase alumina also exists. A nearly linear composition density gradient from pure alumina to pure YSZ is also present. These topics are discussed in much more detail in section 5 of this report.

3. Modeling

Modeling Technique

An atomistic simulation of the deposition process complemented the experimental work. Direct Simulation Monte Carlo (DSMC) modeling of the PVD plume was undertaken using a massively parallel 2-D code, ICARUS, developed at Sandia [11,12]. As an atomistic method, DSMC is ideally suited to deal with complicated physics and chemistry in the gas flow field.

In the DSMC methodology a gas flow is represented by the motion of a number of “computational molecules”, each of which represents a large number of real molecules. A computational molecule travels at constant velocity until it experiences a collision with another computational molecule. Collisions are binary and change the velocities and the internal energies, but not the positions of the colliding pair of computational molecules. It

should be noted that computational molecules have three-dimensional velocity vectors for collision purposes, regardless of the dimensionality of the geometry. The result of this approach is a statistical, physical simulation of the dynamics and interactions of thousands of gas molecules.

A computational mesh is used in the DSMC method for identifying possible collision partners and to accumulate statistical information. Moments of the molecular velocity distribution function are accumulated over one or more time steps within each mesh cell to yield gas quantities such as the number density, velocity and temperature. Forces on molecules, such as gravity or electrostatic forces for ions, can be incorporated. To preclude non-physical behavior, time steps and mesh cells are constrained to be less than about one-third of a collision time and one-third of a mean free path, respectively.

Typically, the transport of 5 million computational particles representing 10^{10} to 10^{14} real molecules are simulated and run using up to a 1000 processors of a 3 Tflop capable ASCI Red massively parallel computer at Sandia National Laboratories. Parametric studies of the oxygen injection, excitation states, chemistry, and thermal management were performed on a 2-d axisymmetric DSMC model of the thermal cage and ingot.

Grid generation

Based on the above considerations the geometry shown in Figure 19 was developed. *Icarus* the DSMC code used for the simulations requires a block structured Cartesian description of the flowfield.

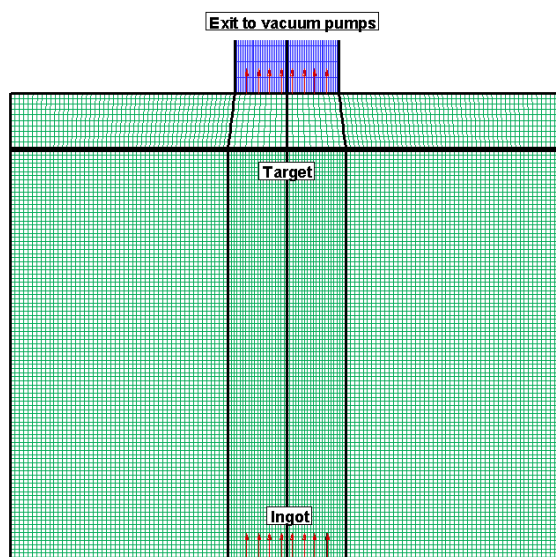


Figure 19. Grid used in the simulations

The flow comes from the bottom of the domain (red arrows) impinges on the target and exits through the blue region (vacuum pumps). The cells used in the simulation were a third of the local mean free path satisfying Bird's goodness criterion for grid resolution.

Description of the Flowfield

Figure 20 presents the number density profile and the contour lines for a double ingot case (Zr/Y and Al ingots). The gases are released from the bottom of the domain. It should be noted that the second plume (Al) is modeled as a ring source surrounding the circular plate Zr/Y source. It is interesting to note the formation of two recirculation zones. The bottom one consists of Al molecules that are “trapped” between the wall of the “doghouse” and the ingot. In a real situation with two ingots this phenomenon wouldn’t have been realized. The formation of this recirculation zone does not affect the rest of the flowfield (close to the target) that is of interest.

The second recirculation zone close to the target is formed by molecules that are trapped between the incoming molecules and the target. This recirculation zone would appear in a realistic three dimensional case. The formation of the recirculation region close to the target enhances the probability of a molecule getting deposited to the target by extending the time molecules spend close to the surface.

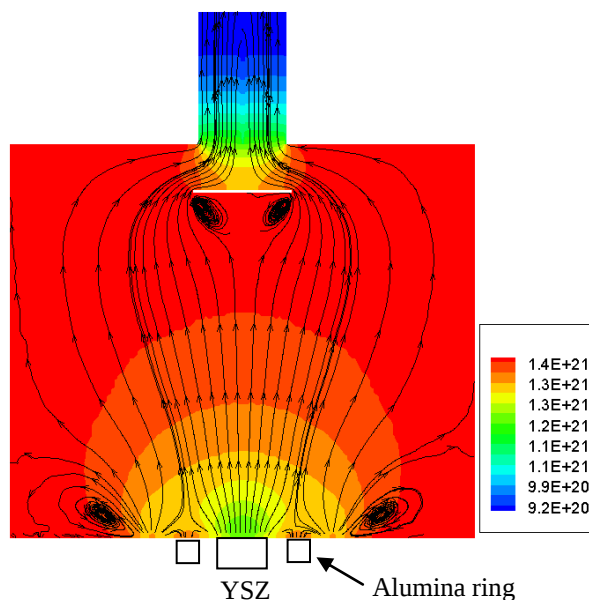


Figure 20. Number density and streamlines for a double ingot case

Thermal equilibria data for YSZ and alumina were obtained from the literature as well as partial pressure curves for Al_2O_3 , ZrO_2 and Y_2O_3 . It was discovered from the experiments that high quality coatings are obtained only when both the YSZ and the alumina ingots are vaporized with sufficient thermal energy to completely disassociate their constituent molecules. The simulations revealed that the PVD process is characterized by almost collisionless transport in the plume. A limited amount of recombination occurs in the plume just above the ingot, forming ZrO ; but fully stoichiometric molecules are only obtained on the hot substrate. The thermal equilibria

data presented in ref. 15 indicate that the evaporation of ZrO is essentially a step function occurring near 2330 K for ZrO_2 . In the case of Al_2O_3 , pure atomic species are evolved above 2170 K. When these curves are correlated with their corresponding vapor pressure curves, it indicates that the window for temperature control of the evaporation rate is quite small; and therefore, only the addition of biasing or IBAD can enhance the control. This is discussed more fully in the results section under Task 2.

Detailed simulation of the processes involved was inhibited by a lack of physical and chemical data concerning the chemical species involved and the chemical reaction rates between them and exposed surfaces. It is worth noting that currently there is no comprehensive theory that allows modeling of these interactions. As a result the numerical investigation was limited to a parametric analysis of the problem.

The topics considered were:

1. *Three vs two dimensionality*
2. *Surface chemistry*
3. *Internal degrees of freedom*
4. *Gas phase chemistry*
5. *Addition of Al in the plume*
6. *Plume effects from electrostatic fields*

The results from each of these topics are discussed below under Task 2.

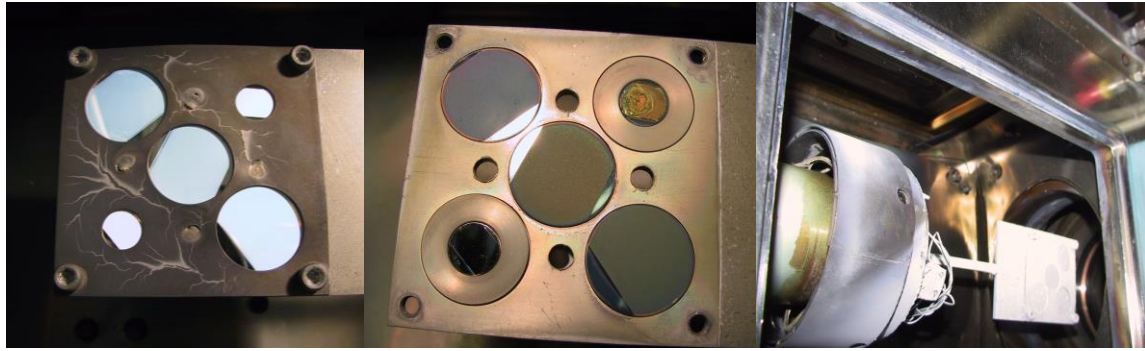
4. Results

Task 1: Periodic Layer Development

Three methods were proposed to control layering on the sub-micron scale. These were substrate pivoting or cyclic rotation, cyclic ion beam-assisted deposition, and cyclic RF biasing. Each method depended on the special capabilities of the EB-1200 PVD coater. Substrate pivoting utilized the water-cooled load-locked parts manipulator known as the “stinger” and its programmable CNC motion controller to rotate the substrate paddle to the orientation desired at the proper time intervals. The cyclic IBAD used the capabilities of the Commonwealth 3-cm hot cathode ion gun and controller to produce a time-gated flux of argon ions on the substrate at the desired duty cycles. The ion gun controller has an extensive recipe library in which the gun parameters could be pre-programmed for easy recall. Although RS-232 computer control is an option, it was not utilized for this project, and the ion gun was manually cycled on and off. In the future, such control could completely automate the ion gun cycling, making such operations much easier to perform. The cyclic RF biasing relies on the Advanced Energy RF power supply and matching network [13]. It also is RS-232 controlled and has an auto-tune feature. Once tuned to the RCL and vacuum conditions, the RF energy can be gated on and off easily either manually or by computer command.

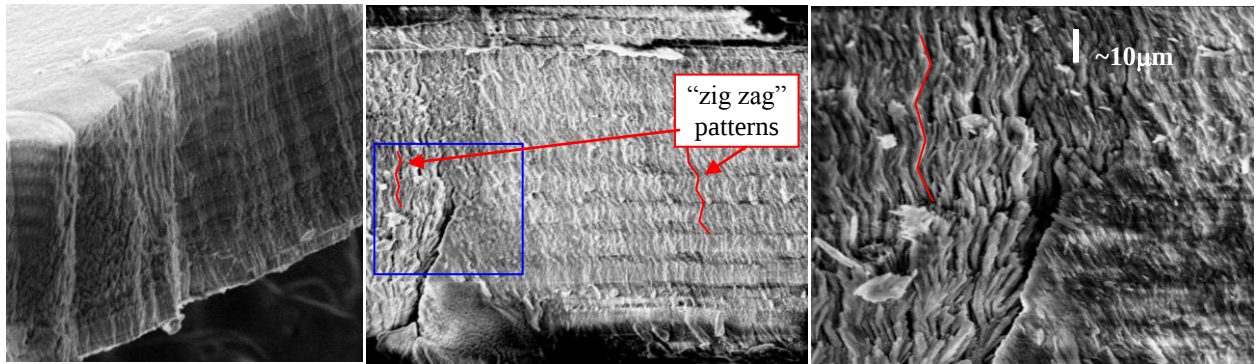
Although the equipment was partially installed to perform the RF biasing experiments, the technique was not applied in this project due to time and funding limitations. A rotatable, RF vacuum feedthrough must be developed for the stinger shaft to allow the RF connection to the substrate paddle. It is anticipated that this will be accomplished in a follow-on program.

Fortunately, the first two techniques proved very successful. Figure 21 shows the substrate paddle at three different stages in the processing. These include the initial loaded condition of clean In-718 substrates, after the heat treatment produced the NiAl bondcoat, and also after the TBC deposition. The first YSZ layered structures produced with 90 s pivoting times at $\pm 30^\circ$ were on a 10 micron scale. SEM micrographs of the YSZ coatings appear in Figure 22. By reducing the dwell times to 10 s, we were able to produce the 0.5 micron layered structures in Figure 23. The micrograph in Figure 23 also shows the effects of cyclic IBAD using 90 s duty cycles. The effect of 10 s pivoting and 20 s IBAD duty cycles produced the morphology shown previously in Figure 15. It was very easy to adjust the cycle times to produce the desired microstructure, since the periodicity is an inverse function of the dwelltime.



(a) aluminum-coated In-718 (b) Ni₂Al₃ bondcoat, post heat treat (c) post TBC deposition

Figure 21. Substrates during various stages in the processing



(a) layered morphology (b) higher mag. reveals pivoting features (c) close-up of columnar grains

Figure 22. Multi-layer YSZ coating on the 10 µm scale

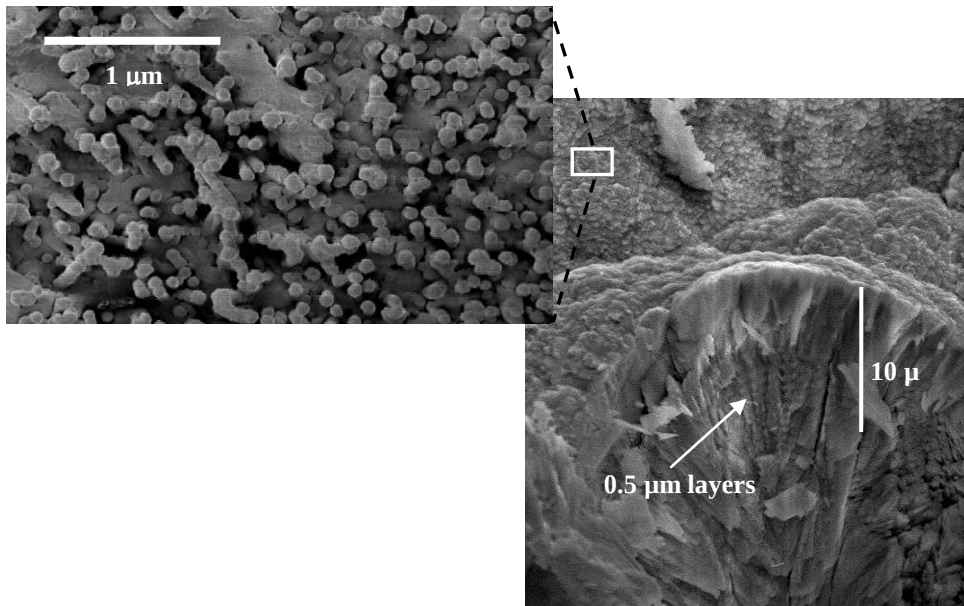


Figure 23. Multi-layer YSZ coating on the 0.5 µm scale

These techniques helped to keep the columnar YSZ grains in the growing film small and the number of grains large. The pivoting produced more void space between grains to inhibit photon transport (radiation) in the matrix while the ion bombardment from the ion gun produced periodic variations in YSZ density. This helped to refract phonon waves and thus decrease thermal conduction.

Figure 24 shows typical 3ω characteristic curves for the layered structure. All thermal conductivity measurements reported here were performed near room temperature. Ideally, the thermal conductivity should be measured all the way to 900 °C. In the near future Sandia will have such high temperature capability, but at the time of these experiments, only low temperature (<200 °C) measurements were possible.

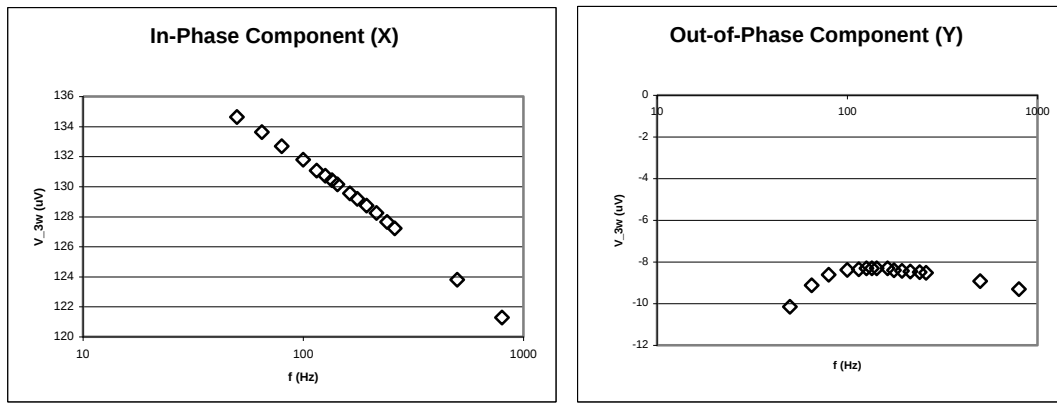


Figure 24. Typical 3ω characteristic for thermal conductivity measurements

The thermal conductivity is determined from the following relation by measuring the change in 3ω voltage at two different frequencies, i.e. the slope of the linear portion of the in-phase component shown in Figure 24.

$$k = \frac{V_{rms}^3}{4\pi R^2 L} \frac{\partial R}{\partial T} \frac{\ln\left(\frac{f_1}{f_2}\right)}{(\Delta V_{3\omega_rms})_2 - (\Delta V_{3\omega_rms})_1} \quad (1)$$

V_{rms} and R are the test section driving voltage and resistance, respectively; L is the length of the test section, and $\partial R/\partial T$ is the derivative of the test section resistance with respect to temperature. Use of the 3ω technique is discussed in more detail in section 5. For further background, the reader is referred to an unpublished report by Graham and Olson [14].

Task 2: Direct Simulation Monte Carlo Plume Modeling

Results from a multitude of parametric transport studies using the 2-d DSMC code ICARUS were obtained despite the lack of fundamental physics data such as chemical reaction rates and wall sticking coefficients. As noted earlier, thermal equilibria data for YSZ and alumina were obtained from the literature as well as partial pressure curves for

Al_2O_3 , ZrO_2 and Y_2O_3 [15]. Figure 25 presents the partial pressures of alumina and zirconia. High quality coatings are obtained only when both the YSZ and the alumina ingots are vaporized with sufficient thermal energy to completely dissociate their constituent molecules. While the process is characterized by almost collisionless transport in an unbounded plume, a limited amount of recombination occurs just above the ingot, forming ZrO . Fully stoichiometric molecules of ZrO_2 form almost entirely on hot surfaces. Figure 26 and Figure 27 present the thermodynamic equilibrium curves from ref [15] for alumina and zirconia, respectively. These data indicate that the *in vacuo* sublimation of ZrO is essentially a step function occurring near 2330 K for ZrO_2 . In the case of Al_2O_3 , pure atomic species are evolved above 2170 K. The vapor pressure for alumina is about 30 times higher than zirconia over a broad temperature range and that means the source temperatures must be maintained carefully with a 500 to 600 K difference between the two, depending on the desired vaporization ratio. This makes the control of dual-source vaporization quite difficult for this material system. The addition of biasing or IBAD can enhance control at the lowest alumina rates by dissociating molecules in the plume near the substrate and providing enough momentum at the substrate to produce the desired $\alpha\text{-Al}_2\text{O}_3$ phase below 1100 °C.

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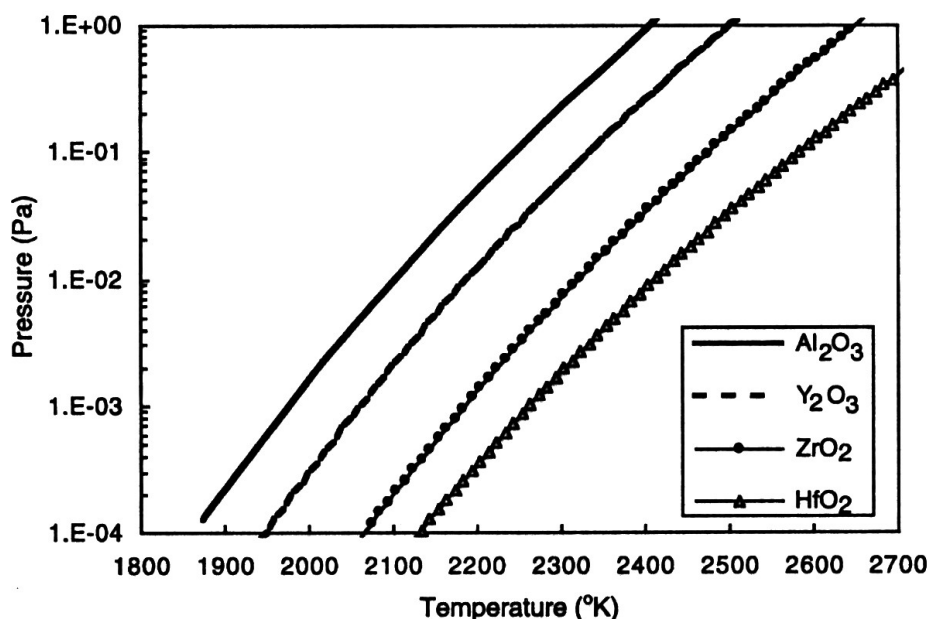


Figure 25. Vapor pressure curves for common TBC materials

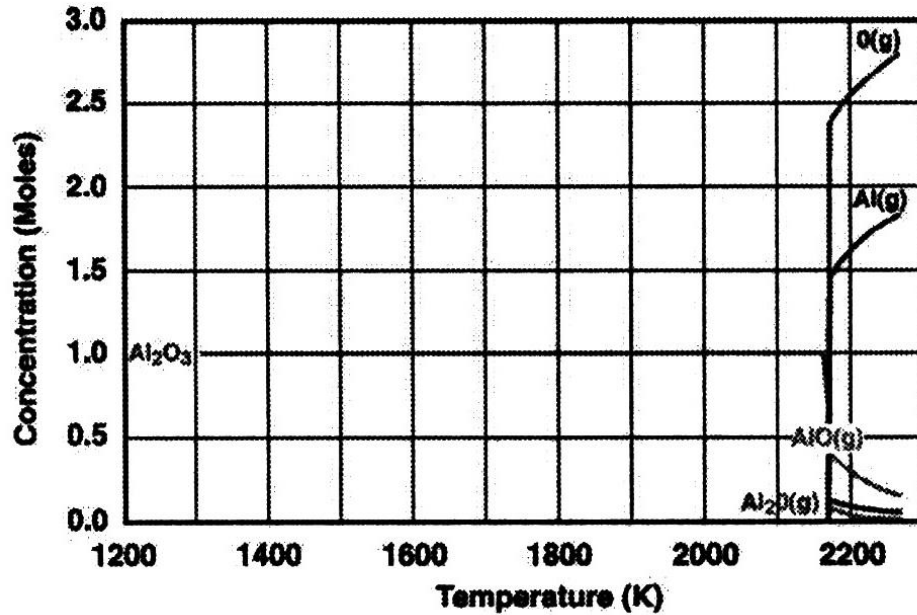


Figure 26. Thermal equilibrium diagram for alumina

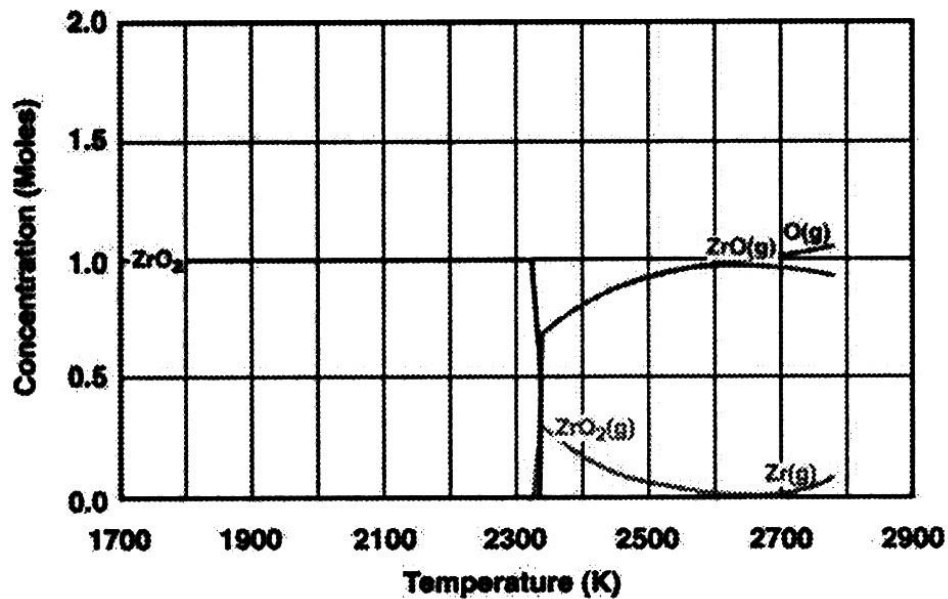


Figure 27. Thermal equilibrium diagram for zirconia

1. Effects of three dimensionality of the flow

Although the geometry modeled is three dimensional, for the purposes of this analysis simplifications were made that would allow faster computation times. As noted earlier one of the concerns of the numerical analysis was the computational time required.

Increasing the dimensionality of the problem by one increases the computational load by one order of magnitude. Such a computation would be marginally possible on the current computational facilities.

As a compromise, a 2-D axisymmetric geometry equivalent was used. The decision to do that was based on the fact that a single plume geometry is by default axisymmetric. Simulating the “doghouse” with a cylindrical axisymmetric geometry doesn’t affect the flowfield either because of the large mean free paths (low collisionality) that makes the trajectories of the molecules almost ballistic once they leave the area of the plume.

2. Surface Chemistry

Wall sticking coefficient data for ZrO were not readily available in the literature. Characterizing this process is far from trivial, since the surface buildup is effectively a transient phenomenon. The first ZrO molecules hitting the surface will form chemical bonds with the metal molecules of the surface. These ZrO molecules will form bonds with other ZrO molecules already deposited there. Experimental observations indicated significant ZrO buildup on both sides of the paddle. Calculations indicated that significant buildup on the backside of the paddle could only be caused as ZrO molecules diffusely reflected from the walls impinge on the backside of the paddle. This indicates that the sticking coefficient on the doghouse walls was less than unity. The back side of the paddle is not in the line of sight of the plume. Therefore for molecules that impinge there can come from two sources: molecules reflected from the walls and molecules that changed their trajectory because of collisions. The latter class of molecules is not large as was discussed earlier and it couldn’t have accounted for the buildup observed in the experiment.

The paddle was equipped with backside substrates as shown in Figure 28. Weight gain determined the percentage of reflected condensate. Quantitative comparison between the deposited mass on both sides of the paddles and DSMC simulations performed indicated that an average sticking coefficient of 70% was adequate to simulate the process.

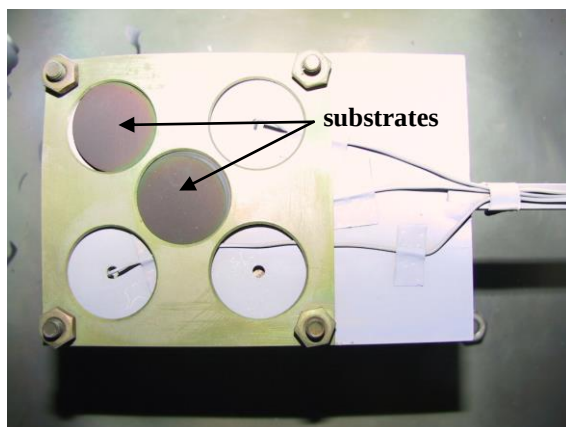


Figure 28. Backside paddle substrates used to determine sticking coefficients.

3. Internal degrees of Freedom

Molecular species may evaporate from the source if enough thermal energy is not available. The internal mode excitation of molecules (Al_2O_3 , ZrO , ZrO_2 , Y_2O_3) can influence their transport because these modes (rotational, vibrational) can store significant amounts of energy. Excitation of these modes during molecular collisions depletes translational energy from the molecules. Such events result in the reduction of particle flux density to the surface with a subsequent reduction in the deposition rates. The process was modeled at two extremes, allowing either full excitation of the internal modes or inhibiting the internal excitation of these molecules. The results of the simulations indicated that even if molecular species are generated, the transport effect is small as long as the background pressures are low.

Most of the plume expansion takes place in the near free molecular regime reducing molecular collisions and therefore the probability of energy exchange.

4. Gas phase chemistry

These observations about the collisionality of the flow relate to the issue of gas phase chemistry. At the pressures of the order of magnitude less than 1 Pa where these processes typically take place, gas phase collisions are rare indicating that chemical reactions could only occur at a significant rate on or near the surfaces.

5. Background gas effect

The role of background gases, particularly the judicious addition of oxygen is of interest since high background pressure can affect electron beam operation and shorten e-gun filament lifetimes. Since commercial PVD operations typically are done at pressures of a few Pa, gas phase collisions in the plume away from the ingots, the paddle and the walls will be rare and chemical reactions with oxygen will only occur at a significant rate on or near surfaces.

Industrial experience has shown that a small addition of oxygen improves the quality of the deposited film. The release of molecular oxygen in the chamber was examined numerically by varying the release rates from 6 to 120 sccm. Such variations to the release rates were found to be insignificant to the deposition rates. It is our assumption that the oxygen addition compensates for the loss of oxygen due to the faster diffusion of oxygen into the vacuum pumps and, therefore, helps to maintain stoichiometry in the coating. Increasing the amount of molecular oxygen above the compensation level has no effect on the coatings.

6. Wall temperature

The effect of the wall temperature was also examined numerically. The conclusion was that keeping the wall temperature at around 550 °C makes the “doghouse” walls act as a temperature device balancing the temperature of the cold oxygen gas and the relatively hot plume gases. Oxygen molecule collisions with the walls appeared to be a lot more frequent than gas-phase collisions increasing in this way the temperature of the oxygen background gas and therefore the collisionality of the mixture. The conclusion was that keeping the wall temperature near 550-600 °C reduces atomic oxygen recombination at

the walls and increases the collisionality in the thermal cage, in addition to its primary function of radiatively heating the substrates.

7. Effect of Al

The final part of the numerical investigation was the addition of Al_2O_3 to the plume and the search for an optimal electron-beam timesharing between the $\text{ZrO}_2/\text{Y}_2\text{O}_3$ and Al_2O_3 sources that would produce the desired film properties. Alumina has higher thermal conductivity than YSZ. Therefore, the thickness of the alumina layer must be limited to about 1 μm , and the timesharing during the deposition of the graded layer must maintain each source at the proper temperature to produce the desired ratio of vaporization rates. Timesharing is controlled by several properties, the specific heats, the melting points and the variation in vapor pressure between the two source materials. However, in mixed plumes, more collisions can occur between heavy ZrO molecules and lighter Al atoms near the ingots. This has a preferential effect on the transport. The deposition rates no longer follow the evaporation rates as in pure plumes, meaning the evaporation rates (source temperatures) must be adjusted accordingly.

Two cases were investigated. The first one assumed an equal evaporation rate of Al_2O_3 and $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ into the plume. The second used an Al_2O_3 evaporation rate comprising only 10% of the total. We note that the deposition rates are almost a linear function of the evaporation rates for each of the separate plumes. However, this is not the case for mixed plumes due to collisions that take place near the surface between species with different diffusion properties. Light/fast diffusing species form a “protective” layer around the target hindering the heavy ones from approaching. However, once a layer with heavy atoms or molecules (ZrO , Y_2O_3) is developed collisions of the relatively lighter atoms (Al) with the heavy atoms results in the lighter ones preferentially bouncing back. Therefore, the aluminum deposition flux is suppressed in relation to its vaporization rate due to the higher ZrO content in the plume.

Figure 29-Figure 33 present the contour lines of the main chemical species for cases described above (Left handside 50/50 timesharing; right handside 90/10 timesharing). At this point it should be stressed that the test case is not a free plume expansion because of the presence of the vacuum pumps. Therefore, the background pressures in these two cases are not the same. For all the simulations the vacuum pumps were set to simulate the vacuum pumps used in the experiment running at optimal speed. Since pressure is a function of the number density of the flow the case where timesharing was 50/50 resulted in higher pressures in the chamber. This is because the dissociation of Al_2O_3 introduces 5 atoms in the system vs. three of ZrO_2 .

Figure 33 shows that the concentration of molecular oxygen released in the chamber for both cases is almost the same. This supports the finding of section 5 i.e. that molecular oxygen does not take part in chemical reactions in the gas phase. Its sole role is to compensate the higher losses of oxygen due to diffusion.

Figure 34 and Figure 35 show the corresponding deposition rates (in molecules per unit time) vs. distance from the YSZ ingot center. Comparison of Figure 34 and Figure

35 shows that the higher Al evaporation rate will result in higher deposition rates. It must be stressed that because of the collisions that take place near the surface of the paddle the relationship between the evaporation and deposition rates is not linear. The Al evaporation rate of Figure 34 is 5 times that of Figure 35. However, the deposition rate is 8 to 10 times higher. This is due to the fact that Al atoms are lighter than Zr/Y ones diffusing faster to the paddle. The ratio is a function of the density and temperature in the chamber. The lower these parameters are the closer we get to a free molecular paradigm and the relationship becomes more linear. As these parameters increase the collisionality of the flow increases and the relationship becomes more complicated. Another parameter that can affect this ratio is the three dimensionality of the flow. In the present example the Al plume brackets the Zr/Y one increasing the Al deposition at the edge of the paddle. In a more realistic three dimensional example this symmetry will disappear.

It is also interesting to note that enhanced Al_2O_3 evaporation results in higher levels of atomic oxygen in the flow (see Figure 32). In this case the release of molecular oxygen is superfluous and will not influence the quality of the film.

The separation distance between ingot and Al_2O_3 crucible was optimized to provide as much vapor plume mixing as possible using a model of the dual-source $\text{Al}_2\text{O}_3/\text{YSZ}$ geometry. With guidance from the modeling results, experimental trials were performed to determine the best electron beam settings to obtain the correct evaporation rate from each source. Dual-source evaporation runs indicated that graded YSZ/alumina coatings were possible using the prescribed setup.

8. Effect of plume ionization-Electrostatic fields to control deposition.

Ionizing the plume with the aid of the electron gun and using electrostatic fields to guide the plume was suggested as one technique that could be used to control the deposition process. The ionization potentials of the Zr/Y and Al atoms differ significantly. It was suggested that advantage could be taken of that, by ionizing the Al atoms (Al being a metal has a lower ionization potential) and then using electrostatic fields to control the flow of Al to the surface.

It is evident that a fully ionized flow can be controlled effectively by electrostatic fields. However, using the electron gun as a mechanism to ionize the flow cannot produce ionization levels more than 5-10%. For this technique to work one would rely on collisions between accelerated ions and neutral molecules to accelerate the flow in the desired direction.

Simulations where the degree of ionization was 10% were performed with an electrostatic field accelerating the ions towards the target. In these simulations no significant changes to the deposition rates were observed. This should be expected for the particular cases in question where the collisionality (secondary acceleration mechanism) was low reducing the efficiency of the whole process.

9. Film uniformity

To optimize the coating process advantage can be taken of gas molecules deposited on both sides of the target. Figure 36 and Figure 37 have the backside points added. We note that lower (50-30%) but significant deposition rates are achieved. By moving the target away from the vacuum pump duct the back side deposition rates could be further increased if so desired.

10. Plume modeling-Final assumptions

The conclusion of this analysis was to adapt the following assumptions as the best way to approximate the plume:

- 1) Zr and Y stick to the walls with 70% probability
- 2) O_2 reflects diffusely of the walls
- 3) The plume of the ingot consists of Zr and Y. 100% efficient reactions turn Zr and Y to ZrO and YO respectively in the plume as it approached the surface
- 4) ZrO_2 and Y_2O_3 are formed on the surface
- 5) Correct modeling of all these should lead to stoichiometric ZrO_2 and Y_2O_3 on the surface, i.e. the fluxes of ZrO and YO should equal the flux of O_2

This leads to a closed set since the oxygen fluxes should equal the ZrO and YO fluxes to the surface. Balancing the fluxes will imply that the system is modeled in a self-consistent way. The spectroscopic measurements allowed a qualitative verification of these assumptions by determining the composition of the plume at the ingot.

11. Future work

The analysis performed here was basically qualitative, and its purpose was to identify the major physical parameters that influence the deposition process. Future work should deal with the extension of the present models to three dimensions to allow for a more realistic representation of the plume interaction. As noted earlier the second plume was assumed to be coming from a ring-shaped source that is clearly leading to a more uniform distribution at the substrate. The recirculation region below the paddle is also expected to disappear. In this case to increase film uniformity, even lower chamber pressures may be necessary to reduce the interaction between the two plumes.

To improve the quality of the simulations more quantitative, detailed comparisons with experimental data are necessary. The lack of physical and chemical data can only be compensated with detailed comparisons between experimental data and realistic simulations. At this point, it should be noted that performing three-dimensional simulations is not trivial since it challenges the most modern computational platforms.

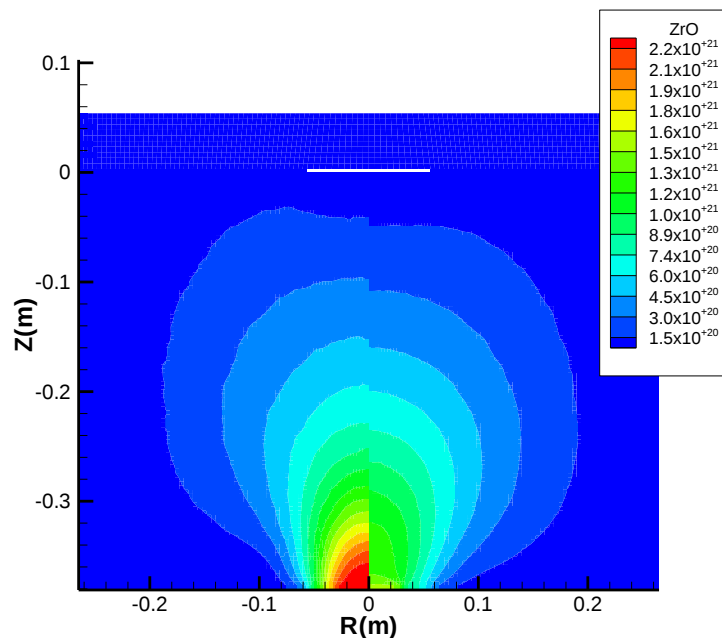


Figure 29. ZrO density profiles for equal (left) and a 90/10 evaporation ratio between YSZ/alumina show only a small difference in density variation well above the source. The YSZ ingot is centered at $R=0.0$ m, the alumina is at $R=0.1$ m.

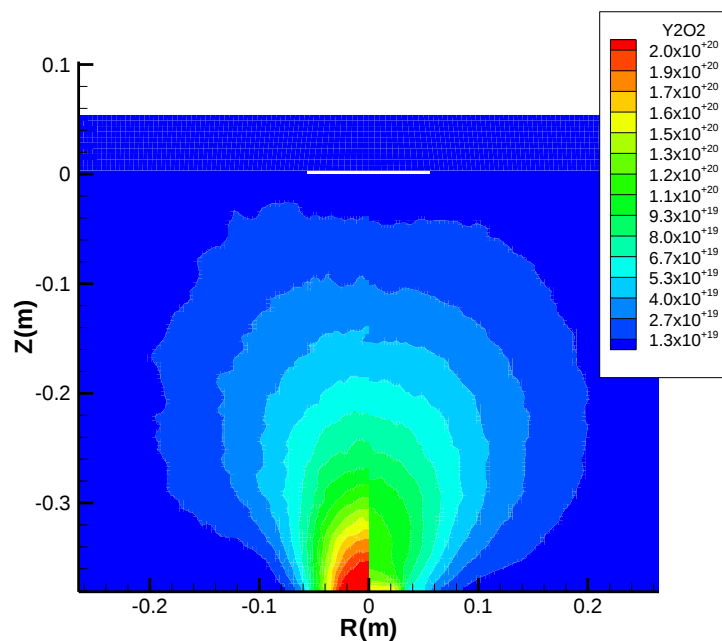


Figure 30. Y_2O_2 density profiles for equal (left) and a 90/10 evaporation ratio between YSZ/alumina show only a small difference in density variation well above the source. The YSZ ingot is centered at $R=0.0$ m, the alumina is at $R=0.1$ m.

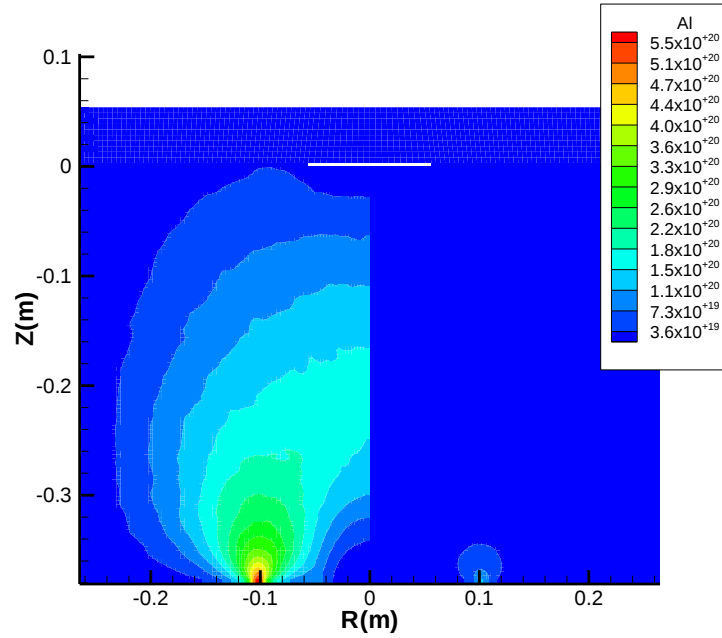


Figure 31. Al density profiles for equal (left) and a 90/10 evaporation ratio between YSZ/alumina show a large increase in density variation well above the source. The YSZ ingot is centered at $R=0.0$ m, the alumina is at $R=0.1$ m.

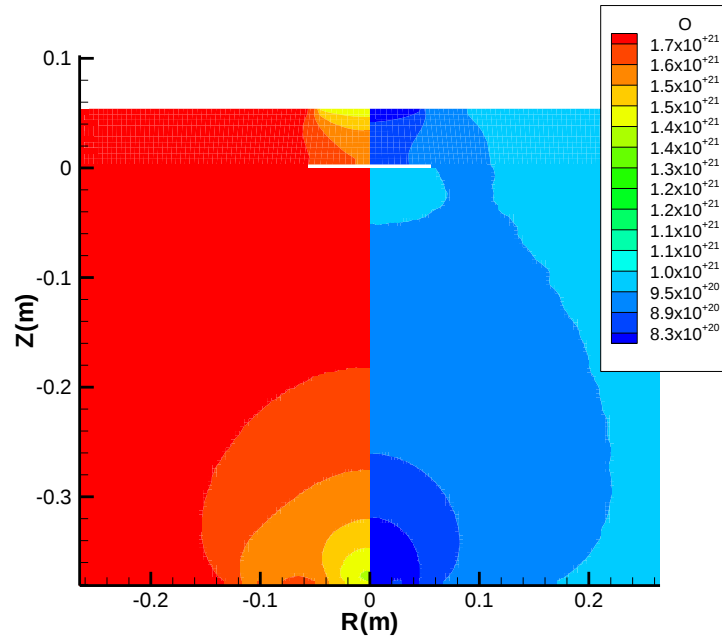


Figure 32. O density profiles for equal (left) and a 90/10 evaporation ratio between YSZ/alumina show a large increase in O concentration in the former case. This is due to the O atoms released by the Al_2O_3 dissociation.

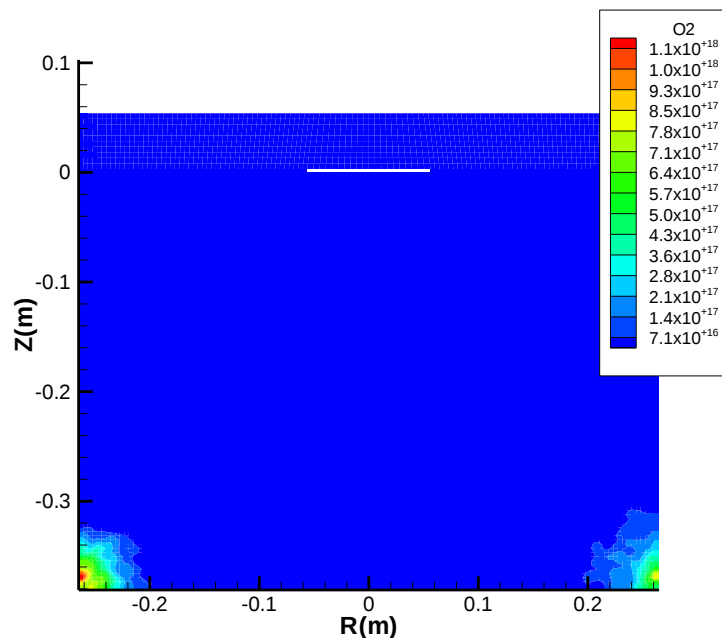


Figure 33. O_2 release density profiles for equal (left) and a 90/10 evaporation ratio between YSZ/alumina. O_2 does not participate in any reactions so its concentration remains the same for both cases. The sole role of O_2 is to compensate for the faster diffusion

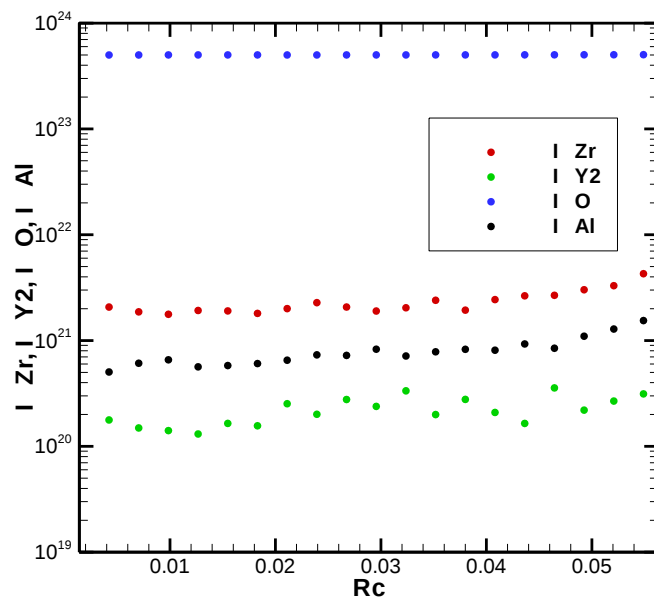


Figure 34. Deposition rates ($m^{-2}s^{-1}$) of constituents with equal evaporation rates between YSZ and alumina indicate an arrival ratio between ZrO/Al of 3/1. The YSZ ingot is centered at $R=0.0$ m, the alumina is at $R=0.1$ m.

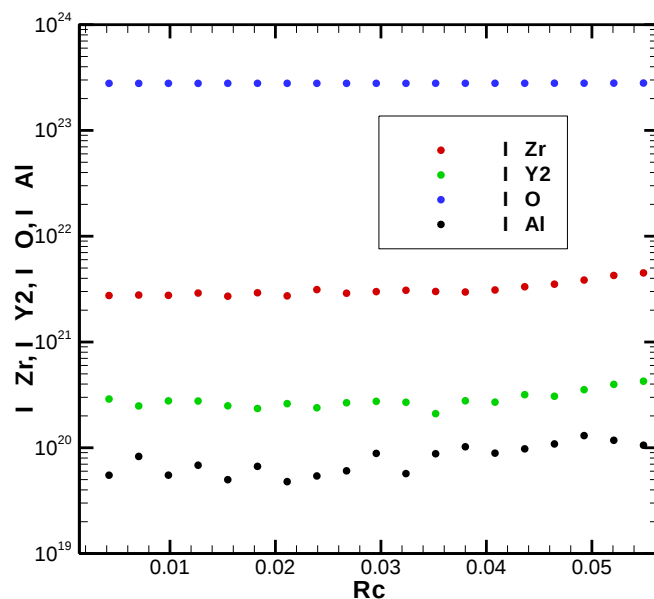


Figure 35. Deposition rates ($\text{m}^{-2}\text{s}^{-1}$) of constituents with a 90/10 evaporation ratio between YSZ and alumina indicate an arrival ratio between ZrO/Al of almost 300/1. The YSZ ingot is centered at $R=0.0$ m, the alumina is at $R=0.1$ m. Al oscillations caused by DSMC statistical fluctuation.

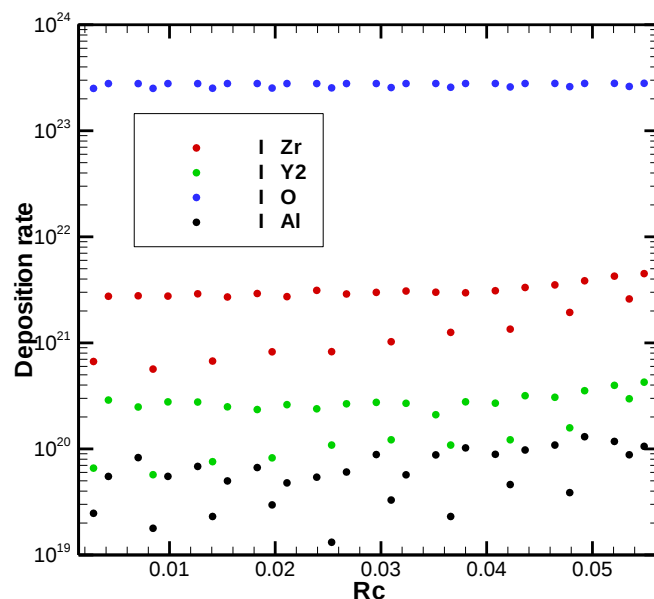


Figure 36. Same as Figure 34. The additional points correspond to the back of the paddle. Apart for the O atoms that diffuse fast enough to equalize their deposition on both sides of the paddle the deposition on the back side is almost half of that on the front side.

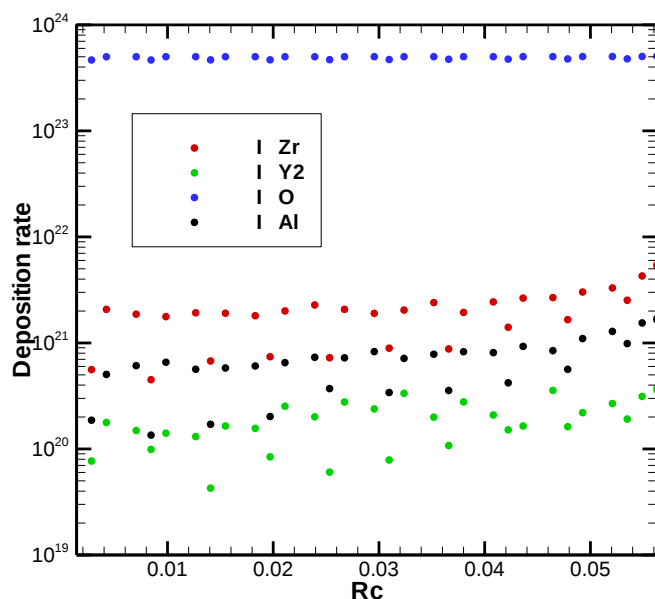


Figure 37. Same as Figure 35. The additional points correspond to the back of the paddle. Apart for the O atoms that diffuse fast enough to equalize their deposition on both sides of the paddle the deposition on the back side is almost half of that on the front side.

Task 3: Mixed Layer Development

A photograph of the dual source configuration after the first mixed layer deposition run is shown in Figure 38. The alumina source was placed in an uncooled graphite crucible positioned next to the YSZ ingot. Note the melted alumina and the melt pool location on the YSZ ingot surface. The entire face of the YSZ ingot was not fully melted during the primary evaporation and thus required special edge cleaning patterns. Mixed layer processing was performed with the beam power from gun #1 time-shared between the two sources.



Figure 38. Evaporant sources after a mixed layer deposition.

The ability to perform the EB-PVD deposition of graded layers relies entirely on the digital rastering control system for the EB-1200 electron guns. During the depositions, the evaporation rates are determined by a source material's surface temperature through its vapor pressure. The source temperature is controlled by the total power absorbed by the ingots. During the course of a deposition the gun power can be raised or lowered accordingly. However to share the electron beam between two dissimilar source materials requires that the time slice on each ingot be carefully controlled and easily adjustable.

The EB-1200 rastering program, named "Prometheus," permits the operator to setup various pattern steps that are combined into sequences of steps in advance and choose those sequences on the fly. Prometheus was developed specifically for EB-PVD applications, but is also used for melting, refining and high heat flux testing at Sandia. The GUI appears in Figure 39. The program allows the operator to choose the position, size, rotation and type of pattern for each source material. The pattern distortion caused by the sector-magnet-induced beam bending is compensated for by adjusting the aspect ratio of the initial pattern. But, most importantly, Prometheus allows the operator to switch from pattern to pattern at frequencies as high as 1 kHz. More time can be spent on source materials with lower vapor pressures and higher melting points compared to others. Thus one can carefully tailor the beam sharing to produce the desired evaporation rate that leads to a desired deposition rate. However, one must take into account the preferential transport that occurs for atoms of different mass and the differences in wall sticking coefficients for various species as illustrated in the mixed plume DSMC simulations. Because mixed plume deposition rates are not linear functions of the

constituent evaporation rates, the massively parallel DSMC calculations were both an integral and necessary part of the project.

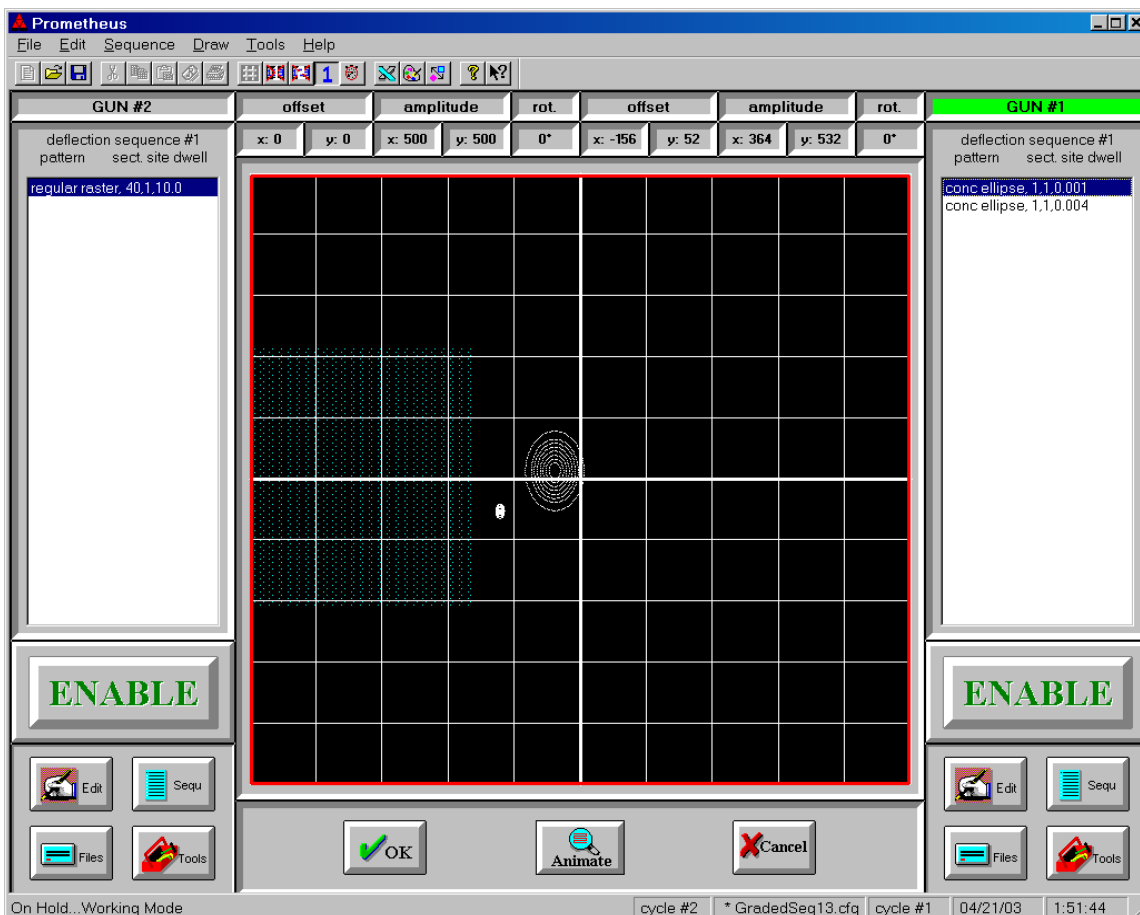


Figure 39. Prometheus application for digital rastering

The first evidence of a composition gradient was obtained from these coatings. EDX scans, taken at several points across a fracture surface, reveal the development of a mixed $\text{Al}_2\text{O}_3/\text{YSZ}$ layer formed during dual-source evaporations. The point scans and an accompanying SEM micrograph were presented earlier in Figure 17 and Figure 16, respectively.

Task 4: Production of Complete, Graded Layer Coatings

More than ten full-scale coatings consisting of the Inconel-718 substrate, a 30 to 50 micron layer of Ni_2Al_3 , a 10 to 50 micron layer of α -alumina, a 50 micron layer of alumina mixed with YSZ, and finally a 10 to 20 micron top coat of YSZ were deposited *in situ* in one chamber pumpdown. The Ni_2Al_3 layer was created by first depositing a 30 micron thick coating of pure aluminum onto the Inconel substrates using a small commercial PVD system. The coated substrates were then loaded into the stinger by securing them with a mask to the substrate paddle or sample holder. The paddle was instrumented with three type-K thermocouples. The substrates were then heated to 850

°C within 30 minutes and held at this temperature for 2.5 hours. This permitted the aluminum to diffuse into the nickel rich Inconel substrate to create a Ni_2Al_3 bondcoat. An XRD 2-theta scan of the heat-treated bondcoat appears in Figure 40. Other nickel aluminides such as Ni_3Al were also present, but to a much lesser degree. Al_5FeNi and FeNi phases from the In-718 substrate are also prevalent. The thickness of the aluminide layer varied slightly from one treatment to the next. Typically it ranged from 30 to 50 microns in thickness as determined by SEM on a cross section. A small percentage of the aluminum that did not alloy with the nickel melted on the surface and evaporated into the stinger chamber.

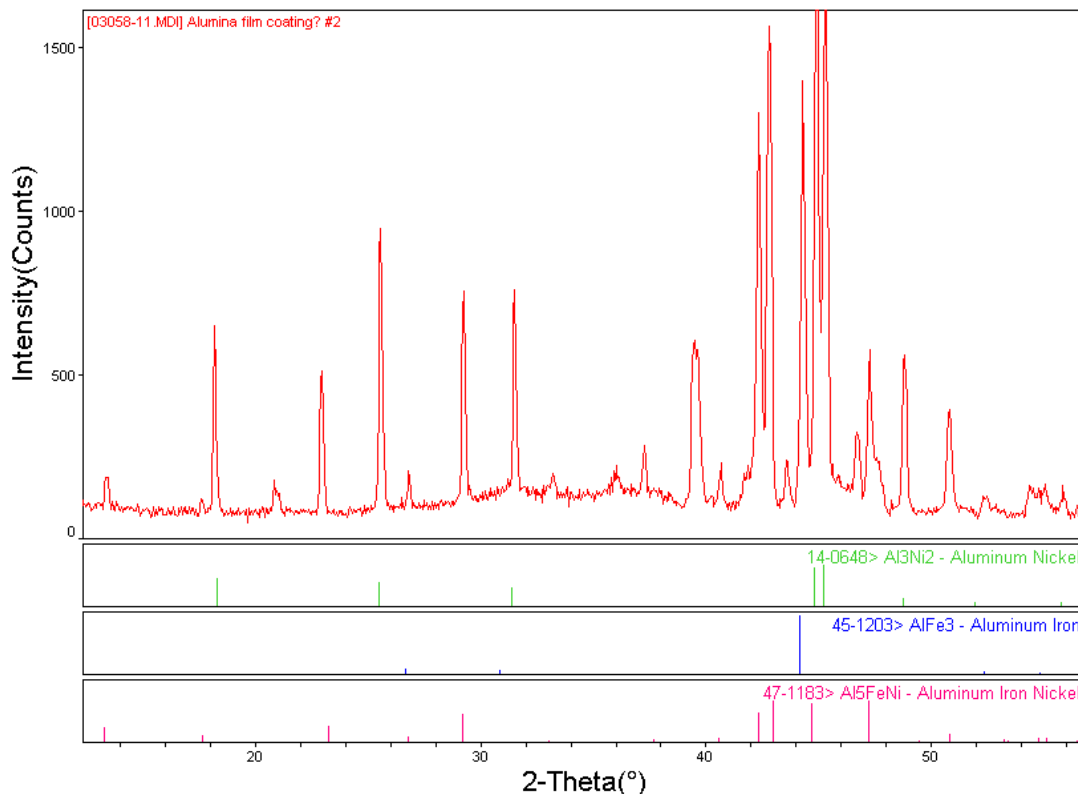
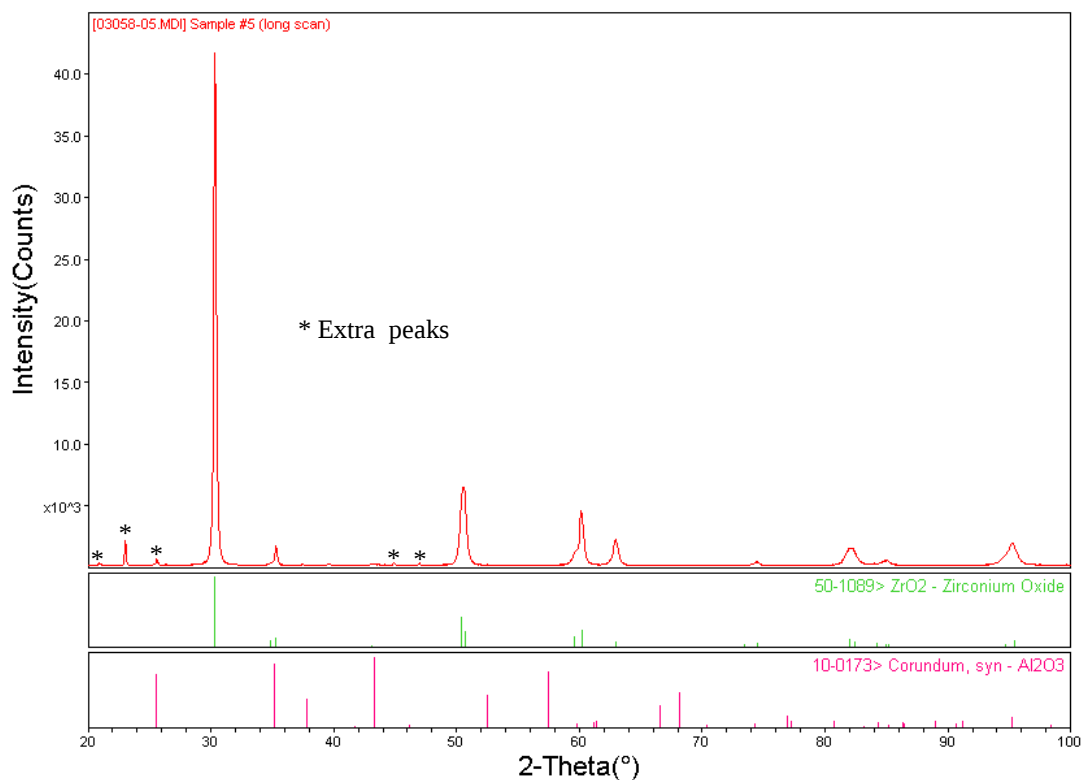


Figure 40. XRD 2θ scan of NiAl bondcoat

Normally a thick alumina layer is grown on a substrate by elevating its temperature to 900 °C and exposing it to an oxygen rich background for several hours. This is known as the thermally grown oxide layer or TGO. In contrast, immediately after reaching a temperature of 900 °C, our substrates were quickly transported into the EB-1200 chamber and exposed to a pure alumina PVD plume for ten to fifteen minutes, while undergoing simultaneous 575 eV argon ion bombardment from the hot cathode 3-cm ion gun positioned 25 cm below the substrates with an angle of incidence near 30°. Modest ion currents of approximately 20 mA were sufficient to transition the deposited alumina on the substrate to α -phase even though the substrate temperature was between 600 and 750 °C. Figure 41 shows an XRD 2-theta scan for a surface deposited without IBAD. Either no significant α -phase (corundum) peaks are present, or the zirconia has completely attenuated the x-ray signal. However, Figure 42 presents the 2-theta scan for the IBAD

sample. Note the strong α -phase peaks. Not all peaks were present indicating a preferred orientation with very large crystallites several microns in size. The predominant orientation was (012). Other peaks in the spectra indicate the presence of another phase, cubic. Therefore, not all the alumina was converted to the α -phase. However, based on the crystallite sizes appearing in the SEM images, one can estimate that 75 to 90% of the alumina was in the α -phase. Note that our substrate temperatures were 400 °C lower than the temperature where thermally induced transitioning can occur. This indicates that no long, high temperature post-deposition heat treatment is required if the alumina is deposited with energetic IBAAD under the proper conditions.



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Figure 41. XRD 2θ scan showing Tetragonal ZrO₂ and no evidence of α-alumina.

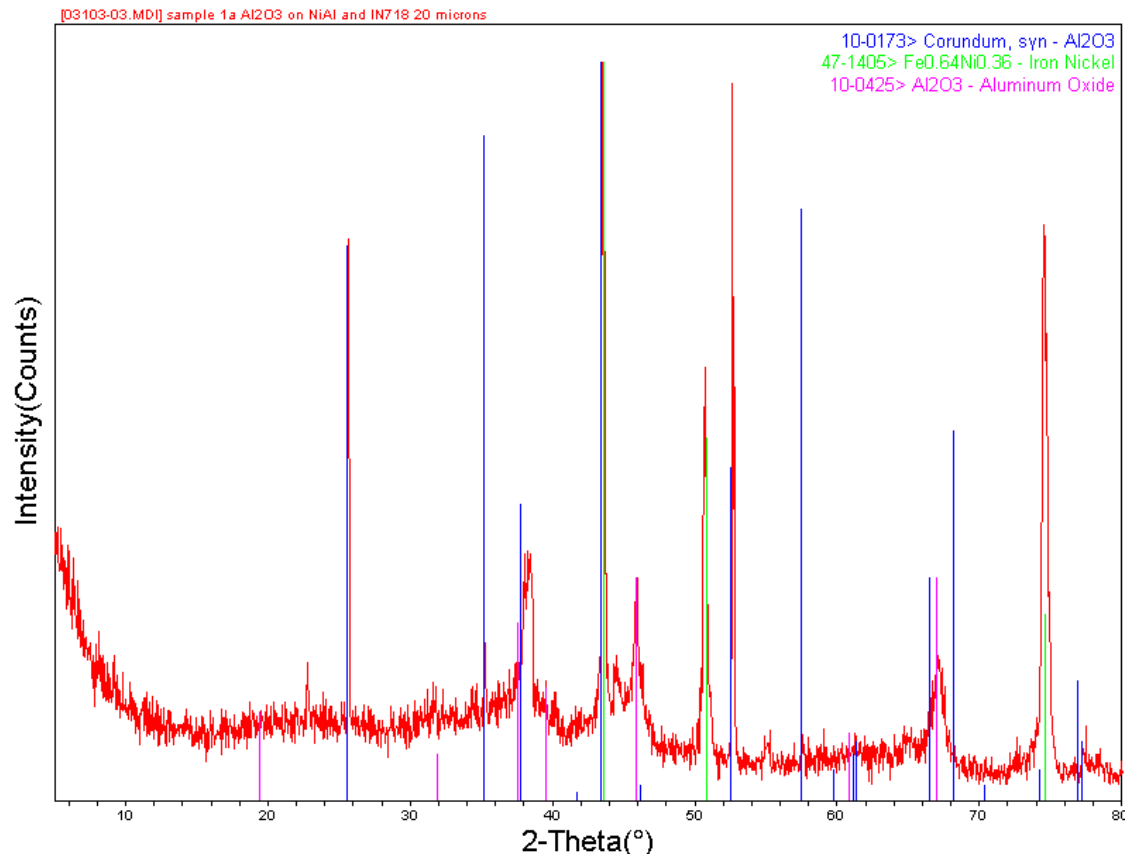


Figure 42. XRD 2θ scan showing α-phase alumina deposited on In-718 substrate with IBAD.

After approximately 15 minutes, the YSZ ingot is brought to evaporation temperature by adjusting the electron beam dwell time and sharing the beam between the alumina source and the YSZ ingot. During the next 30 minutes, the time spent on YSZ ingot is increased while the time on the alumina ingot is decreased. Thus, the YSZ deposition rate increases while the alumina deposition rate decreases, forming a graded layer from pure alumina to pure YSZ. Figure 43 is a micrograph of a fracture surface through the graded layer. Figure 44 shows an EDX scan through the thickness of the graded layer. The backscattered x-ray signal shows that the aluminum content decreases as the zirconium content of the film increases with growth. During this process, the argon ion bombardment remained on. After the YSZ deposition became the dominant species in the plume, a substrate paddle was pivoted back and forth with $\pm 30^\circ$ rotations dwelling for 10 seconds at each angle. The ion gun was also cycled on and off. Many different duty cycles were used. The highest was 20 seconds on and 20 seconds off. The lowest investigated was 120 seconds on and 120 seconds off.

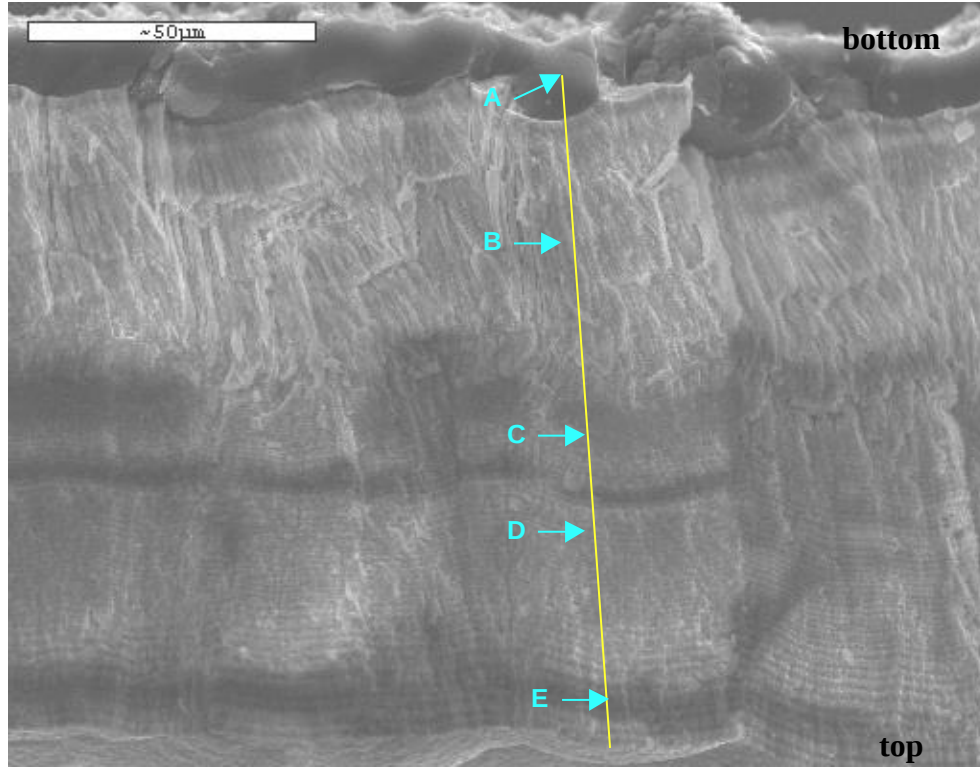


Figure 43. Fracture surface across full TBC loc:A X700; spectra A-E, scan (115 µm start= top)

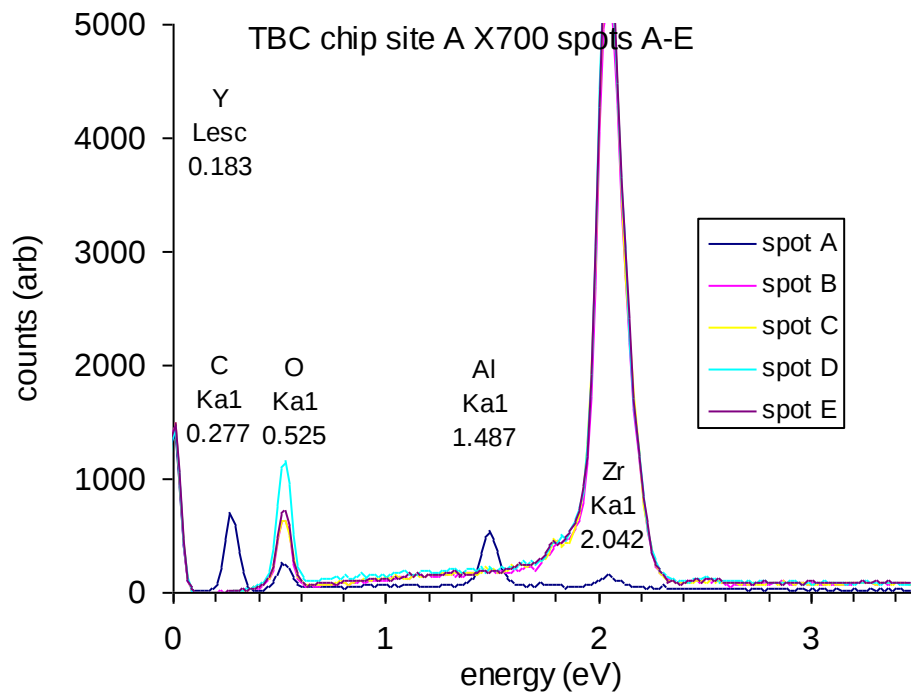


Figure 44. X-ray spectra from spots A-E on Figure 43; only spot A shows Al.

Finally, a pure YSZ top coat was deposited by limiting the electron beam pattern solely to the YSZ ingot. The pivoting and cyclic IBAD were continued during this process which usually lasted ten to twenty minutes. Lower argon bombardment energies below 300 eV produced tetragonal zirconia in the top coat as shown in the 2-theta XRD scan displayed in Figure 45. The XRD peaks are broad indicating fine crystallite size and increased micro-strain. Higher bombardment energies of 575 eV produced cubic phase zirconia as verified by the 2-theta scan shown in Figure 46. The spectrum indicates a strong preference for (111) out-of-plane grain orientation. Thus the coatings have a rough, textured surface, although still much smoother than plasma-sprayed TBCs. A comparison of the two phases is shown in Figure 47.

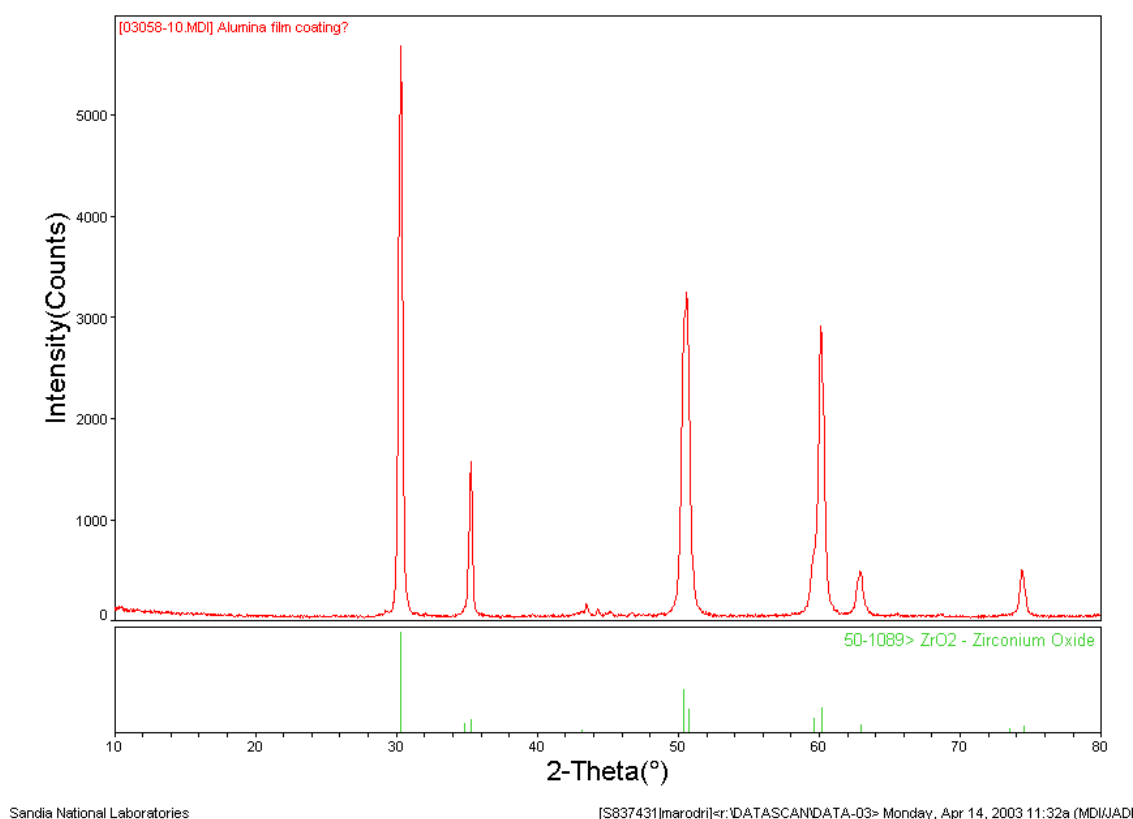


Figure 45. XRD 2θ scan showing tetragonal zirconia phase in top coat.

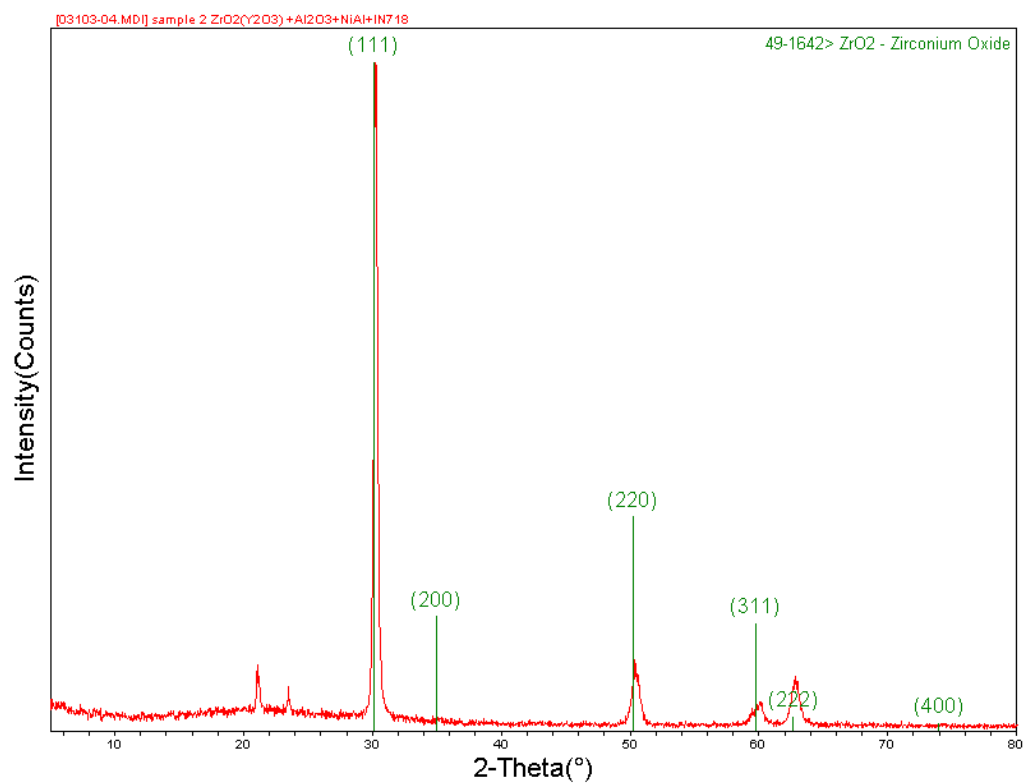


Figure 46. XRD 2θ scan showing cubic zirconia phase in top coat.

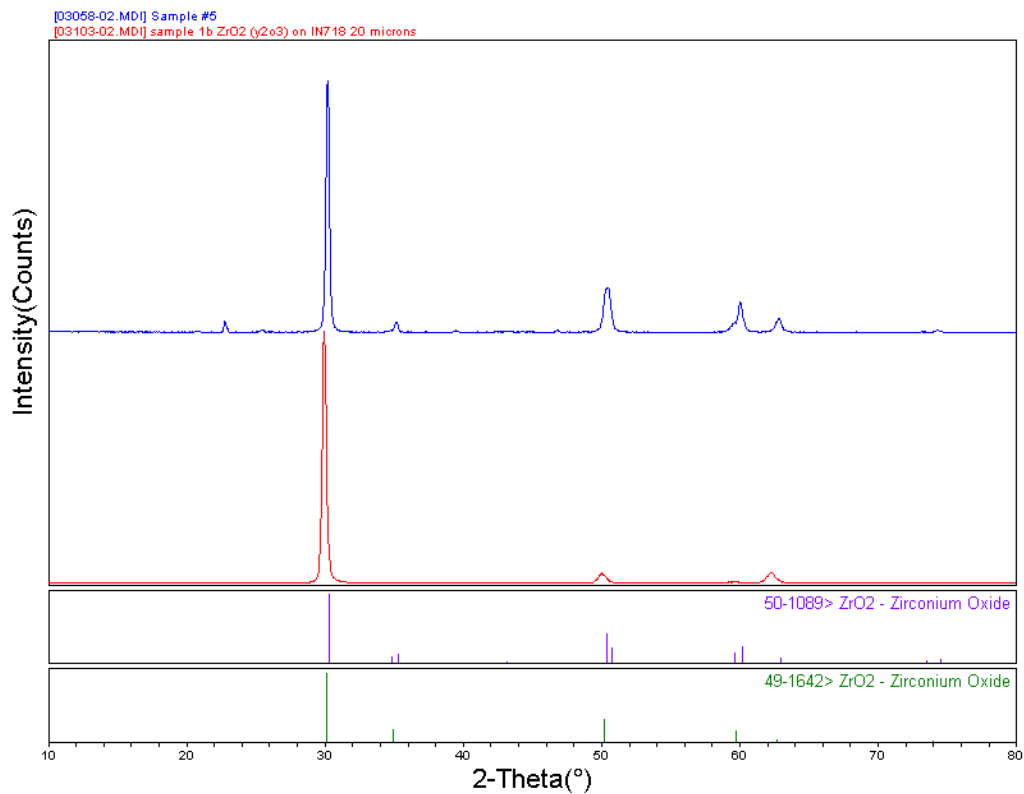


Figure 47. Comparison of XRD 2θ scans for tetragonal and cubic phase zirconia.

The substrate paddle was then extracted by the stinger from the chamber and allowed to cool in the stinger chamber usually overnight before venting with argon. The substrate temperatures dropped precipitously when removed from the EB-1200 chamber, often falling 400 degrees in less than 15 minutes. Although various cooldown rates could have been investigated using the quartz lamps heaters and a programmable controller on the stinger, we had little time to pursue this endeavor. It is believed that better coating adhesion could be obtained if a slow cooldown over several hours was realized.

Task 5: Materials Characterization and Testing of Coatings

Materials characterization of the depositions consisted of SEM and EDX analyses for morphology and composition and XRD analyses for composition and phase. A new micro-electromechanical-systems (MEMS) measurement for thermal conductivity known as the “ 3ω ” techniques was used on the coatings. It is far superior to other techniques like laser flash diffusivity, especially when dealing with thin layers or stacked multi-component layers.

Substrate pivoting has an enormous effect on the coating morphology. Figure 22 in section 4, task 1 showed SEM micrographs of a layered yttria-stabilized zirconia (YSZ) structure produced by the EB-1200 using 30° substrate pivoting at 90-second intervals. Typical columnar YSZ coatings produced by EB-PVD have a thermal conductivity of approximately 1.9 W/m·K [3]. Controlled layering at the micron level for this coating resulted in a thermal conductivity of 1.5 W/m·K as measured using the “ 3ω ” technique at 50°C [16]. The periodic densification and breakup of the PVD columnar morphology caused by cyclic IBAD and 30° substrate pivoting at 10-second intervals was shown in Figure 23. The thermal conductivity of this coating was only slightly lower than the non-IBAD coating, 1.4 W/m·K. The coating was produced with a current density of 1.6 mA/cm² at the substrate, resulting in a ratio of Ar⁺ flux to ZrO flux at the substrate of only 0.1. The composition was the same as the non-IBAD coating.

The 3ω technique can determine a thin film’s thermal conductivity by periodically measuring the surface temperature as the coating is being heated by driving an oscillating current through it. This technique was developed by Cahill [17] and refined by Lu and others [18,19]. An approximate analytical solution is used to derive the thermal conductivity from the third harmonic fluctuation in circuit voltage. This technique exploits the interaction between the changes in electrical resistance due to surface temperature changes and the electrical current which drives the heating. A small, but measurable signal is produced at three times the driving frequency (ω). Thus the technique was appropriately named 3ω .

Obtaining thermal conductivity measurements of multi-layer coatings is extremely difficult. Flash laser diffusivity techniques do not work well for thin films, especially where the specific heat is not known *a priori*. Capacitance techniques require thermocouples for temperature measurements and are not suited to measuring conductivities in thin films. Use of the 3ω technique is challenging, because of the large surface roughness inherent in the tetragonal YSZ columnar structures. This makes it very

difficult to pattern the coatings with the metallic electrode that is often only a few microns thick. Many of the TBC coatings were first polished to reduce the surface roughness from the ten micron range down to tenth micron features. Some measurements simply could not be obtained due to roughness variations across the surface and poor adhesion to the substrate. It is also very important that the thermal conductivity of each dissimilar layer be determined separately; so that more accurate measurements can be made of the full multilayer coating, i.e. each pure layer from the In-718 substrate all the way to the pure YSZ top coat must be measured separately; in order to determine the conductivity across the graded layers in a complete composite coating.

Deposition campaign #4 was separated into three distinct processing runs. One to two substrates from each run were removed from the paddle for separate analyses, while the remainder were included in the next processing step. The first run was the preparation of the NiAl bondcoat by heat treatment of the aluminum-coated Inconel substrates at 850 °C for two hours. The second run deposited the alumina scale and transitioned it to α -phase alumina with IBAD. The final run started with pure alumina and transitioned quickly to pure YSZ during the run duration. SEM/EDX analyses of coatings produced in deposition campaign #4 revealed successful sub-micron layering at modest evaporation rates and the growth of a density graded Al_2O_3 /YSZ coating. Both full substrates and coating chips that delaminated from the substrates were analyzed. The fracture surfaces displayed on the chip edges show the deposited layers clearly as presented in Figure 43. Striations on the edges correlate with the paddle (substrate) rotations. The striations varied from about 0.6 microns during the graded layering to slightly more than 1 micron during the top coat deposition. The light areas shown are indicative of SEM charging effects while the darker areas indicate portions of the coating that may have higher electrical conductivity.

However, Figure 48 does show evidence of morphological changes at depths where the ion flux was on. Such zones show blunted or compacted columnar grains. These are areas where the columns appear to be sintered together, but only in the affected layer. These zones appear to have higher in-plane electrical conductivity and also appear dark in SEM images. No doubt, these regions may also have higher in-plane thermal conductivity. Therefore, one can surmise that too much IBAD may have a negative impact on efforts to reduce the thermal conductivity, and so, it must be used with care.

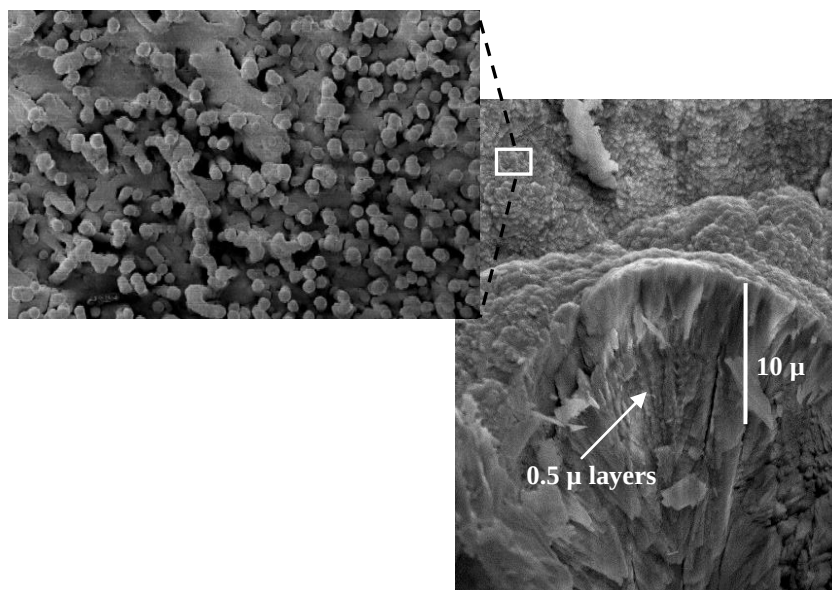


Figure 48. Effect of IBAD on surface morphology

Relative compositions of Al and Zr obtained by EDX along the growth direction are shown in Figure 49 and Figure 50 corrected for backscattering and background. The spectral line ($K\alpha_1$) for Al, which lies close to the $L\alpha_{1,2}$ lines for Zr, has a strong background signal for relatively short exposures. In the data shown, the backgrounds for the Al (Mg window, 130%) and Zr- $L\alpha$ (Sb window, 150%) X-ray windows were subtracted. The data are smoothed to running averages over 5 points for the Al and Zr- $L\alpha$ signals and 10 points for the Zr- $K\alpha$ signals. A nearly linear concentration gradient can be seen over an approximate 200 micron depth. This indicates that the electron beam sharing, and the transition from pure alumina to pure YSZ in the raster pattern sequence was performed quite well. In addition, lower magnification, macroscopic views are presented in Figure 51 to Figure 53 to show global surface features and delamination areas. Figure 54 and Figure 55 show some interesting delamination areas or substrata that span multiple layers of different composition. The delaminations did not appear to favor any particular layer in the coating. Some carbon contamination was found in the full TBC coating that resulted when a portion of the alumina crucible was vaporized inadvertently. This contamination may have played a significant role in the poor adhesion quality of the coatings. Figure 57 shows the porous nature of the NiAl bondcoat, while Figure 58 presents the growth surface of the pure Al_2O_3 layer. Unfortunately, the rough, porous morphology of the bondcoat is propagated to the top coat in PVD. A plasma-sprayed NiCoCrAlY or PtAl bondcoat would produce smoother topcoats. This is obviously one reason why they are the preferred commercial bondcoats in use by industry.

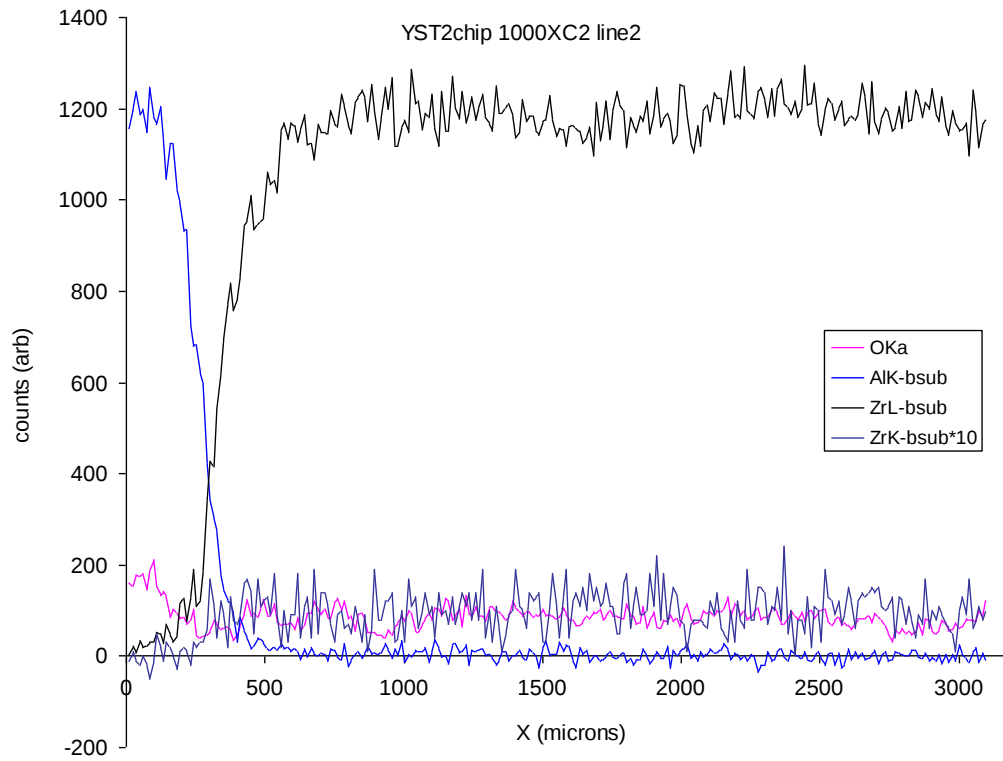


Figure 49. Line scan (Fig. 5, Line 2) - O, Al, Zr-La and Zr-Ka intensities vs. distance

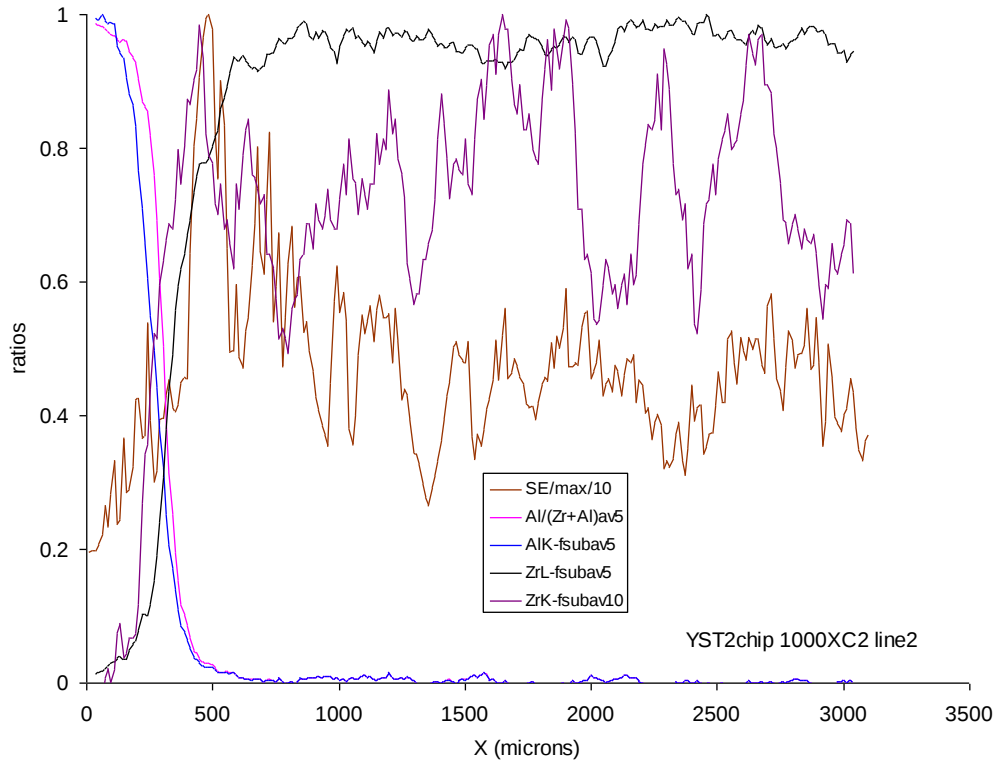


Figure 50. Data from Figure 49 re-plotted as fractions of maxima along path

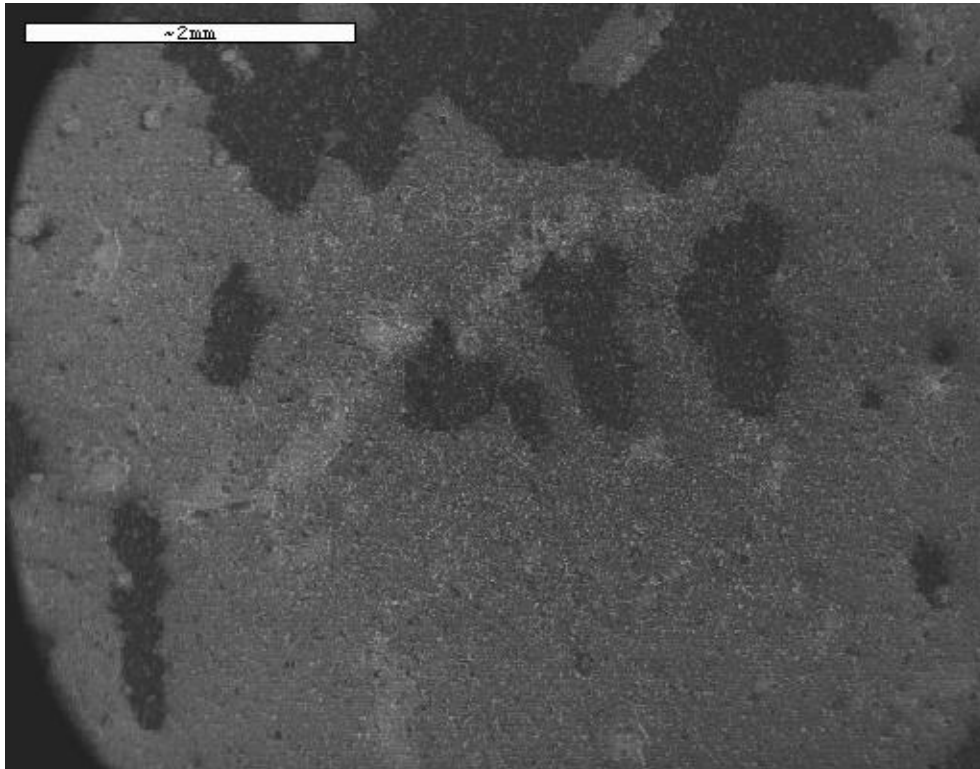


Figure 51. Full TBC coating at X20 showing surface variability

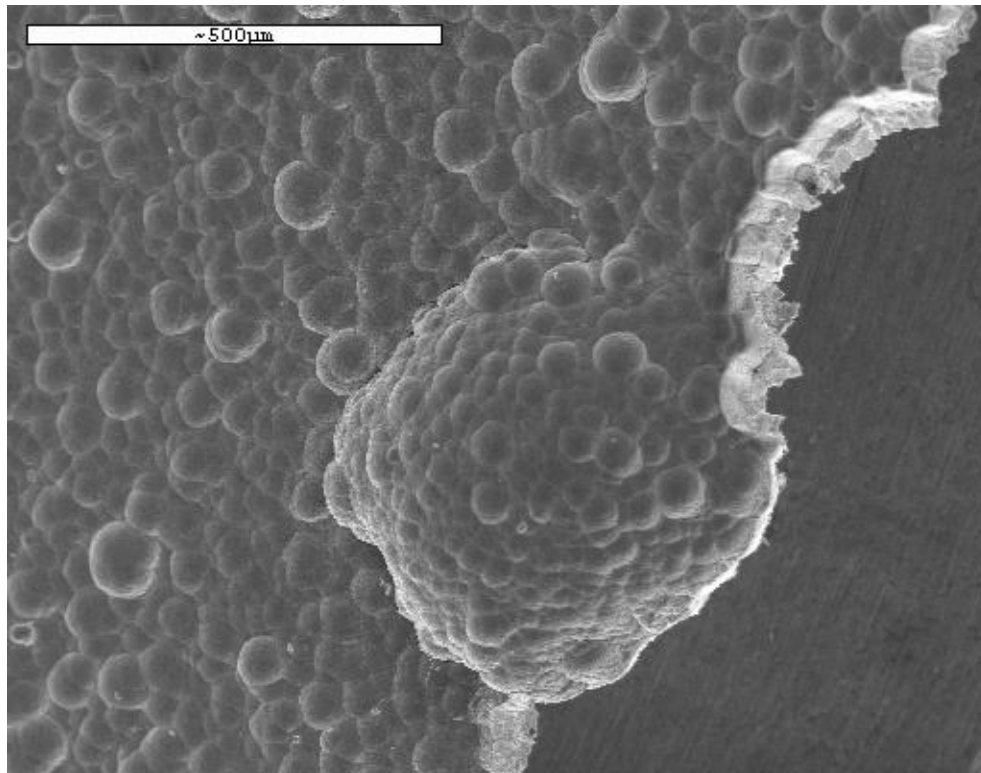


Figure 52. Full TBC coating at X100 showing top of grains

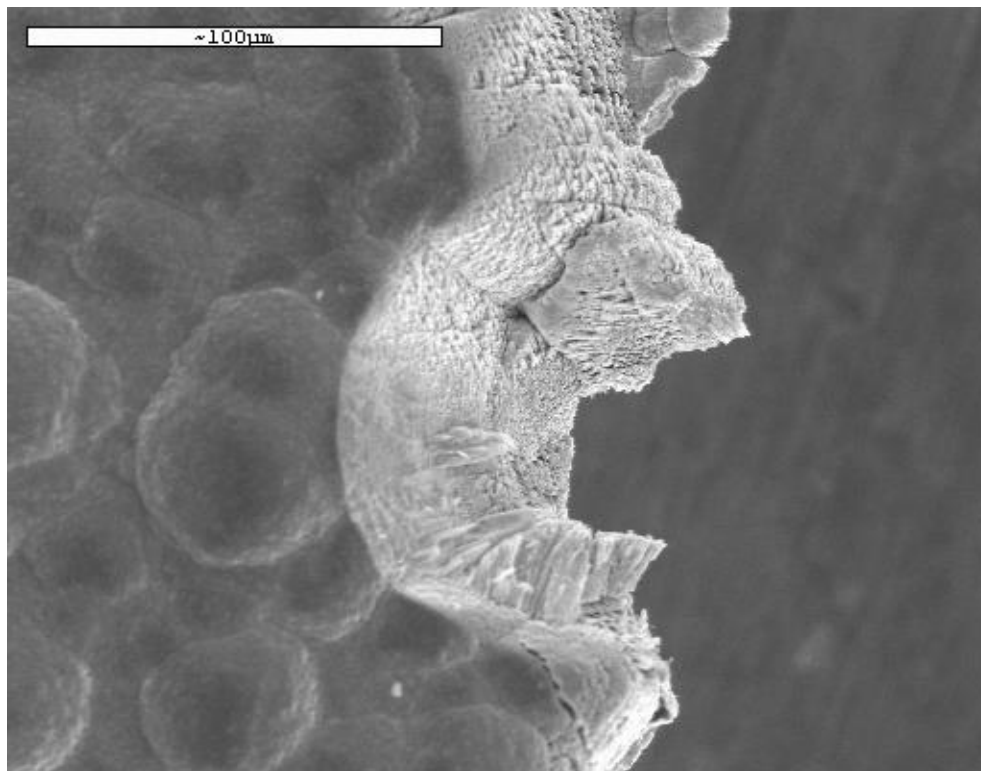


Figure 53. Full TBC coating at X500 showing fracture surface

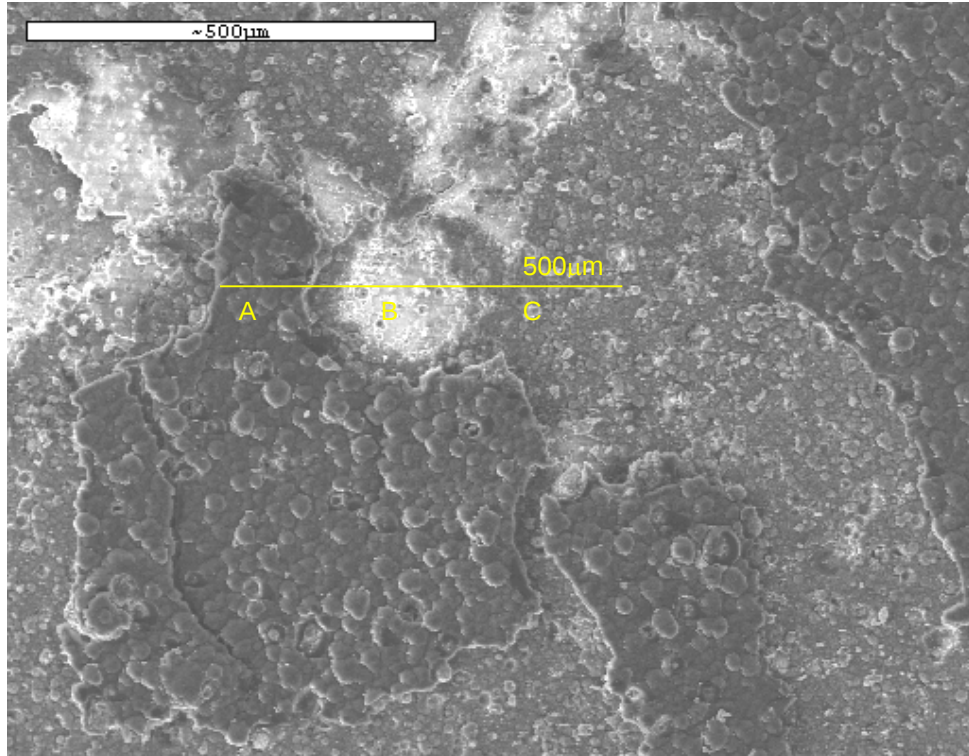


Figure 54. full TBC coating at X100, scan: FTBC button X100A 500micron; Scan showed C+Zr (Region A); Al+O, some Zr (Region B); Al+O (Region C)

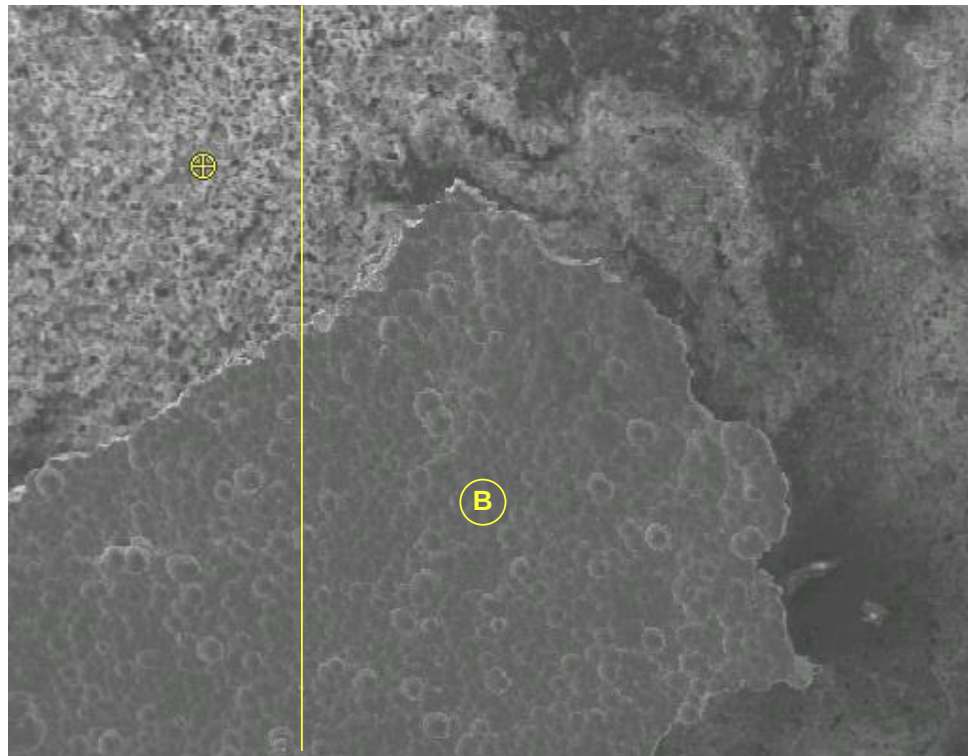


Figure 55. SEM micrograph at 50X site A spot (shown) is NiAl with Ti,Cr,Fe; spot B Z+Y+O

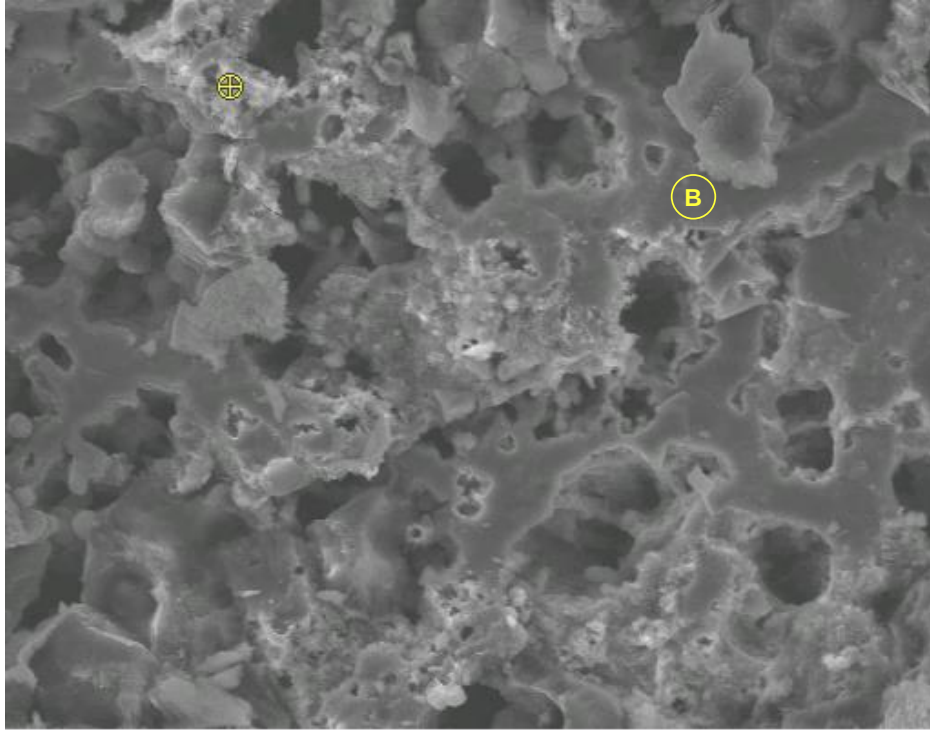


Figure 56. SEM micrograph at 1000X up/left in Figure 55, spots A (cross) and B are similar in Al and Ni.

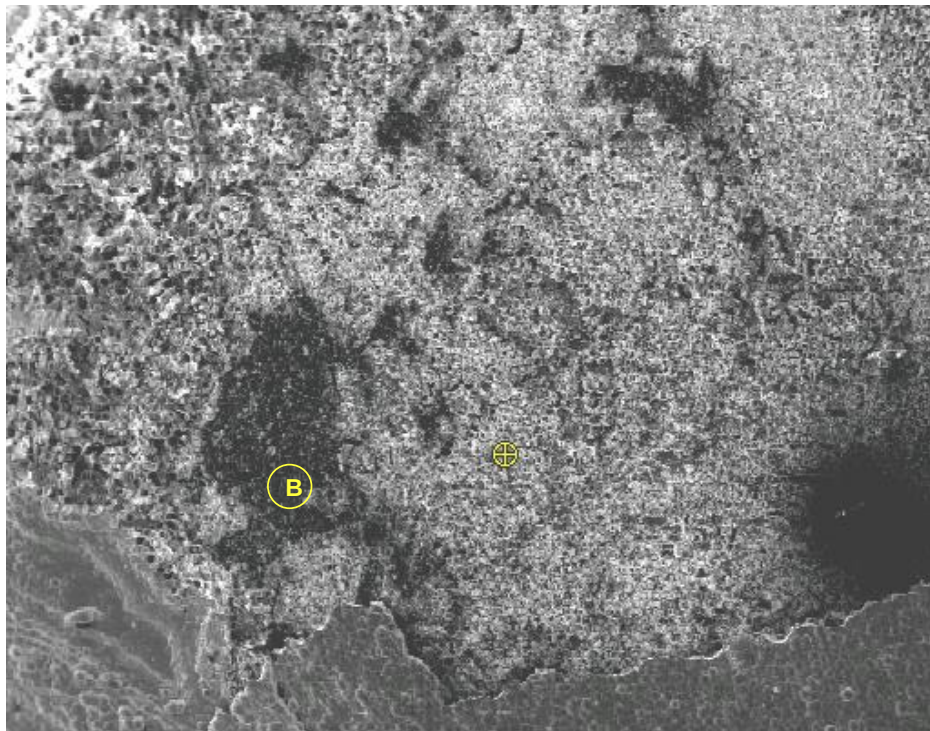


Figure 57. SEM micrograph at 25X, site B and spot A (cross) are mostly Al with Ni+Ti, Cr.

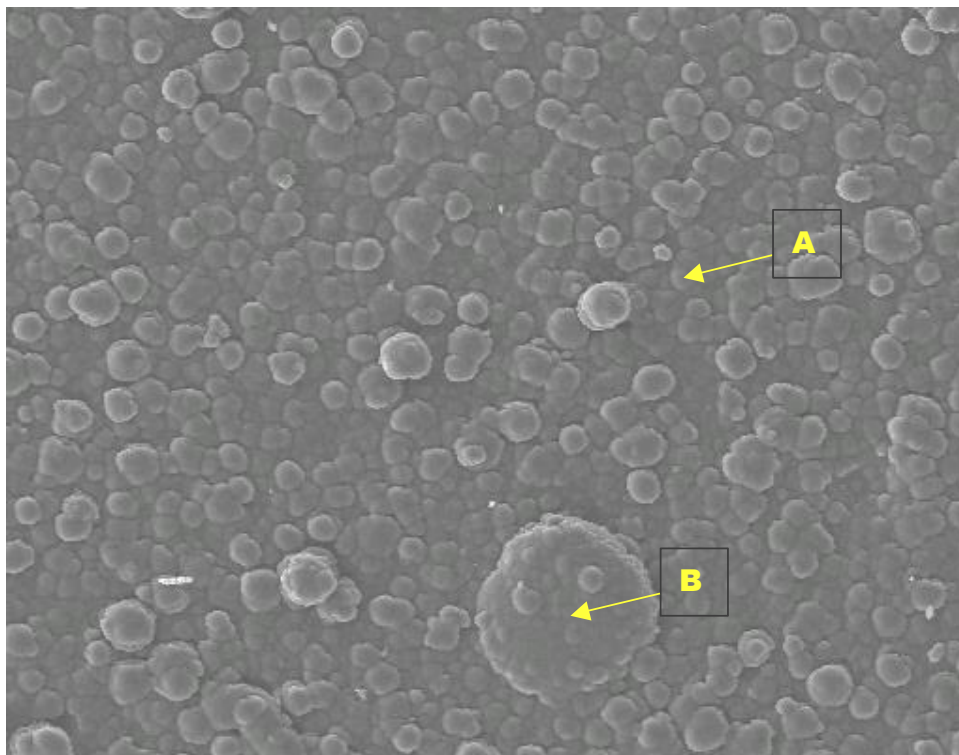


Figure 58. SEM micrograph at 150X showing growth surface of Al_2O_3

Since quite a few of the coatings deposited during the four deposition campaigns exhibited quick delamination and poor adhesion, it was decided to forego any type of quantitative comparison between the coatings. The Figure-of-Merit defined as adhesion strength/thermal conductivity made little sense in light of these developments. Therefore, it was decided to leave the adhesion problems to a larger future project for further investigation and rank the coatings based on thermal conductivity alone.

Optical emission spectroscopy was used to characterize the composition of both YSZ and combined YSZ+ Al_2O_3 plumes. The excitation of the plume by both the primary electron beam and the ion gun produces intense line emissions. A comparison of typical spectra with and without IBAD appears in Fig. 7. Strong emission from ZrO and YO species occurs at the onset of evaporation. During the application of an argon ion flux, atomic Zr and Y lines also appear. The Y line at 597.2 nm, the Zr lines at 677.9 nm and 746.7 nm are suitable for quantitative actinometry. The YO line at 593.9 nm, and the ZrO lines at 622.9 nm and 647.4 nm indicate that a plume exists.

The use of IBAD produced fully stoichiometric YSZ coatings even with the background O_2 pressure reduced by over an order of magnitude, from over 3 Pa to slightly over 0.1 Pa, and the background temperature in the thermal cage reduced by 200 °C. The stoichiometry was verified with 2 θ XRD scans of the coatings that show sharp peaks from the tetragonal (111) ZrO_2 phase. This is further validated by the intense white color of the coating [3]. This is a significant result, since it indicates that a much wider processing window may exist for TBCs. Noticeable density variations in the YSZ

coatings as seen in SEM micrographs were obtained by applying a 20 mA, 500 eV argon bombardment at 30 cm from the substrate in a 133 mPa oxygen background using 20 s on/ 20 s off IBAD duty cycles.

Only a very limited amount of thermal testing was performed on the coatings during the deposition process due to scheduling constraints. Most of the project time was used to deposit more coatings under various conditions. Adhesion of many of the coatings to the substrate was poor. The YSZ top coat would often flake-off of the bondcoat immediately after cool down due to thermal stresses in the coatings. These coatings were not viewed as good candidates for further thermal fatigue testing. Several of the earlier coatings, in particular those that did not have an alumina diffusion barrier, did display good adhesion, and it is hoped that dedicated thermal fatigue testing can be performed in the near future once a new funding source is identified.

5. Accomplishments and Milestones (Executive Summary)

During this two-year project, we completed 19 of the proposed 21 task goals and met all eight project milestones. The first task was completed by using IBAD and substrate pivoting. SEM micrographs of our earlier attempts to produce layered yttria-stabilized zirconia (YSZ) with the EB-1200 using 30° substrate pivoting at 90-second intervals appeared in Figure 22 in section 4, task 1. These features were on the 10 micron scale. Since, we have demonstrated layering to sub-micron levels. Figure 59 below is a recent SEM micrograph of a coating with 0.6 micron layering, and Figure 23 in section 4, task 1 showed layers with a periodic thickness of only a half-micron.

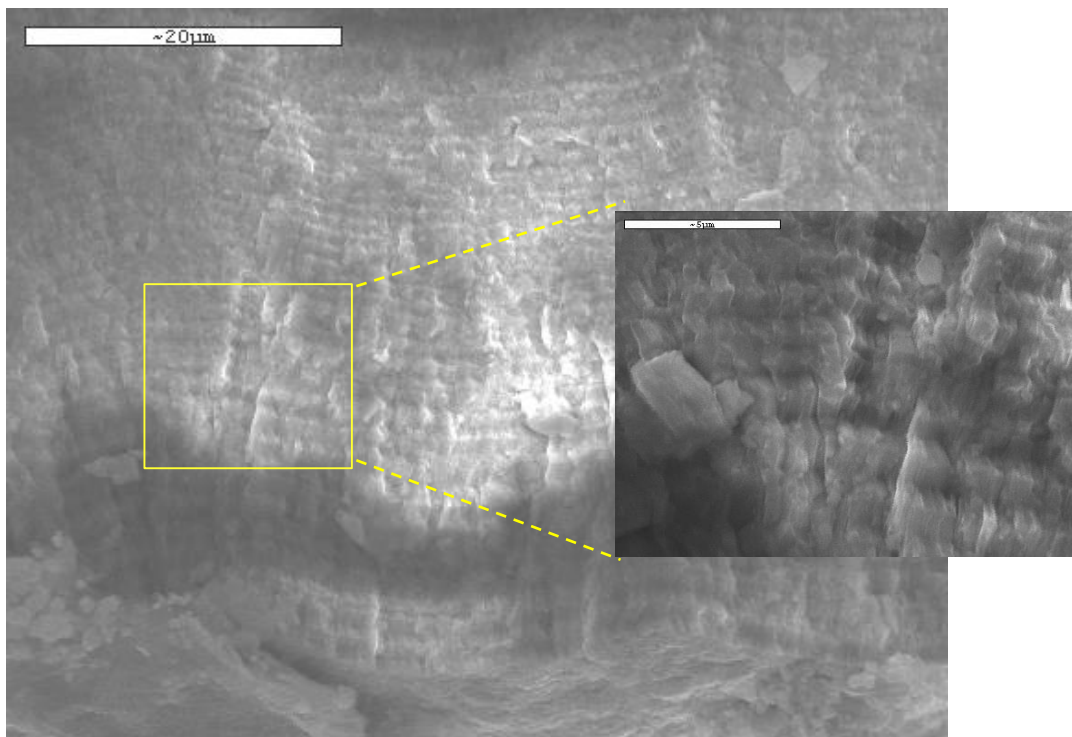


Figure 59. Multi-layer YSZ with 0.6 um layering

In the second subtask of the project, we verified that we could reduce the background O_2 pressure by over an order of magnitude and reduce background temperature in the thermal cage by 200 °C and still produce fully stoichiometric YSZ coatings by using IBAD. This is an extremely significant discovery, since it opens up a much wider processing window for TBCs. We have identified ion gun parameters that produce distinct layering. For example, by applying a 20 mA, 575 eV argon bombardment at 25 cm from the substrate in a 27 mPa (2×10^{-4} Torr) oxygen background, we were able to produce noticeable density variations in the YSZ coating using 20 s on/ 20 s off IBAD duty cycles. Figure 48 presented the surface modification caused by the ion bombardment and subsequent renucleation and growth of new YSZ columns. Because, the results were very favorable, it was decided to continue the work on layered structures, thus satisfying the first official milestone in the project.

On the modeling front, a 2-d DSMC model of the thermal cage and ingot were completed. Parametric studies of the oxygen injection, excitation states, chemistry, and thermal management were completed. Although sensitivities studies reveal the importance of various parameters, lack of fundamental physical data remained a challenge.

The modeling work performed at the beginning of the LDRD was aimed at improving our understanding of the physical processes. Thermal equilibria data for YSZ and alumina were obtained from the literature as well as partial pressure curves for Al_2O_3 , ZrO_2 and Y_2O_3 . In particular, the degree of vibrational excitation of the ZrO_2 and Y_2O_3 and its influence on the deposition rates at the surface were not known. Therefore, two cases were investigated. The molecules were modeled either as fully vibrationally excited using a classical description or as vibrationally cold. Despite differences observed in the shape of the plume the deposition rate on the surfaces was not significantly affected. This means that our lack of understanding regarding the molecular excitation modes of these compounds will not generate much error in modeling of their transport in the plume.

The effect of the wall temperature was also examined numerically. The conclusion was that keeping the wall temperature at around 550 °C enables the thermal cage walls to increase the temperature of the cold oxygen gas and more uniformly distribute O_2 throughout the enclosure. Oxygen molecule collisions with the walls appeared to be a lot more frequent than gas phase collisions. This not only increases the temperature of the oxygen background gas, but also the collisionality of the mixture.

Another open question, relevant to the gas phase collisionality, is that of the gas phase chemistry, since it pertains to the formation of ZrO_2 and Y_2O_3 on the surface. Initially, we made the following assumptions to approximate the plume:

- 1) Zr, Y, ZrO, Y_2O_x , ZO_2 and Y_2O_3 were given a unity wall sticking coefficient.
- 2) O_2 reflects diffusely off the walls, and its sticking coefficient was approximated as zero.
- 3) The plume of the ingot consists of ZrO and Y_2O_x .
- 4) ZrO_2 and Y_2O_3 are formed on the surface.

Correct modeling of all these should lead to stoichiometric ZrO_2 and Y_2O_3 on the surface, i.e. the fluxes of ZrO and Y_2O_x must be less than about half the flux of O_2 .

By balancing the fluxes, the system can be modeled in a self-consistent way, i.e., the molecular oxygen fluxes should at least equal to half the ZrO and Y_2O_x fluxes to the surface. Spectroscopic measurements allowed a qualitative verification of these assumptions by providing more information on the composition of the plume near the substrates. Wall sticking coefficient data were not readily available in the literature. Therefore, we performed a dual substrate weight gain experiment that allowed us to infer the correct sticking coefficients for our process conditions. The experimental value of 0.7 was used for ZrO and Y_2O_x in subsequent DSMC runs and produced good agreement to observation.

A new model of the dual source $\text{Al}_2\text{O}_3/\text{YSZ}$ geometry was completed. The separation distance between ingot and Al_2O_3 crucible was optimized to provide as much vapor plume mixing as possible. This effort completed the fourth subtask. Although the DSMC calculations provided the required evaporation rates for gradient mixing, experimental trials were required to determine the best electron beam settings to obtain the correct evaporation rate from each source. This is especially critical in dual source evaporation where the dissimilar source materials have such widely different melting points and vapor pressures. Based on our preliminary dual-source evaporation runs, it appeared that graded YSZ/alumina coatings were possible. A decision was made to pursue work on optimizing the graded TBC approach. This decision satisfied the second official milestone of the project.

The above subtasks were completed and milestones were attained because significant progress was made in setting up for YSZ deposition using the EB-1200. The geometry of the EB-1200 electron beam system was reconfigured to perform EB-PVD. This included the development and use of PVD sector bending magnet of our own design. It also included the fabrication and operation of our own YSZ ingot feeder, the fabrication of the thermal cage, and the refurbishment of the “stinger” load-locked parts manipulator with 22 kW of pre-heat. Substrate sample holders with thermocouples and masks were fabricated. A large oxygen compatible turbo pump was added to the cathode chamber of EB-1200 gun #1 to handle the oxygen pumping. Real time calorimetry of the hearth and remote control of the ingot feedrate were also completed. An additional infrared camera, a visual video system and two video fiberscopes were added in FY’02 to monitor beam positioning and ingot evaporation. A gridded ion gun was added to the system to perform ion-beam-assisted deposition. Polished Inconel 718 superalloy coupons were coated with 30 and 50 μm of aluminum and used as substrates for our deposited YSZ coatings.

An alumina ingot in a graphite crucible was installed next to the ingot feeder for dual-source evaporations. DSMC modeling was performed to evaluate the vapor phase transport and mixing in the dual-source plume. These results were used to determine the position of the alumina ingot and the relative evaporation rates required to produce the desired gradient in the mixing. Thus, the dwell times required for beam sharing on both ingots were obtained.

The project also faced several operational hurdles that limited the total number of deposition runs. Five major problems developed during the course of the experiments. The biggest was the continued cracking of the quartz windows in the stinger preheat chamber. Thermal expansion of the quartz would lead to high stresses and subsequent fracture in the 1-cm-thick windows that formed the vacuum boundary between the chamber and the quartz lamps. To solve the problem, the entire vacuum boundary was moved behind the lamps and the windows were eliminated entirely. However, a new problem quickly surfaced. The quartz lamps would arc and blow their fuses when the background pressure exceeded a few hundred mPa. This often coincided with a plasma breakdown inside the EB-1200 D-chamber when the stinger gate valve was open. This problem was mitigated by preheating with the gate valve closed. But, substrate outgassing loads at 900 °C were too high for the current stinger pumping system. In the future, a larger turbopump must be installed on the stinger for more reliable operations.

The original tungsten filaments supplied with the 150 kW electron gun cathodes had a short lifetime. They were replaced with homemade tantalum filaments that performed quite well. The ion gun power supplies developed intermittent contact problems that occasionally resulted in poor operation and unreliable cycling. Several of the sockets in the ion gun connector were loose due to thermal fatigue and required repair. The thermal cage temperatures were too hot for the substrate fiberscope; so it was replaced with a simple mirror system to view the substrate surfaces from the bottom of the chamber. Unfortunately, the mirrors were subject to coating by the evaporants. Finally, it was difficult to maintain an even melt pool over the entire YSZ ingot. This created sidewalls of unmelted ceramic around the edges that were not easily removed. Continual feeding of the ingot to maintain the pool elevation sometimes resulted in blocking the sightline for the spectroscopy fiber directly above the hearth. Proper e-beam clean-up procedures to remove these unmelted edges have yet to be perfected.

An extra cylindrical shield was added to the thermal cage to protect the stinger shaft from becoming coated with YSZ. On the first deposition, the coating on the shaft caused the shaft to bind against the vacuum seals and jammed the stinger so substrates could not be removed from the EB-1200 D-chamber. A picture of the coated shaft appears in Figure 60. The new shield performed quite well, but still a thin coating was deposited on the shaft near the substrates, and this often made retrieval of the substrates difficult.

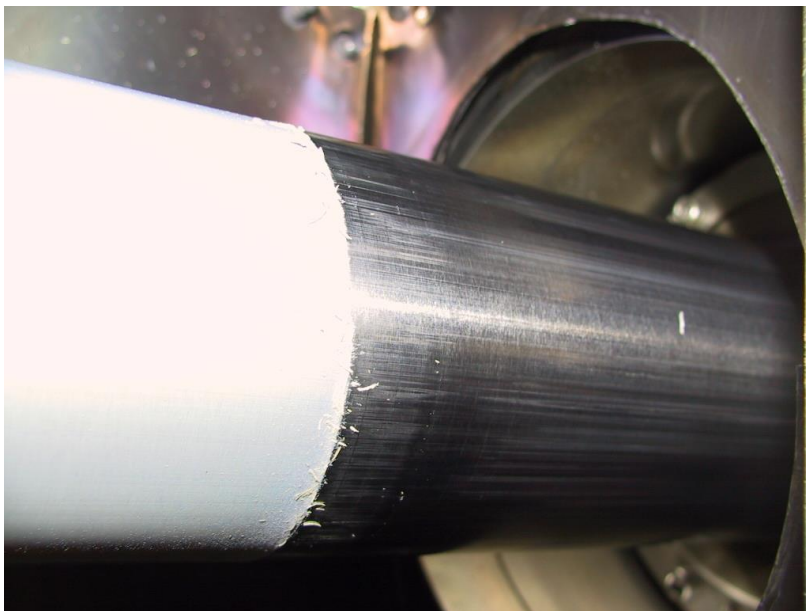


Figure 60. Thick YSZ coating deposited on stinger shaft

During the first series of depositions, it became apparent that the spot size of the EB-1200 electron gun was too large for acceptable raster control across the 70-mm-dia YSZ ingot. To remedy this problem, a modification kit was installed in gun #1 of the EB-1200 that reduced the cathode size from a 19 mm diameter to a 9 mm diameter. This reduces the spot size from 12 mm in diameter down to 5 mm at a cost in the reduction of maximum gun power from 600 kW to 150 kW. The smaller spot size was rastered over both the 70-mm-dia YSZ ingot and the 28-mm-dia Al_2O_3 ingot with good control of the temperature distribution using our advanced digital rastering system. The maximum 150 kW power level proved more than adequate to evaporate both YSZ and Al_2O_3 during the dual-source evaporations.

Both tetragonal ZrO_2 and cubic ZrO_2 top coats could be deposited in the EB-1200 depending on the oxygen background pressure, the ion flux and the substrate temperature. Higher chamber pressures (133 mPa, 1×10^{-3} Torr) and lower substrate temperature ($<600^\circ\text{C}$) without IBAD produced predominantly tetragonal ZrO_2 phase; whereas, lower chamber pressures (27 mPa, 2×10^{-4} Torr) and higher substrate temperatures ($\sim 750^\circ\text{C}$) with IBAD produced mostly cubic phase. A comparison of the XRD spectra for these two cases was shown in Figure 47.

A very significant discovery was the validation that we could indeed produce α -phase alumina using IBAD directly by depositing amorphous alumina in the presence of an ion flux. A patent disclosure for this technique has been issued to the Sandia Patent and Licensing office.

Our intention to use Laser Atomic Absorption Spectroscopy for plume characterization was abandoned, when it was learned that the only system in existence tuned to YSZ plumes was dismantled at Lawrence Livermore National Laboratory. However, optical

emission spectroscopy was successfully performed in the harsh, 900 °C environment of the PVD plume. Spectra for various operating parameters were obtained for both IBAD and non-IBAD plumes. Figure 61 below shows a typical spectrum that contains both atomic Zr and Y lines as well as molecular lines of ZrO and YO. OES was used to characterize the composition of both YSZ and combined YSZ+Al₂O₃ plumes. The excitation of the plume by both the primary electron beam and the ion gun produces intense line emissions. Strong emission from ZrO and YO species occurs at the onset of evaporation. During the application of an ion flux, atomic Zr and Y lines also appear. The Y line at 597.2 nm, the Zr lines at 677.9 nm and 746.7 nm are suitable for quantitative actinometry. The YO line at 593.9 nm, and the ZrO lines at 622.9 nm and 647.4 nm indicate that a plume exists.

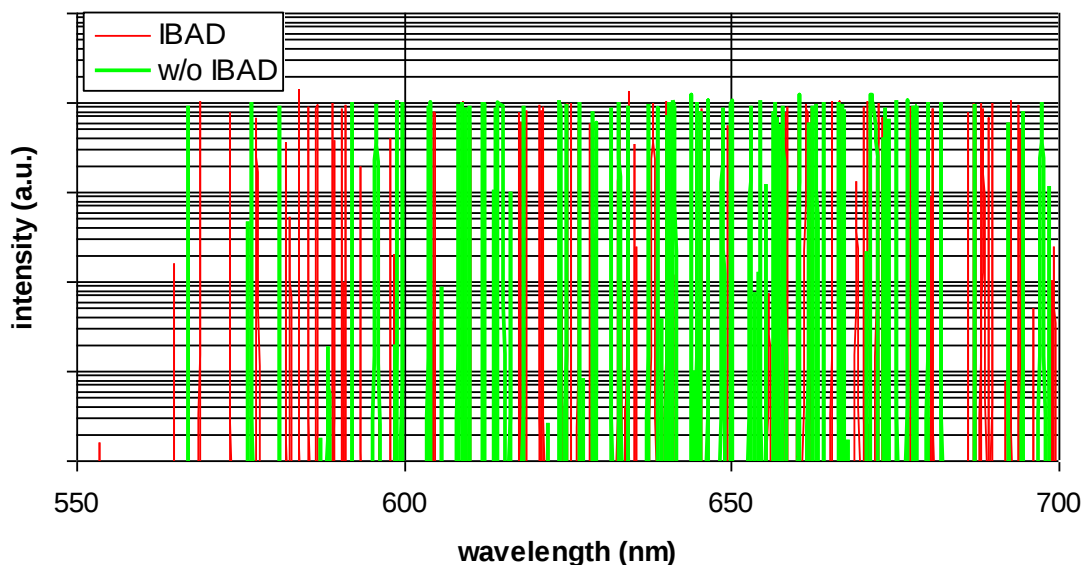


Figure 61. Typical optical emission spectroscopy spectra both with and without IBAD

The best samples produced to date were identified and their material properties such as composition and phase were measured with EDX and XRD, and the thermal conductivity was measured using the 3 ω technique.

A final SAND report was written by the close of FY'03 and submitted for printing.

6. Conclusions

It has been demonstrated that IBAD and substrate pivoting can create a layered morphology on the sub-micron level in YSZ that results in reduced thermal conductivity compared to commercially available EB-PVD coatings. The pivoting changes the grain orientation and increases the number of grain boundaries, while the periodic IBAD layers keep the PVD columnar grains from growing too large, thus maintaining the higher intergranular porosity that impedes thermal conduction. Reduced conductivities as low

as 1.4 W/m²K were obtained. Although much improved, these conductivities remain higher than typical plasma-sprayed YSZ coating values near 0.9 W/m²K [3].

An easily controllable process for transitioning physical vapor deposited amorphous alumina to α -phase alumina has been demonstrated using IBAD. This technology greatly reduces the processing time from the several hours used to thermally grow the oxide layer and the post processing heat treatment to perform the transition to only a few minutes. The ion gun and vacuum parameters used for the process are patentable, and a technical advance has been submitted to Sandia National Laboratories for the protection of this intellectual property.

The use of DSMC simulations has revealed the loss of oxygen from the ingot, the importance of thermal management during the deposition process, and the plume composition during dual source evaporation. IBAD produced fully stoichiometric YSZ films at a lower thermal cage temperature of 600 °C compared to 800 °C. The DSMC calculations also revealed that a sticking coefficient for ZrO on stainless steel at 600 °C of approximately 0.7 produced non line-of-sight depositions consistent with experimental observations.

Currently, we are working to identify a follow-on CRADA partner for this research. The technology developed for EB-PVD of land-based IGT blades is commercially valuable. Several industrial TBC vendors have expressed interest in the results of this project, and negotiations are underway to continue the effort. Sandia now has access to a new 3-d DSMC code developed at NASA that could advance the plume modeling beyond the current state-of-the-art. The use of IBAD to form the α -alumina scale via PVD is a significant development with licensing potential.

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Appendix: Presentation at International Conference on Metallurgical Coatings and Thin Films – 2003 (American Vacuum Society), April 30, 2003



A3-3-9

**Effects of Ion Beam Assisted Deposition, Beam Sharing
and Pivoting in EB-PVD Processing of Graded Thermal
Barrier Coatings**

ICMCTF 2003

D. L. Youchison, M.A. Gallis, R.E. Nygren, J.M. McDonald, T.J. Lutz
Sandia National Laboratories

San Diego, CA
April 30, 2003

 Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000. 

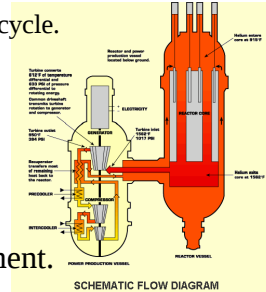
OUTLINE

- A. Objectives of EB-PVD TBC Research**
- B. DSMC plume modeling to improve processing**
- C. Capabilities of Sandia's EB-1200 system**
- D. Layering results and coating characterization**
- E. Concluding remarks**

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Highly efficient IGTs coupled to HTGRs are one possible solution to the nation's energy needs both in electricity and hydrogen production.

DOE is involved in a holistic approach to the nuclear fuel cycle.



IGTs require further EB-PVD process development.

1. Bend horizontal electron beams for under-rake access
2. Understand transport in large plumes for uniform coatings
3. Reduce processing temperatures, improve thermal management
4. Reduce EB-PVD TBC thermal conductivity by layering to increase phonon and photon scattering (pivoting, DC and RF biasing, IBAD)
5. Streamline processing times to improve throughput of larger parts.
(replace TGO with IBAD α - Al_2O_3 and a graded YSZ/ Al_2O_3 system)

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3



Utilized 2-d and 3-d DSMC modeling of plume transport to improve processing.

- Massively parallel computing permits the use of Sandia's ICARUS and PEGASUS DSMC codes on EB-PVD plumes.

(5 million computational particles representing $>10^{10}$ real molecules are used on 1000 processor 3 Tflop ASCI red computer.)

- free-molecular to continuum flow fields can be modeled
 - multiple species, internal energy modes, chemistry, and transport are modeled.
 - particles are independent during transport
 - particles are collided using probabilistic techniques
 - complex gas and surface chemistry is possible if reaction rates known
- Due to lack of physical data, we investigate parametric extremes.

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DSMC studies reveal development path for graded layer TBCs.

- effect of oxygen injection and location
 - O_2 compensates for preferential pumping
 - Injection location not significant
- effect of thermal cage, i.e. thermal management
 - Required to increase collisionality
 - Reduces adsorption
- transport in mixed plumes ($7YPSZ + Al_2O_3$)
 - Mass screening in plume skews deposition rates
- surface chemistry, sticking coefficients
 - YSZ sticking coefficients near 0.7 on s.s. at 600 C
 - Full stoichiometry restored at the substrate
- control of incident flux through RF-biasing or plume ionization.
 - Promoting dissociation of molecules opens the window for control of deposition rates in the YSZ/ Al_2O_3 system.

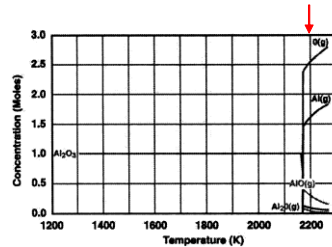
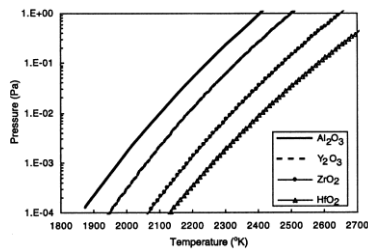
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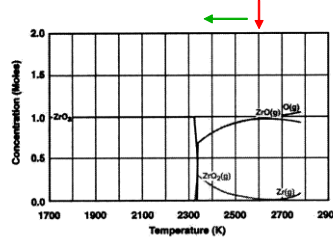
Need high temperatures at ingot for complete dissociation of molecules.

G.D. Alton et al. / Nuclear Instruments and Methods in Physics Research A 438 (1999) 190–209



But, need to control ratio of fluxes to the substrate for grading.

IBAD: An energetic Ar^+ flux can promote dissociation in the plume



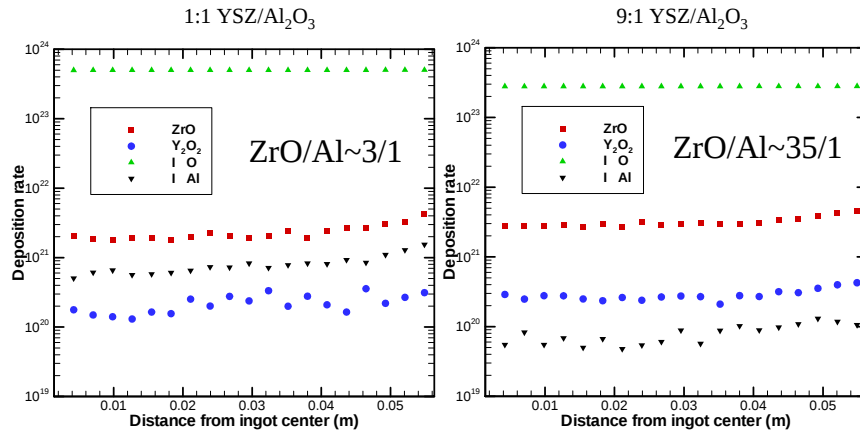
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6



Thermally excited deposition rate is almost linear function of evaporation rate except for mixed plumes.

Transport is mostly collisionless and line-of-sight at the **substrate**, but not near the ingots.



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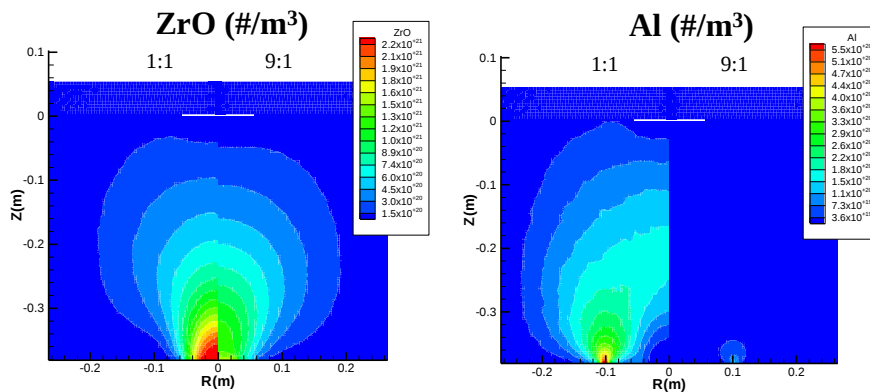
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Most collisions occur near the sources and this hampers transport of lighter molecules.

Evaporation ratios:

Left: 1:1 ratio of YSZ/Al₂O₃ Right: 9:1 ratio of YSZ/Al₂O₃



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EB-1200 as a PVD coater



ingot feeder

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9



EB-1200 System has flexibility.

Beam Current	15+ amperes each gun
Angle of Beam Incidence	0° to 90 °
Cathode Lifetime	> 200 hours
Magnetic Lenses	2 coils
Magnetic Deflection	2 coils, orthogonal directions
Max. Angle of Beam Deflection	±30° at < 200 Hz ±7° at 10 kHz
Maximum Raster Frequency	10 kHz
Unrastered (pulsed) Spot Diameter at 600 kW and a Distance of 1.5 m	3.5 cm
Maximum Heat Flux (unrastered)	>1000 MW/m ²
Maximum Heated Area @ 1.5 m, and 10 kHz	37 cm x 37 cm
Heat Flux @ Maximum Area	8.7 MW/m ²
Maximum Pressure in Chamber	< 3 Pa
Cooling Water Consumption	2.2 m ³ /hr

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10



EB-1200 has a variety of diagnostics.

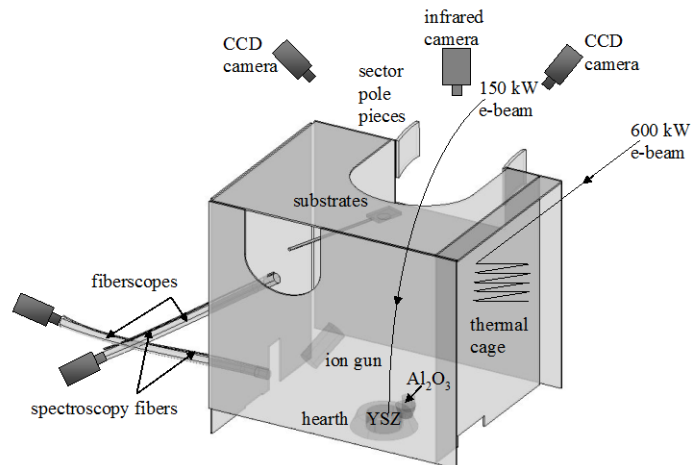
<u>Diagnostic</u>	<u>Purpose</u>
Pyrometers (4)	Surface temperatures
Infrared Camera & video digitizer (2)	Surface temperature profiles
x-ray CCD camera	Composition, thickness
Laser-Induced Fluorescence	Composition, density, velocity distributions
Thermocouples (48)	Bulk temperatures
Strain gauges, LVDTs	Bulk response
Residual Gas Analyzer	Partial pressures
Water calorimetry	heat removal capability
Bore scopes (3)	<i>In situ</i> surface observations
TV monitoring system	Visual records
Fiberscopes (2)	
<i>Optical Emission Spectroscopy (OES)</i>	<i>Plume Composition</i>

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11



High temperatures in thermal cage make diagnostics challenging.



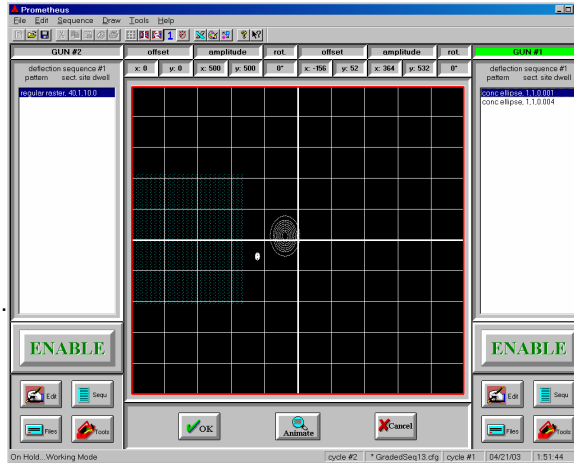
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12



Exotic raster patterns and high-speed pattern switching make beam sharing possible.

- The EB-1200 is equipped with digital rastering.
- The "Prometheus" program can raster at 10 kHz and pattern switch at 1 kHz from one source to another.
- Two gun control
- Size, position rotation and aspect ratio can be controlled.
- 40 sections, 3 sequences, 10 steps, 2000 point max.
- Different dwelltimes can be set for each section.

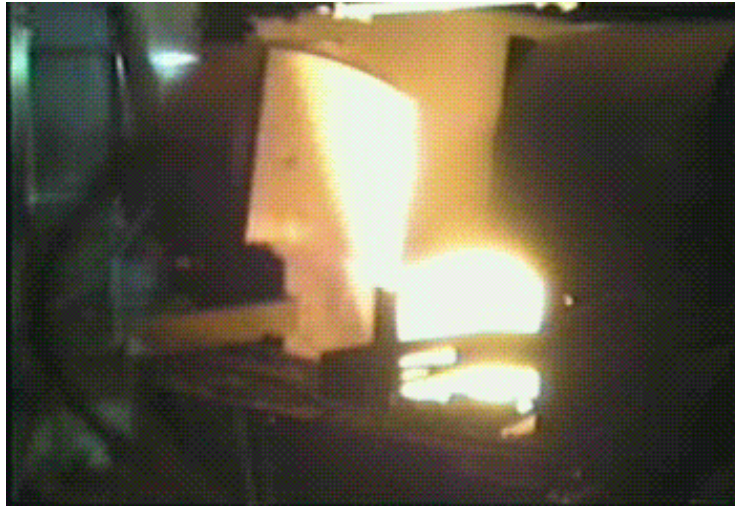


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13



Beam sharing and sizing are critical.

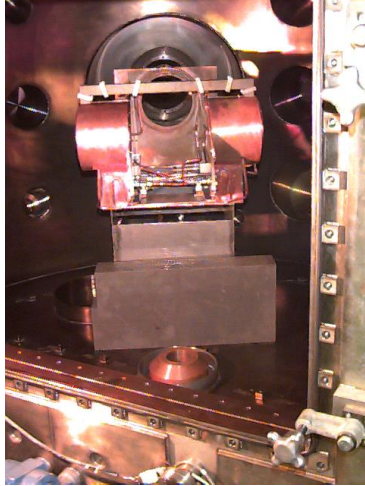


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Bending magnet and hearth installed in EB-1200.



- Water-cooled, vacuum compatible 70° bending magnet
- 2.5" DIA water-cooled hearth with calorimetry
- load-locked ingot feeder with 12" of ingot feed
- load-locked, rotatable parts manipulator with preheat
- Digital rastering with high-speed pattern switching, 2-gun operation
- 3 IR cameras & 4 pyrometers, OES diagnostic

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15



Beam bending after pattern requires good optics.

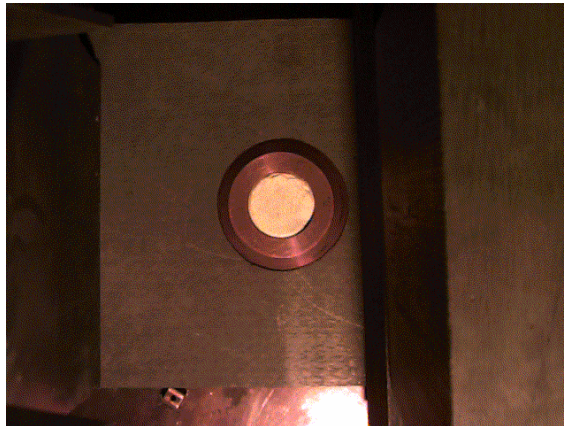


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Water-cooled hearth with YSZ ingot as seen from IR camera port.

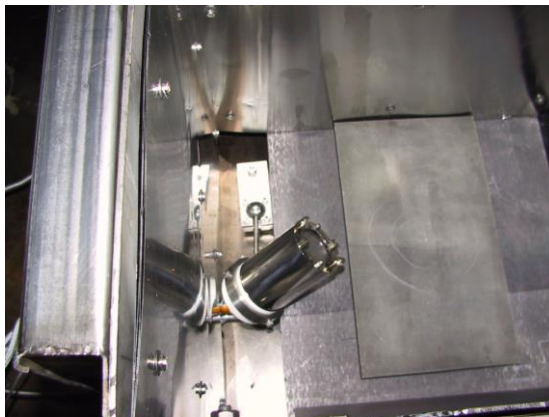


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Surface Modification



- IBAD with 3-cm Kaufman Gun (Veeco Iontech with ID-2500 P.S., dual Mo grids)
- Pivoting with Parts Manipulator
- RF-biasing

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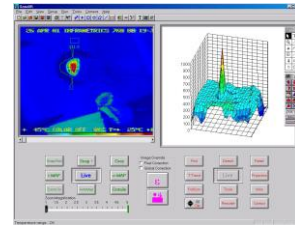
18



Thermography and calorimetry used to characterize processing.



IR camera view of ingot, hearth and paddle



Paddle w/ 5 substrates
Kaufman gun

Magnet pole piece

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Good substrate control and diagnostics are essential.

Load-locked, 3-d parts manipulator with programmable rotation (30 rpm max), 1000 C, 22 kW of preheat, 1 m of stroke and 4 TCs.



5 coupon substrate holder (paddle) with YSZ-coated Inconel 718 substrates

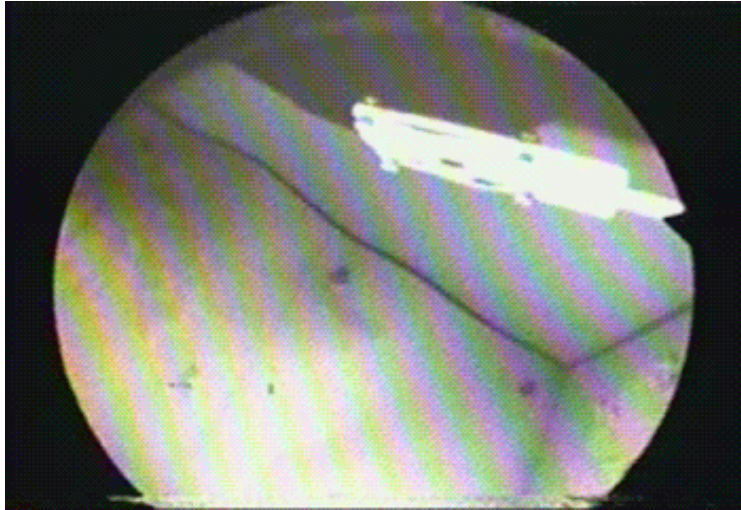


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20



Viewing substrate pivoting is difficult at 700 C.



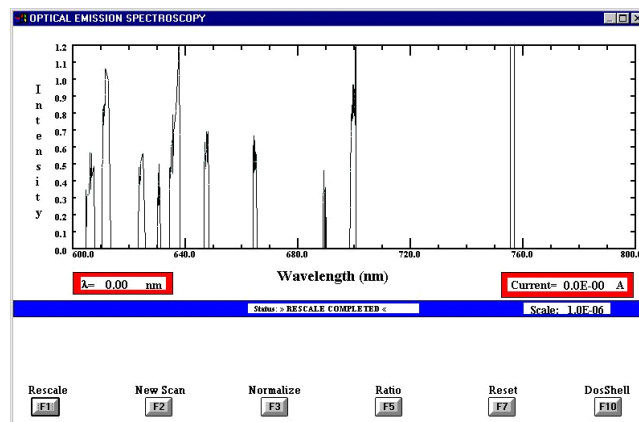
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21



Diagnostics used to benchmark modeling and develop process controls.

- Optical Emission Spectroscopy – 0.3 m focal length, 1200 g/mm
- Water calorimetry of hearths
- IR thermography of melt pool

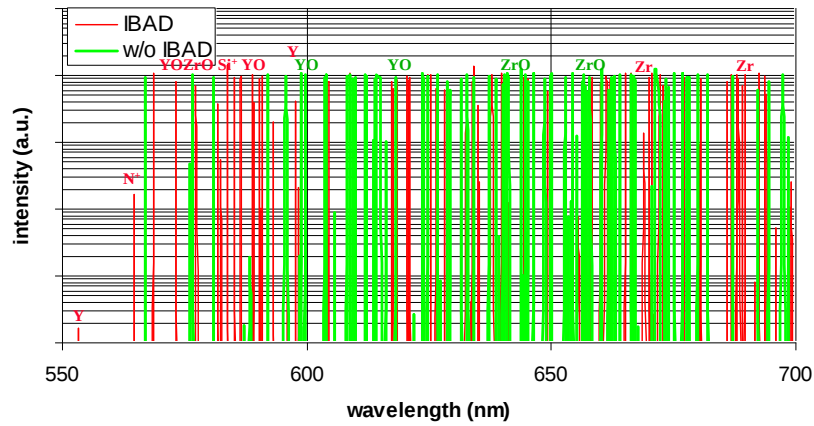


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22



Argon ions disassociate molecules in the plume.

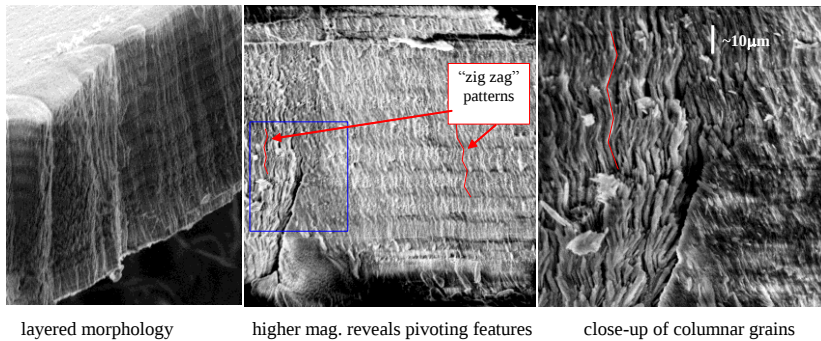


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TBC layering studies included 30° substrate pivoting using 90 s dwelltimes.



layered morphology

higher mag. reveals pivoting features

close-up of columnar grains

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Diffusion of Aluminum can cause poor adhesion at interface.

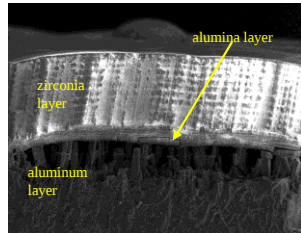
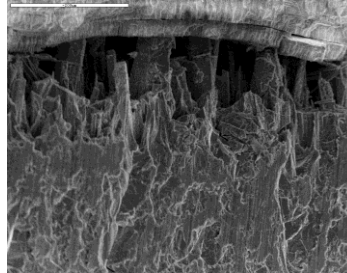


Fig. 1. 5C100E Zirconia layer (~450 μ m) with underlying layers of alumina (~20-25 μ m) and aluminum (~400-500 μ m).



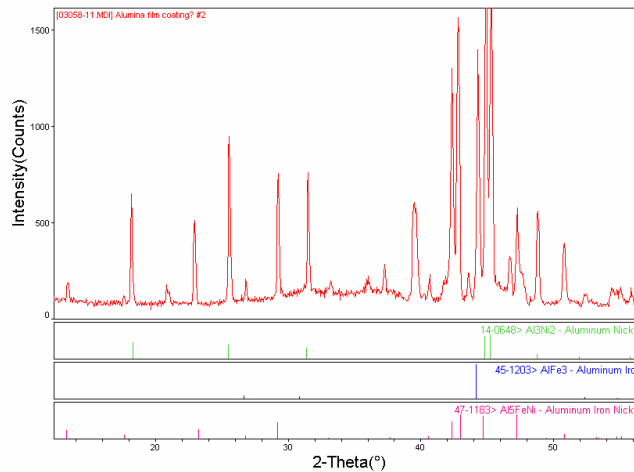
450 μ m	TBC, YSZ
400 μ m	TGO, alumina
	BondCoat, Al_2Ni_2
	Substrate, In718

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Aluminides formed on the Inconel surface.

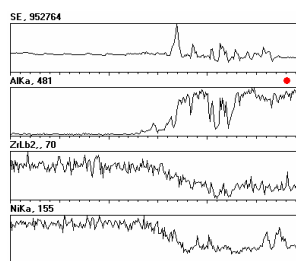
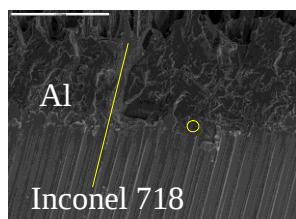


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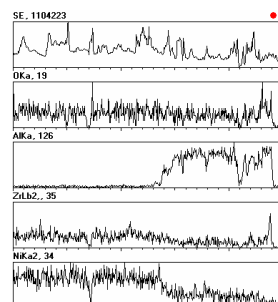
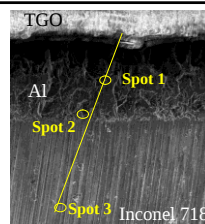


EDX used to characterize interfaces.

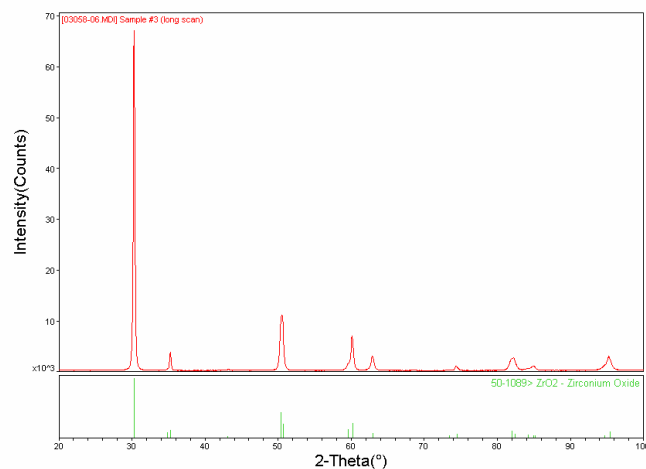


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XRD spectra confirm Tetragonal ZrO₂.



Sandia National Laboratories

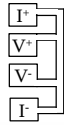
[S837431]merodil+cr:DATASCANDATA-03+ Tuesday, Apr 01, 2003 10:38a (MCM/AD6)

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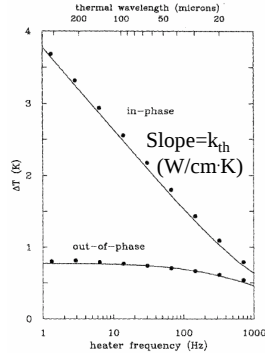
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3 ω MEMS technique used for thermal conductivity measurements of coatings.



I at ac frequency ω heats the metal line at 2ω .
R goes as 2ω . Voltage varies as 3ω .



$K_{th} = 1.5 \text{ W/m}\cdot\text{K}$ at 50 C. (pivoting only)

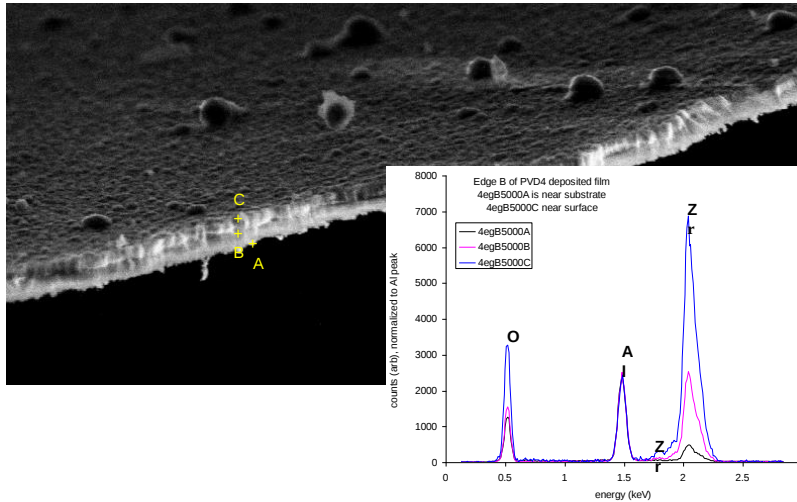
D.G. Cahill, *Rev. Sci. Instrum.* **61**, 804 (1990)

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Evidence of a graded YSZ/ Al_2O_3 coating

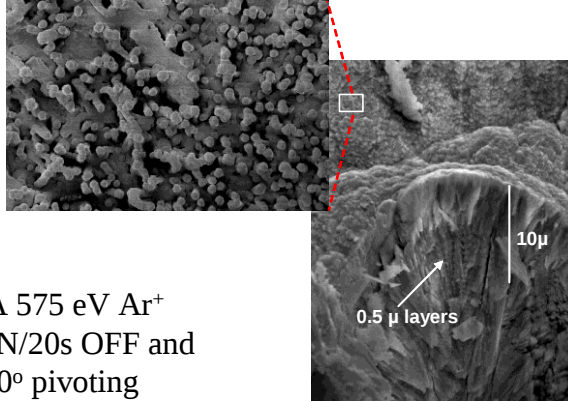


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Cyclic IBAD combined with pivoting has a dramatic effect on coating morphology.



20 mA 575 eV Ar⁺
20s ON/20s OFF and
10 s 30° pivoting

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Concluding Remarks

- DSMC modeling useful for setup and process insight
- Sub-micron layers obtained in YSZ coatings with pivoting
- IBAD successfully combined with pivoting to create layering
- IBAD changes plume chemistry
 - IBAD assists in grading from Al₂O₃ to YSZ
 - Can reduce thermal cage/substrate temperatures
 - Can reduce oxygen makeup
- Only nominal reduction seen in thermal conductivity

Future efforts will focus on the use of IBAD to create α-Al₂O₃ below 1100 C.

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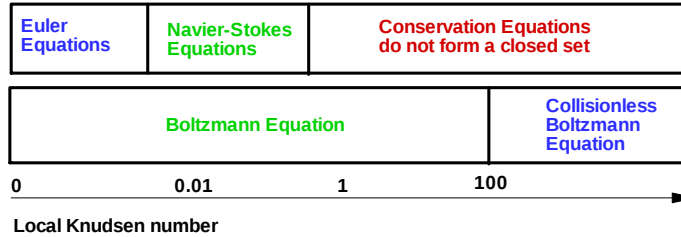


Mathematical models for gas dynamics

$$Kn = \lambda / L$$

λ : local mean free path

L: characteristic length



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The Boltzmann Equation

$$\frac{\partial}{\partial t}(nf) + \vec{v} \cdot \frac{\partial}{\partial \vec{r}}(nf) + \vec{F} \cdot \frac{\partial}{\partial \vec{v}}(nf) = \left[\frac{\partial}{\partial t}(nf) \right]_{collision}$$

f : distribution function

n : number density

F : external force

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Microscopic description of gases

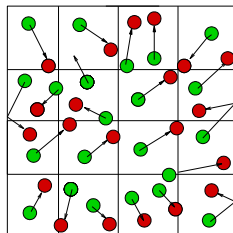
- The rarefied regime is described by the Boltzmann equation
- Particulate nature of gas
- Gas is described by the position, velocity, energy of an ensemble of molecules in a statistical manner
- The microscopic description describes physical processes regardless of the mathematical complexity of the problem

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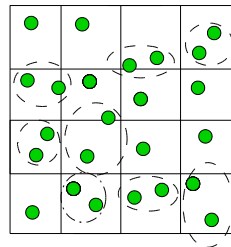
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The Direct Simulation Monte Carlo Method



Move phase (deterministic)



Collide phase (stochastic)

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Applications of DSMC and typical length-scales

- Hypersonics (m)
- Microelectronics manufacturing processes (cm)
- Physical, Chemical vapor deposition (cm)
- MEMS (microns)
- Non-equilibrium chemistry (atomic level)

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The limitations of DSMC

- The computational load increases with the density of the flow
- Statistical error decreases as a function of the *square root* of the number of samples
- DSMC can carry more information than actually needed for some applications
- DSMC is an MMP empowered technology

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