CHEMICALLY VAPOR DEPOSITED YSZ FOR THERMAL AMD ENVIRONMENTAL BARRIER COATINGS

T. M. Besmann
Metals and Ceramics Division, Oak Ridge National Laboratory

V. Varanasi and T. J. Anderson
Chemical Engineering Department, University of Florida

T. L. Starr and W. Xu
Chemical Engineering Department, University of Louisville

ABSTRACT

Yttria-stabilized zirconia (YSZ) has been used as a thermal/environmental barrier coating for gas turbine engine blades. Current methods of fabrication include air plasma spraying (APS) and electron-beam physical vapor deposition (EB-PVD). The APS technique results in a coating that loses effectiveness with thermal cycling. The EB-PVD technique deposits a columnar microstructure which accommodates thermal expansion mismatch, but the process is capital intensive and also line-of-sight. A technique currently being investigated is chemical vapor deposition (CVD), which can reduce the need for costly capital equipment, is simpler, and can deposit high quality coatings on hidden surfaces. Further, CVD coatings can act also as a top coat to seal an EB-PVD coating from ingress of damaging salts from the combustion environment. In our continuing work, YSZ has been successfully deposited on α-Al_2O_3 and the turbine blade material (Mar-M247) with reasonable agreement between modeled and experimental results.

INTRODUCTION

Thermal barrier coatings, or TBC's, are excellent materials for improving the performance, longevity, and overall costs of gas turbine engine (GTE's) lifetimes (Haynes 1997). These ceramic coatings, made of yttria-stabilized zirconia (YSZ), improve GTE lifetimes by reducing the turbine blade temperature and preventing turbine blade failure (Haynes 1997). A schematic of the TBC system is shown in Figure 1.

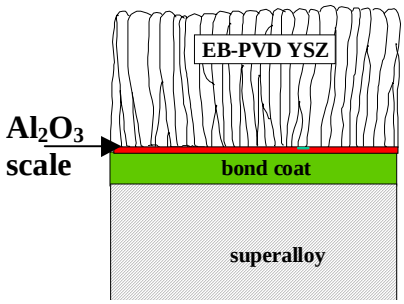

Figure 1: Schematic of TBC. *(After J. A. Haynes)*

The nickel- or cobalt-superalloy turbine blade is protected by three coating layers: an oxidation-resistant aluminum-rich bond coat, a thermally-insulating YSZ top coat, and an α-alumina scale interface (Haynes 1997). The aluminum-rich bond coat is an alloy of MCrAlY (M= Ni or Co), and is coated onto the blade by plasma spraying (Haynes 1997). The YSZ top coat is typically zirconia (ZrO_2) stabilized by six- to eight-weight percent (3.5- to 5.5-mole percent) yttria (Y_2O_3), and is currently deposited onto the bond coat by electron-beam, physical vapor deposition (EB-PVD) (Haynes 1997).

There are several advantages to using a YSZ top coat for the superalloy blade. The decrease in blade temperature of as much as 167°C improves the blade lifetime by three- to four-fold. This top coat can even improve fuel consumption by more than one percent. In addition, less air-cooling will be required, thus increasing the GTE thermal efficiency and reliability (Haynes 1997).

There are two methods by which YSZ is fabricated: (1) plasma spraying and (2) EB-PVD (Haynes 1997). Upon thermal cycling, plasma sprayed YSZ tends to promote a rough top coat-scale interface. This rough coating has a strong tendency to spall due to inadequate thermal expansion match between the YSZ and the alumina. The EB-PVD YSZ has a columnar microstructure which can allow grains to separate to accommodate substrate expansion, and a much smoother top coat-scale interface. Since this EB-PVD coating has a desirable columnar microstructure, there tends to be less of a thermal mismatch issue between the YSZ top coat and the underlying bond coat and scale interface. Since the EB-PVD technique allows for reduced thermal match mismatch stess and improved chemical adhesion between the top coat and scale interface, this technique is preferred over plasma spraying (Haynes 1997).

EB-PVD, however, is very costly. An alternative is metallorganic chemical vapor deposition (MOCVD) of the YSZ top coat. This is potentially a much cheaper technique, in which transport and kinetic control can help to fabricate tailored YSZ coatings. The goal is to obtain the 100 to 250 μm YSZ coatings, with a similar microstructure to that of EBPVD, but at a much lower cost. In addition, the technique can allow coating of surfaces that are unavailable to EB-PVD and can produce a uniform seal-coat on top of an EB-PVD layer.

EXPERIMENTAL DESIGN

The MOCVD experimental design is based on several factors. First, low cost and effective precursor. Second, a controlled oxygen source. Third, a substrate that simulates the scale interface or blade material. Finally, a flow system and reactor design that is gas-diffusion deposition rate-limited.

For the zirconium and yttrium metal sources, $Zr(tmhd)_4$ and $Y(tmhd)_3$ were chosen due to their adequate closeness in vapor pressure, their high thermal stability (up to 500°C), their cost, and their success as a precursor for YSZ thin films and $YBa_2Cu_3O_7$ superconductors. The oxygen source was chosen to be pure O_2 and the reactions are as follows:

$$Zr(tmhd)_4(g) + xsO_2(g) \rightarrow ZrO_2(s) + \text{waste organics} \quad (1)$$

$$Y(tmhd)_3(g) + xsO_2(g) \rightarrow Y_2O_3(s) + \text{waste organics} \quad (2)$$

To complement this choice of precursors and oxygen source, a stagnation flow design was employed because it allows the determination of the rate-limiting processes and promotes efficient deposition. Stagnation flow offers design flexibility by controlling residence time, prevents pre-reaction of metallorganic precursors, provides for high deposition rates, and promotes deposition uniformity. Furthermore, stagnation flow allows growth rates to be gas-diffusion limited as opposed to surface-reaction/kinetics limited.

In a stagnation flow reactor the gas mixture with a laminar flow profile approaches a gas-distributing nozzle in a cylindrical flow tube reactor (Fig. 2, A). The gas-distribution nozzle "breaks up" the laminar flow profile of the gas stream (B) which enters the region above the substrate (C). In this region, the velocity, temperature, and reactant concentration gradients of the forced-convective gas stream are independent of the substrate diameter. As the gases approach the substrate, heterogeneous reactions occur on the substrate to form the coating (D). The coating thickness is independent of the substrate diameter and grows in the axial direction. Moreover, the coating growth rate depends solely on the gas flow.

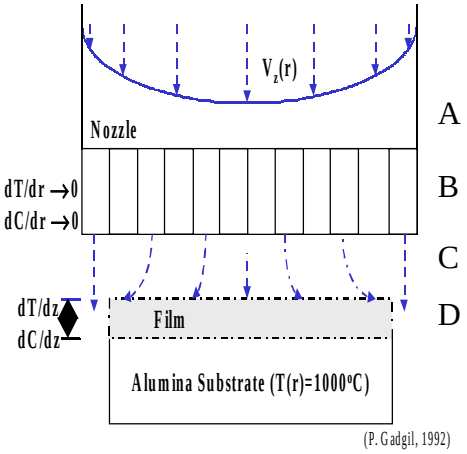

Figure 2: Schematic of stagnation-pont flow reactor. *(After P. N. Gadgil)*

A reactor and flow system have been developed for the deposition of YSZ (Figure 3). The precursors were dissolved in tetrahydrofuran (THF) and continuously injected through a check valve into the reaction chamber by a syringe pump. To ensure quick evaporation of the precursor and solvent, the precursor solution was fed to an ultrasonic nozzle. The axygen carrier gas was fed through heated gas lines and into the stainless steel injector. The gas streams mix and flow through the injector (maintained at 200^{o}C by a heating jacket of silicone oil) toward the substrate. The substrate (inductively heated by a radio frequency coil heating a Mar-M247 susceptor) was maintained at 900^{o}C for the set of experiments described in this report. Waste gases were trapped in an isopropanol-dry ice bath. The deposition time was typically one hour.

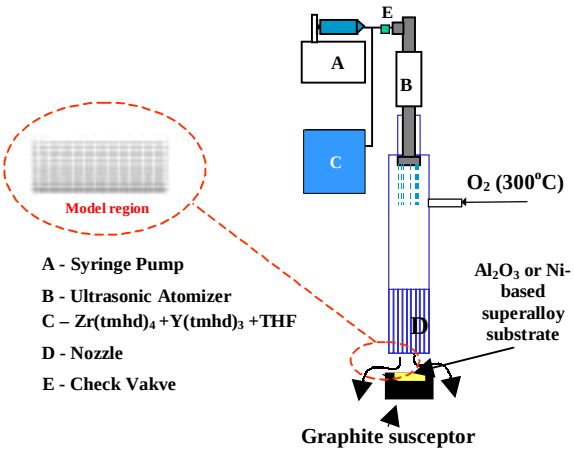

Figure 3: Flow schematic of MOCVD reactor.

RESULTS AND DISCUSSION

X-ray diffraction (Cu K-α,θ-2θ) revealed that the deposition of 8 wt % YSZ (tetragonal) was successful on the superalloy (Figure 4) and alumina. Scanning electron microscopy (Hitachi S800) showed the coatings were 3 to 4 μm thick on the alumina (Figure 5) and 4 to 5 μm thick on the superalloy (Figure 6).

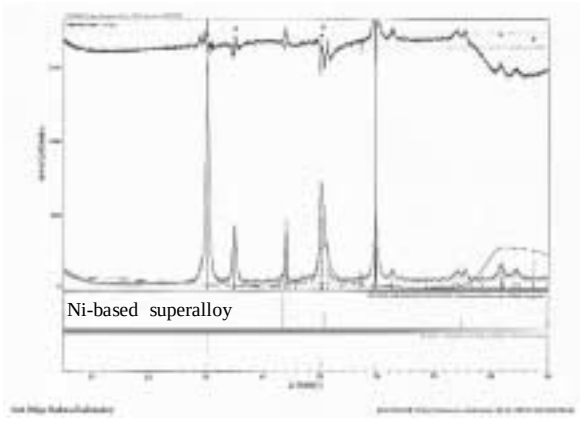

Figure 4: Results of XRD.

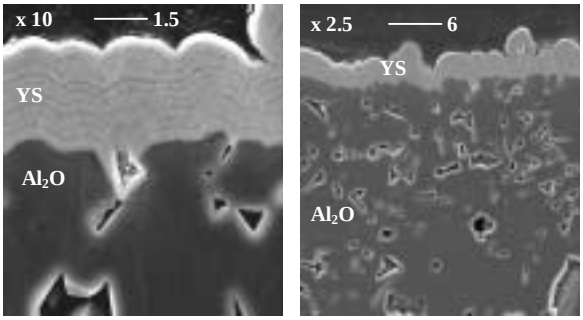

Figure 5: Micrograph of YSZ on alumina

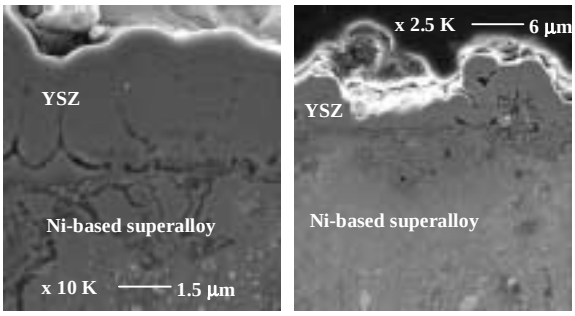

Figure 6: Micrograph of YSZ on the superalloy

Using these experimental conditions, detailed modeling predicted deposition rate and uniformity shown in Figure 7. On one hand, there is moderately good agreement between experimental deposition rates and modeled deposition rates (12 to 13 μm/hr). . On the other hand, there was some variation in the coverage of the coating technique. Experimentally, the coating is uniform with only a 0 to 15 % difference in thickness between the edges and the middle of the substrate whereas modeling predicted a 2 to 5 % difference.

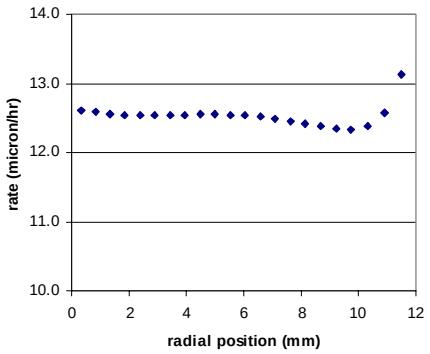

Figure 7: Modeled results of experimental conditions.
Conditions: Ts=960 ^{o}C, P=18 torr, 0.87 ml/min THF soln. with X(tmhd) at 0.04 g/ml, Y/(Y+Zr)=0.165, 100 sccm O_2. (*After T. L. Star*)

FUTURE WORK

While successful, these preliminary results indicate that more work is needed to optimize the precursor delivery system so as to obtain better control of the rate of precursor flow to the substrate. A critical next step in the effort is to develop an understanding of how deposition parameters can control microstructure and can deposit columnar structures. A kinetics parametric study will allow improvement in the parallel modeling effort, and this has a high priority.

SUMMARY

The need to reduce the cost of TBC fabrication is necessary for the commercialization of these coatings for gas turbine engines. MOCVD offers a cost effective, non-"line-of-sight", uniform deposition technique that can either replace or supplement EB-PVD coatings. A stagnation flow reactor was used to successfully deposit YSZ on alumina and a nickel-based superalloy. Results of XRD and SEM show that YSZ coatings were successfully obtained with a thickness of 3 to 4 μm on alumina and 4 to 5 μm on the superalloy for a one hour deposition time. Future efforts will require refining the precursor delivery system and obtaining an understanding of the microstructure-deposition parameter relationship and the kinetics of deposition.

REFERENCES

Gadgil, P. N. "Single Wafer Processing in Stagnation Point Flow CVD Reactor: Prospects, Constraints and Reactor Design". *Journal of Electronic Materials*, Volume 22, Number 2: 1992.

Haynes, J. A. *Oxidation and Degeneration of Thermal Barrier Coating System*. University of Alabama at Birmingham. Birmingham, Alabama: 1997.

Matsuno, S., F. Uchikawa, and S. Utsunomiya. "etalorganic Chemical Vapor Deposition Using a Single Solution Source for high J_C $Y_1Ba_2Cu_3O_{7-X}$ Superconducting Films". *Applied Physics Letters*. Volume 60, Number 19, pp. 2427-2429: 1992.

Jiming Zhang, Robin A. Gardiner, Peter S. Kirlin, Robert W. Boerstler, and John Steinbeck. "Single liquid source plasma-enhanced metalorganic chemical vapor deposition of high-quality $YBa_2Cu_3O_{7-x}$ thin films". *Applied Physics Letters:* Volume 61, Number 24, 1992.

Starr, T. L. ibid. 2002