METAL-ORGANIC CHEMICALLY VAPOR DEPOSITED YTTRIA-STABILIZED ZIRCONIA (YSZ) FOR THERMAL BARRIER COATINGS

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ABSTRACT

The current metal-organic chemical vapor deposition (MOCVD) process utilizes a cold wall reactor with liquid delivery of a metal-organic precursor solution to deposit YSZ. Thick thermal barrier coatings with a columnar structure have been successfully deposited on developmental FeCrAlY material. TBC coupons were tested under thermal cycling and resisted spallation through 1000 cycles of 1 hour to a temperature of 1100°C when the deposit was on a pre-oxidized surface. The MOCVD system is being scaled-up to deposit coatings on prototypical turbine blade width sections. Components have been constructed and operational testing is beginning. One of the scale-up issues has been adequate and accurate delivery of precursor solution to a vaporization system, and this has been solved through installation of a continuous, non-pulsating liquid delivery pump. Interactions with Pratt & Whitney have resulted in an informal agreement on testing prototype YSZ coatings.

INTRODUCTION

Yttria-stabilized zirconia (YSZ) is used as a thermal barrier coating (TBC) to protect super-alloy blades such as Mar-M247 or Rene-N5 during engine operation. The current method for YSZ fabrication for TBC applications is by air-plasma spraying (APS) or electron beam-physical vapor deposition (EB-PVD).[1-5] APS gives reasonable deposition rates, but has a more limited life with aging effects due to its porous and lamellar structure. EB-PVD coatings are more stable and can accommodate larger thermomechanical stresses due to their characteristic strain-tolerant, columnar microstructure. EB-PVD and APS are, however, line-of-sight deposition processes, which often leave “hidden areas” uncoated. EB-PVD in particular has only modest throughput, and high capital cost. The process of metal-organic chemical vapor deposition (MOCVD) is being investigated as an economical alternative to EB-PVD and APS, with the potential for better overall coverage as well as the ability to produce thick (>250 μm), strain-tolerant, columnar coatings.

MOCVD of YSZ involves the use of zirconium and yttrium metalorganic precursors reacting with an oxygen source. Previous researchers have used a variety of metalorganic and chloride precursors.[6-9] These precursors have low transport rates due to their low carrier solvent solubility.[10] Solvated zirconium and yttrium butoxide precursors were investigated here due to their higher vapor pressures and high solvent solubility. This work uses previously performed predictive equilibrium modeling and experiments involving butoxide precursors for tetragonal YSZ fabrication.[11]

EXPERIMENTAL

YSZ was deposited in the MOCVD reactor shown in Fig. 1. Substrates included alpha-alumina (99.6 % purity: Coors) and a a developmental FeCrAlY alloy whose composition is given in Table 1. The precursors were Y- and Zr-tert butoxides dissolved in toluene and n-butanol, respectively. The precursors were pre-solvated and their solubility was 0.5 M Y in toluene and 2.23 M Zr in n-butanol. From the as-delivered batches, the reactants were mixed together based on their solubility and the desired coating composition. The solution was delivered continuously by a gear pump that allows continuous flow from a reservoir through a poppet-seal relief valve into the deposition chamber. To ensure efficient vaporization, the solution was made an aerosol using an ultrasonic atomizing nozzle. The vapor was carried by argon and mixed with 300°C O_2 in the reactor and allowed to flow to the substrate. The substrate was held at temperature by contact with an inductively heated Mar-M247 susceptor.

The CVD chamber wall and susceptor holder were made of fused silica glass. A thermocouple was placed within the susceptor to control the susceptor temperature, while the substrate temperature was read using an optical pyrometer and the temperatures correlated as during deposition the substrated surface is typically not visible. From an equilibrium analysis[10] a minimum of 18 moles of molecular oxygen is required for every mole of Y-butoxide + Zr-butoxide (O/(Y+Zr)=35) to ensure formation of tetragonal YSZ at 950°C. To assure full oxidation, the oxygen flow rate was selected to be twice the minimum, O/(Y+Zr)=72. Samples were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Stability of the coatings on FeCrAlY susbstrates was determined by thermal cycling, with each cycle involving holding the sample at 1100°C in flowing oxygen for 50 min followed by 10 min cooling in flowing room temperature air. Weight loss was periodically determined and reported.

RESULTS

The replacement of the previously used syringe pump with a continuous gear pump for providing the precursor to the MOCVD reactor allowed deposition times of up to 4 h, with longer periods possible but not yet attempted.

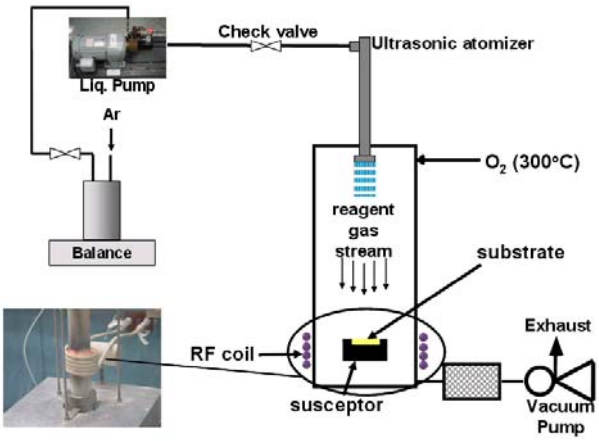

Fig. 1. Schematic of MOCVD system.

Table 1. FeCrAlY composition

	wt %
Fe	74.50
Cr	20.07
Al	5.08
Y	0.140
Cu	0.010
N	0.0003
O	0.0035
S	0.0010

Results of thermal cycling tests of YSZ-coated FeCrAlY samples are presented in Fig. 2. The uncoated sample experienced slow oxide scale growth, which resulted in small weight gains. A YSZ-coated FeCrAlY sample, on which no polishing or pre-oxidation was performed before coating, suffered substantial weight loss over the thermal cycling period due to severe spallation of the coating. A second substrate with a polished surface that was pre-oxidized in 1 kPa oxygen at 1000°C for 1 h prior to coating to form the desired alumina surface oxide performed significantly better, with minimal weight loss to 1000 cycles. Optical images of the coating that showed little weight loss indicated no perceptible damage (Fig. 3). Polished cross-sections of the coating showed retention of the columnar microstructure and porosity within the grains (Fig. 4).

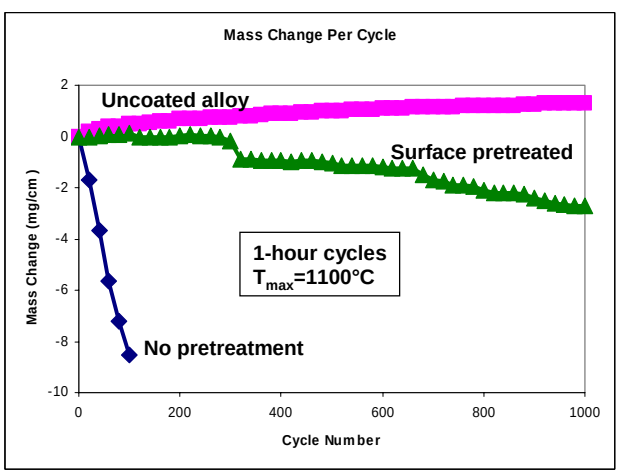

Fig. 2. Mass change as a function of thermal cycles

Fig. 3. Optical images of thermally cycled coating on pretreated surface.

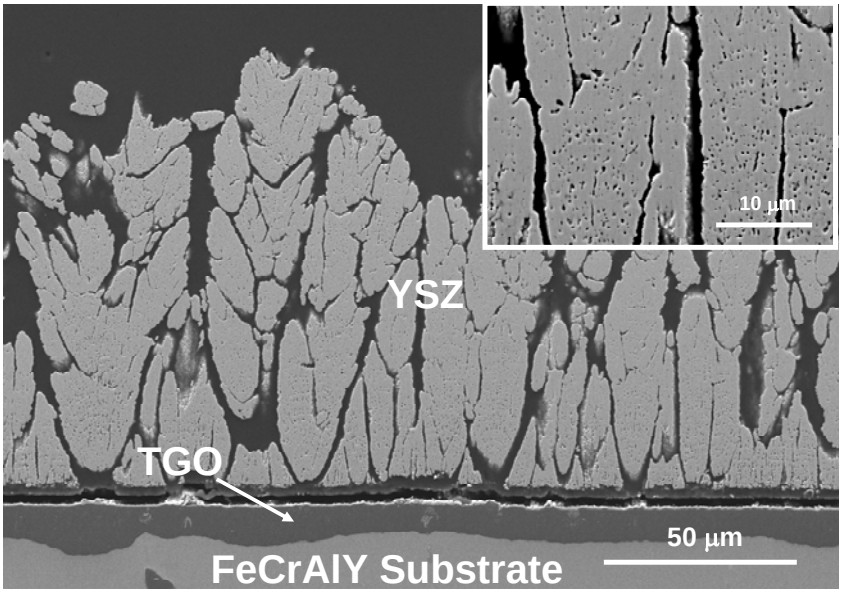

Fig. 4. Scanning electron images of the thermally cycled YSZ coating on the FeCrAlY substrate material.

Modeling work has provided guidance for development of a scale-up system to deposit YSZ uniformly on prototypical land-based turbine blade widths (Fig. 5). Two concentric injectors will be used to provide vapor to either side of the substrate, with oxygen and precursor flowing through each of the concentric tubes, mixing only after reaching the reactor. The vapor source will consist of a heated vessel into which an ultrasonic nozzle will inject precursor aerosol.

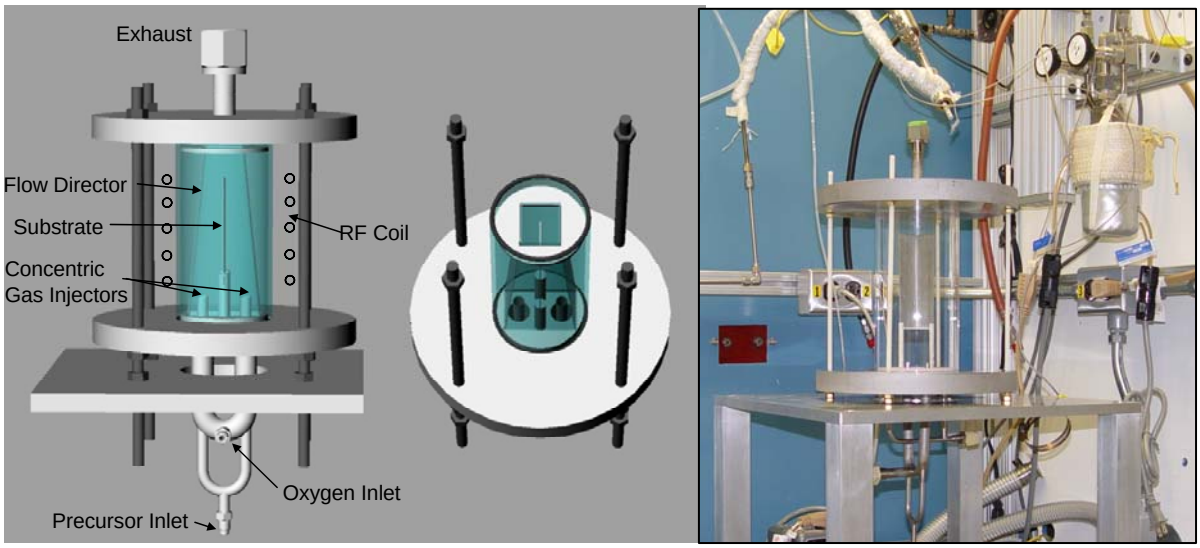

Fig. 5. Computer-generated image of the scale-up reactor based on the modeling results and a photograph of the system for coating prototypical blade width (12 cm) completing construction.

DISCUSSION

The results of the thermal cycling of MOCVD YSZ on FeCrAlY substrates is very encouraging. APS coatings typically survive approximately 700 cycles and EB-PVD coatings survive 1200. These, however, are on my traditional superalloys with aluminized bond coats, and this difference can also be important. Investigation of the interfaces in the current system show neither the rumpling or the bowing that has given rise to failure in the commercial systems. This may be attributed, at least in part, to the greater ductility of the FeCrAlY alloy over typical nickel superalloys. There is also, however, good evidence that the adhesion of the MOCVD YSZ is excellent. Although separation is seen in the micrographs, such as in Fig. 4, this is likely due to stresses from potting and curing the epoxy mounting media as no failure is seen in thermal cycling.

The scale-up design in Fig. 5 has been developed based on computational fluid dynamics modeling coupled with chemical kinetic information. The coating of large surfaces using MOCVD, however, is challenging and even the current design may have difficulties. An option that will be pursued with the current system is pulse deposition, which has been demonstrated particularly by Krumdieck et. al, and that capability is being built into the design. Digitally controlled valving will allow the reactor to be closed to the precursor injection system and therefore evacuated, the reactor would then be isolated from the vacuum system, and finally the precursor allowed to rapidly transport into the reactor since the chamber will be at a significantly lower pressure than the precursor vaporizer. Thus precursor vapor can fill the chamber more quickly than deposition can occur, overcoming mass transport limitations and resulting in uniform coatings. Repeated cycling will allow the rapid deposition of thick YSZ coatings.

Interactions with Pratt & Whitney have resulted in an informal agreement on testing prototype YSZ coatings. Pratt & Whitney will be supplying standard burner rig test substrates for coating at ORNL. These will be then provided to Pratt & Whitney for burner rig testing. Samples will be shared for evaluation.

SUMMARY

The relatively thick columnar YSZ thermal barrier coatings deposited by MOCVD on an FeCrAlY have been shown to successfully survive 1000 thermal cycles. The coatings retained their columnar structure, and small-scale porosity within the grains that is advantageous for reducing thermal conductivity. A scale-up system to coat the width of prototypical land-based turbine blades (12 cm) has been designed utilizing computational fluid dynamics and kinetics information. The system has been largely constructed and installed and will include capability for pulsed deposition to improve uniformity. Burner rig testing of samples at Pratt & Whitney will be used to evaluate future coatings.

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REFERENCES

1. J. R. Nicholls, "Advances in Coating Design for High-Performance Gas Turbines," *MRS Bull.*, **28** 659-670 (2003).
2. D. R. Clarke and C. G. Levi, "Materials Design for the Next Generation Thermal Barrier Coatings," *Annu. Rev. Mater. Res.*, **33** 383-417 (2003).
3. A. G. Evans, D. R.Mumm, J. W. Hutchinson, G. H. Meier and F. S. Pettit, "Mechanisms Controlling the Durability of Thermal Barrier Coatings", *Progr. Mat. Sci.*, **46** 505-553 (2001).
4. N. P. Padture, M. Gell and E. H. Jordan, "Thermal Barrier Coatings for Gas-Turbine Engine Applications", *Science*, **296** 280-284 (2002).
5. P. K. Wright and A. G. Evans, "Mechanisms Governing the Performance of Thermal Barrier Coatings" *Curr. Opin. Sol. State Phys.*, **4** 255-65 (1999).
6. G. W. Wahl, W. Nemetz, M. Giannozzi, S. Rushworth, D. Baxter, N. Archer, F. Cernuschi, and N. Boyle "Chemical Vapor Depostion of TBC: An Alternative Process for Gas Turbine Components," *Transactions of the ASME*, **123** 520-4 (2001).
7. G. Wahl, Ch. Metz, and S. Samoilenkov "Thermal Barrier Coatings," in Proceedings: Thirteenth European Conference on Chemical Vapor Deposition, EDP Sciences, Les Ulis, France, 2001, pp. Pr3-835-46.
8. H.Yamane and T. Hirai, "Yttria Stabilized Zirconia Transparent Films Prepared by Chemical Vapor Deposition." *Journal of Crystal Growth*, **94** 880-4 (1989).
9. S. P. Krumdieck, O. Sbaizero, A. Bullert, R. Raj, "YSZ Layers by Pulsed-MOCVD on Solid Oxide Fuel Cell Electrodes." *Surf. Coat Tech.*, **167** 226-33 (2003).
10. V. G. Varanasi and T. M. Besmann, "Parametric Study of the Chemical Vapor Deposition of Yttria-Stabilized Zirconia From Organometallic Precursors," in Proceedings of the Electrochemical Society: Chemical Vapor Deposition XVI and EuroCVD 14, Vol. 2, The Electrochemical Society, Pennington, NJ, 2003, pp. 783-9.
11. V. G. Varanasi, T. M. Besmann, J. J. Henry, Jr., T. L. Starr, W. Xu, T. J. Anderson, "Yttria-Stabilized Zirconia Thermal Barrier Coatings By Metal-Organic Chemical Vapor Deposition," pp. 595-601, in *Proc. 5th Int. Conf. On High Temp. Ceramic Matrix Composites*, eds. M . Singh, R. J. Kerans, E. Lara-Curzio, R. Naslain, American Ceramic Society, Westerville, OH, 2004.