

CHEMICALLY VAPOR DEPOSITED YTTRIA-STABILIZED ZIRCONIA (YSZ) FOR THERMAL AND ENVIRONMENTAL BARRIER COATING

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INTRODUCTION

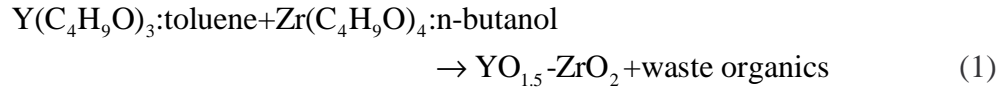
Yttria-stabilized zirconia (YSZ) is used as a thermal barrier coating (TBC) to protect super-alloy blades such as Mar-M247 or Rene-N5 during engine operation. The current method for YSZ fabrication for TBC applications is by air-plasma spraying (APS) or electron beam-physical vapor deposition (EB-PVD) (Haynes 1997). APS gives reasonable deposition rates, but has a limited life and aging effects due to its porous and lamellar structure. The EB-PVD coatings are more stable and can accommodate thermomechanical stresses due to their characteristic strain-tolerant, columnar microstructure. EB-PVD, however, is primarily line-of-sight, which often leaves “hidden areas” uncoated, has low throughput, and has high capital cost. The process of metal-organic chemical vapor deposition (MOCVD) is investigated here as an economical alternative to EB-PVD and APS, with the potential for better overall coverage as well as the ability to produce thick (100-250 μm), strain-tolerant, columnar coatings.

MOCVD of YSZ involves the use of zirconium and yttrium organometallic precursors reacting with an oxygen source. Previous researchers have used β -diketonate or chloride precursors and oxygen (Wahl et al. 2001a, Wahl et al. 2001b, Yamane and Harai 1989). These precursors have low transport rates due to their low carrier solvent solubility (Varanasi et al. 2003). Solvated zirconium and yttrium butoxide precursors were investigated here due to their

higher vapor pressures and high solvent solubility. This work uses predictive equilibrium modeling and experiments involving butoxide precursors for tetragonal YSZ fabrication.

EQUILIBRIUM ANALYSIS

In this work an equilibrium analysis was used to determine the minimum oxygen requirement needed to efficiently deposit YSZ. Since a large portion of the precursors is carbon, it will also be necessary to ensure that the deposit does not a carbon phase. The overall reaction is



We focused on preparing 4 mole percent Y_2O_3 , tetragonal YSZ. For ease of control it is desirable to obtain the same coating $\text{Y}/(\text{Y}+\text{Zr})$ ratio as that of the inlet $\text{Y}/(\text{Y}+\text{Zr})$ ratio.

The thermochemical properties (Barin 1989, Kubaschewski et al. 1996, Sundman 1985) and solid solution model (Du et al. 1992) were collected and organized into a ThermoCalc database. Figure 1 shows the effect of the temperature and inlet $\text{O}/(\text{Y}+\text{Zr})$ ratio. If no oxygen was added to the system, a minimum inlet $\text{O}/(\text{Y}+\text{Zr})$ ratio of five was imposed on the system since oxygen is present in the precursors at this ratio. Two more restrictions imposed on this system are the mole fraction of hydrogen and carbon, which are introduced solely through the precursors. Thus, the carbon to metal ratio ($\text{C}/(\text{Y}+\text{Zr})$) and the inlet hydrogen to metal ratio ($\text{H}/(\text{Y}+\text{Zr})$) were fixed at 30 and 60, respectively. In Figure 2, it can be seen that as long as the temperature is 950°C and the inlet $\text{O}/(\text{Y}+\text{Zr})$ ratio is greater than 30, carbon will not form with tetragonal YSZ.

EXPERIMENTAL

From the equilibrium analysis a minimum of 18 moles per minute of molecular oxygen is required for every mole per minute 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, $O/(Y+Zr)=72$.

The YSZ was deposited in the stagnation flow MOCVD reactor shown in Figure 2. Substrates included alpha-alumina (99.6 % purity: Coors) and Rene-N5 (Howmet). 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 syringe pump through a poppet-seal relief valve into the deposition chamber. To ensure efficient vaporization, the solution was then misted using an ultrasonic atomizing nozzle. The misted solution was carried by 300°C O₂ at 1200 sccm to the substrate through a stainless-steel stagnation flow nozzle. The substrate was inductively heated using a 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. Samples were then analyzed using X-ray diffraction (XRD) to identify the phases. Scanning electron microscopy (SEM) revealed coating thickness and microstructure. In addition, electron probe microanalysis (EPMA) was used to determine the relative homogeneity of yttrium and zirconium throughout the as-deposited coating.

RESULTS AND DISCUSSION

Figure 3 shows a YSZ deposit with a columnar microstructure on an alpha-alumina substrate. In this electron micrograph, initial lamellar layers of YSZ form, and then the columnar structure forms. To the right of the electron micrograph are EPMA intensity maps. The lighter the region, the higher the concentration of the atom in that region. In this case, there is reasonable uniformity of Y and Zr atoms in the columnar coating. The banded layers show varying intensity of Y and Zr atoms relative to the columnar structure, indicating some non-uniformity. At the top of the coating, areas of high Zr or Y appears to be the result of powder formation. The powder formation may be indicative of separate zirconia and yttria phases being produced.

Figure 4 shows the YSZ coating on a Ni-based super-alloy substrate. Although the coatings are predominantly columnar, powder may be trapped within the columnar regions and within the gaps between columnar grains. This was attributed to pre-reaction of the precursors due to a failure to maintain cooling oil to the injector. There also appears to be a porous YSZ layer formed near the interface between the substrate and YSZ. This porous initial YSZ layer may have resulted from insufficient scale growth prior to deposition. Again banding is seen within the coating layers, which may be due to non-uniformity of yttrium and zirconium composition.

X-ray diffraction (XRD) results can be seen in Figure 5. The peaks represent the CVD YSZ coating and positions of the standard peaks for 3.25 mole percent yttria YSZ are shown below the pattern. The standard and the coating peaks match reasonably well.

SUMMARY

Results of equilibrium modeling predicted carbon-free tetragonal YSZ formation and experiments demonstrated tetragonal YSZ formation with columnar grain structures and high deposition rates ($\sim 45 \mu\text{m hr}^{-1}$). These coatings showed reasonable Y and Zr uniformity throughout the columnar region, although were not entirely uniform. Future work will include parametric studies to improve the coatings quality followed by scale-up to larger substrate and blade geometries.

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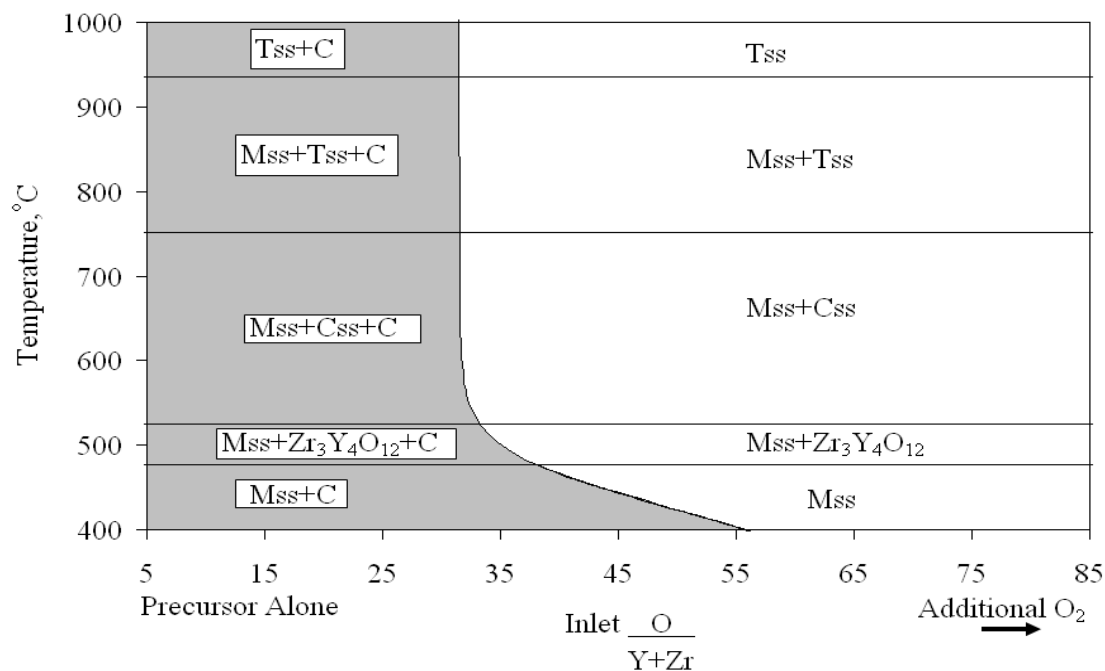


Figure 1. Equilibrium analysis of using Y- and Zr-butoxide precursors.

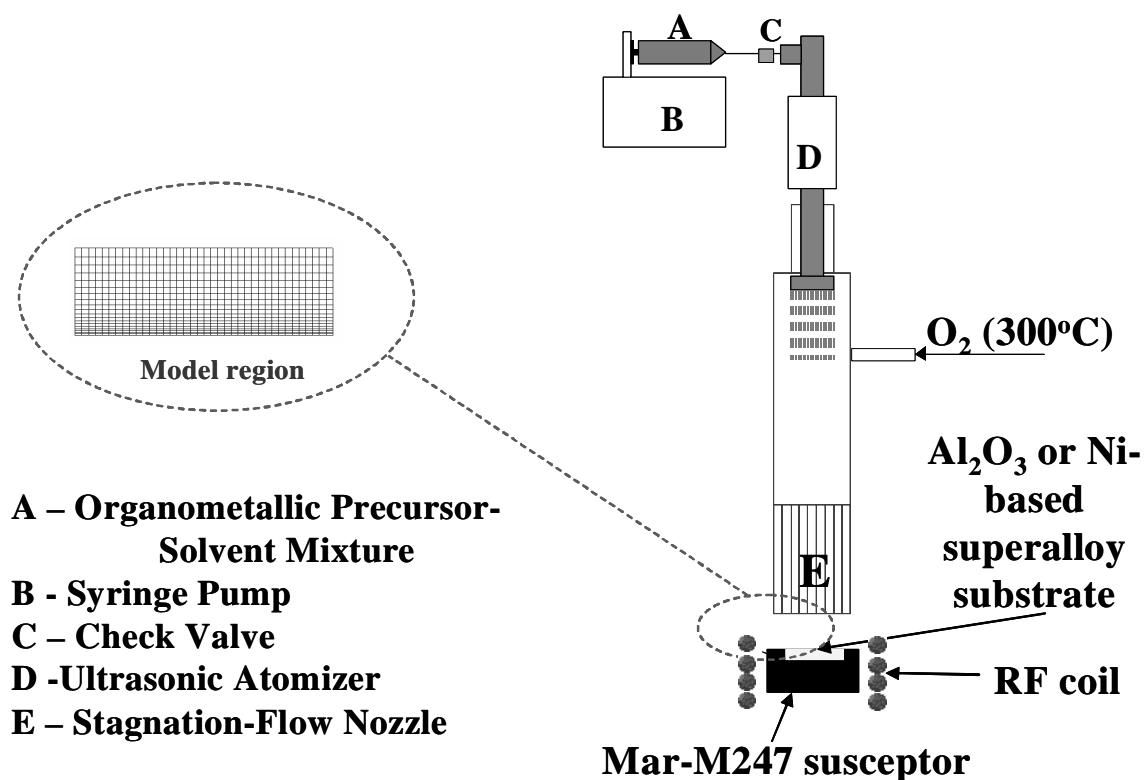


Figure 2. MOCVD reactor developed at Oak Ridge National Laboratory.

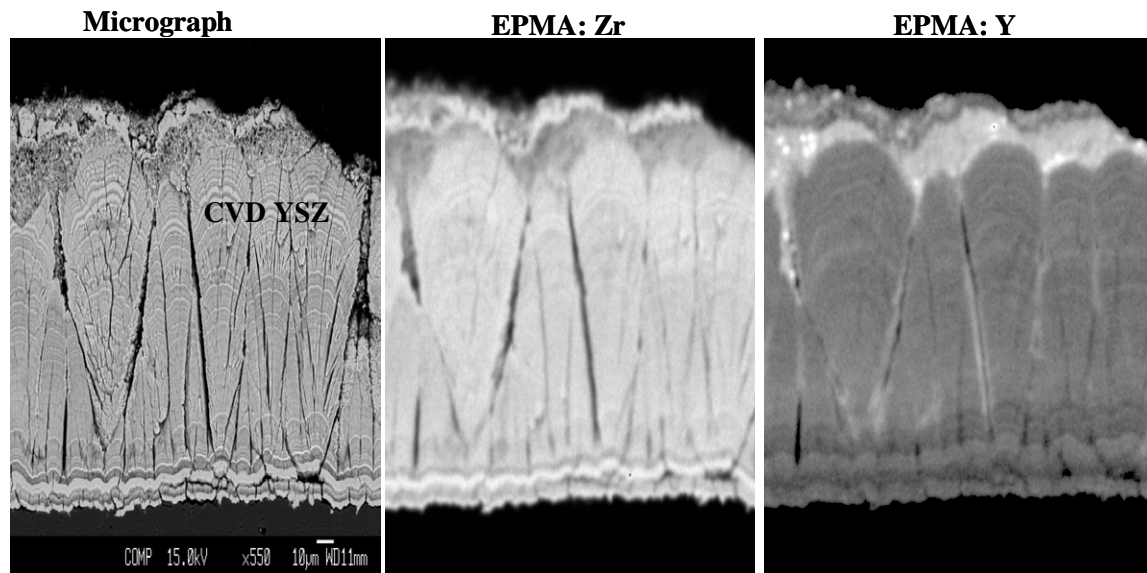


Figure 3. Micrograph of YSZ with EPMA intensity maps for Zr and Y as-deposited on alpha-alumina substrate.

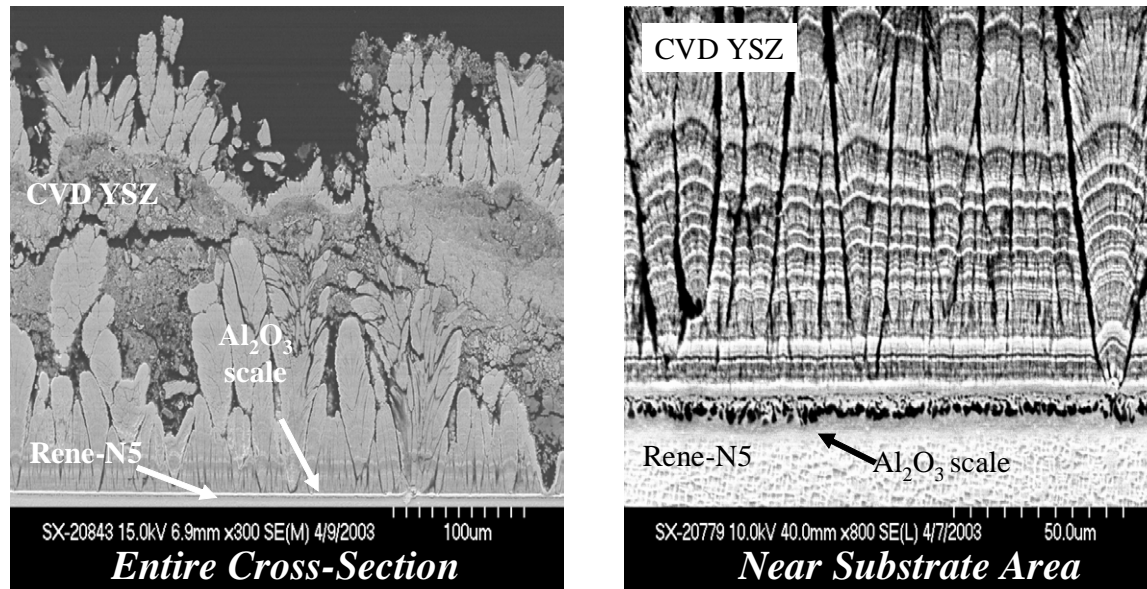


Figure 4. SEM micrograph of YSZ as-deposited on Rene-N5, Ni-based superalloy substrate.

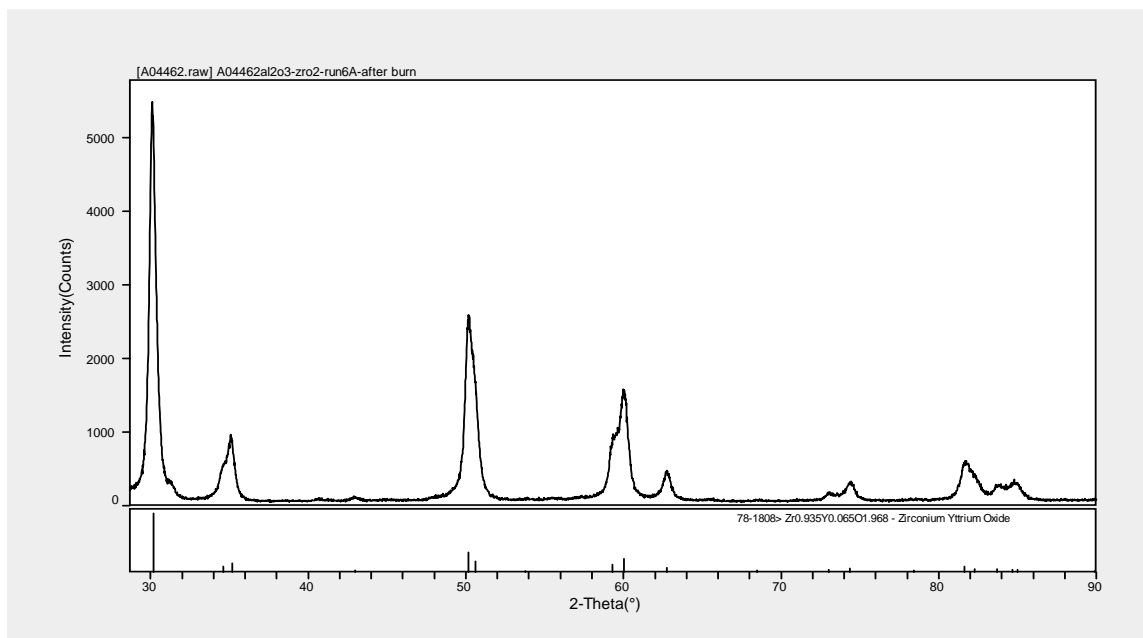


Figure 5. XRD of tetragonal YSZ coating (at 3.25 wt% Y_2O_3) on Ni-based superalloy.