

HIGH-TEMPERATURE STABILITY OF AMORPHOUS Al_2O_3 DEPOSITED ON Si AND CeO_2 -STABILIZED ZrO_2 BY METALORGANIC CHEMICAL VAPOR DEPOSITION

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ABSTRACT

Aluminum acetylacetonate and water vapor were used to deposit an amorphous Al_2O_3 seal coating on Si and CeO_2 -stabilized ZrO_2 (CSZ) produced by air plasma spray. The Al_2O_3 coating prepared at $\sim 500^\circ\text{C}$ was $\sim 2.5\mu\text{m}$ thick, uniform, and non-porous. The crystallization and adhesion characteristics of the Al_2O_3 coating were examined by thermally annealing the Al_2O_3 -coated Si and CSZ substrates in air. The amorphous coating crystallized to metastable Al_2O_3 phases within 20 hours at temperatures as low as 700°C . The coating on Si spalled upon annealing whereas the coating on CSZ did not spall, but microcracked extensively due to the significant volume shrinkage associated with crystallization.

INTRODUCTION

Thermal barrier coatings (TBCs) have been developed to improve the performance of aircraft engines, power generation gas turbines, and diesel engines [1-3]. For diesel engines, CeO_2 -stabilized ZrO_2 (CSZ) is applied by air plasma spray (APS) over a graded NiCrAlY bond coating to insulate and protect cast iron components from high-temperature combustion environments [2]. The APS-CSZ coating is intentionally made porous for strain tolerance and for enhanced adhesion at the metal-ceramic interface region. However, recent engine test results have shown that the porous CSZ coating may absorb fuel prior to ignition in the combustion chamber and thus may adversely affect overall engine efficiency [2,3].

A pragmatic solution to the fuel entrainment problem is to seal the CSZ surface with a thin coating. Such a seal coating must be non-porous, impermeable, conformal, adherent, and stable upon thermal cycling from 800 - 900°C . Another major constraint is that the seal coating must be prepared at temperatures below 500°C to avoid tempering of cast iron components.

Al_2O_3 is an ideal candidate coating material because: (1) it is one of the most thermochemically stable materials with respect to ZrO_2 -based ceramics as well as in high-temperature corrosion environments and (2) it has a coefficient of thermal expansion (CTE) similar to that of CSZ ($\sim 8 \times 10^{-6}$ versus $\sim 10 \times 10^{-6} \text{ K}^{-1}$, respectively). However, these attractive properties are mainly reserved for crystalline $\alpha\text{-Al}_2\text{O}_3$ which is the thermodynamically stable polymorph of Al_2O_3 . It is generally known that $\alpha\text{-Al}_2\text{O}_3$ is a difficult material to prepare by chemical or physical vapor deposition processes unless deposition temperatures above 1000°C are used [4]. From this perspective, the main objective of this work was to explore the possibility of using an amorphous Al_2O_3 prepared by metalorganic chemical vapor deposition (MOCVD) at $\sim 500^\circ\text{C}$ with emphasis on evaluating the coating's physical integrity upon exposure to high-temperature environments. In particular, the significant volume shrinkage expected from the crystallization of the amorphous Al_2O_3 coating ($\sim -9\%$) [5] was a great concern.

EXPERIMENTAL

$\text{Al}(\text{acac})_3$ (aluminum acetylacetonate: $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$) was chosen as an Al precursor because it decomposes readily (well below 500°C) but is a relatively stable solid at room temperature [5-7]. Furthermore, this precursor is relatively non-toxic, insensitive to moisture, and inexpensive. Despite these advantages, carbon contamination and low growth rates were previously observed by Kim, *et al.* [7]. Also, it was found that inclusion of water vapor in the precursor stream helped eliminate the carbon contamination problem and increased growth rates [7].

In this work a cold-wall MOCVD reactor, shown in Figure 1, was used. The reactor was constructed of a stainless steel chamber with an internal resistance substrate heater. The reactor was equipped with two external vaporizers to store $\text{Al}(\text{acac})_3$ and distilled water. The $\text{Al}(\text{acac})_3$ was sublimed at $\sim 135^\circ\text{C}$ (vapor pressure = 0.0047 kPa) and the water was vaporized at 26°C (vapor pressure = 3.2 kPa). Both vapors were carried by Ar (99.999%) and fed into the reactor. To minimize condensation of the $\text{Al}(\text{acac})_3$ vapor, the gas line from the vaporizer to the reactor inlet was heated using heating tapes. With these precursors, growth rates of 0.3 to $0.5 \mu\text{m/h}$ were typically obtained at a deposition temperature of $505 \pm 5^\circ\text{C}$ and a total reactor pressure of 1.33 kPa.

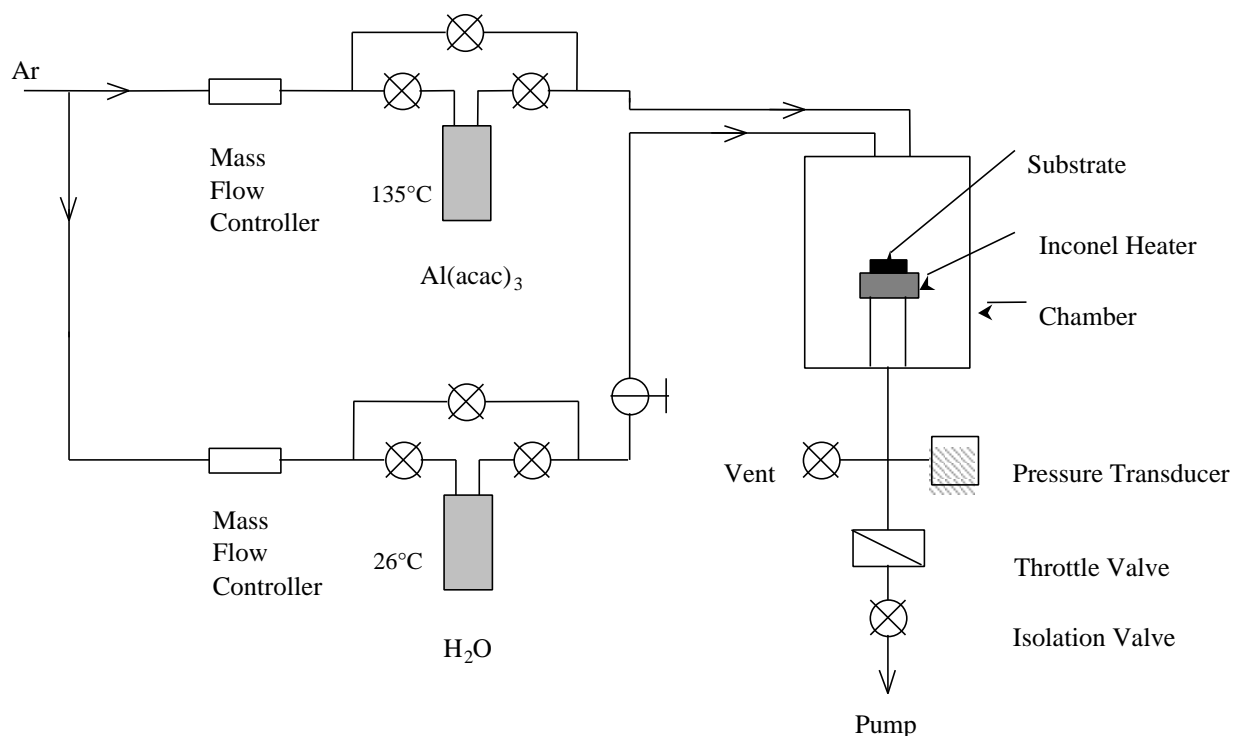


Figure 1. Schematic diagram of the MOCVD system used to deposit amorphous Al_2O_3 .

For thermal annealing experiments, substrates were coated to a thickness of $2.5 \pm 0.25 \mu\text{m}$. CSZ-coated cast iron flexure bars and free-standing CSZ coupons were used as substrates. In addition, Si substrates were used for ease of characterization during initial coating preparation and evaluation. The coated specimens were annealed in air for 20 hours using a small furnace over a range of 700 to 1200°C . The as-prepared and annealed coating specimens were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

RESULTS AND DISCUSSION

The as-deposited coating on Si, shown in Figure 2a, was smooth and conformal. Annealing of the coated Si substrates at temperatures of 700 to 1200°C resulted in extensive spallation, as shown in Figures 2b and 2c. The coated specimens annealed at 700°C and 800°C exhibited somewhat less severe spallation than those annealed at the higher temperatures. The coating spallation reduced the signal-to-noise ratio of XRD $\theta/2\theta$ scans. XRD analysis was further complicated by the appearance of several metastable Al_2O_3 phases (such as θ , β , κ , δ) with their peaks in high proximity to each other. Despite these complications, Figure 3 shows that the crystallization of the amorphous coating to metastable- and α - Al_2O_3 occurred rapidly during the thermal exposures.

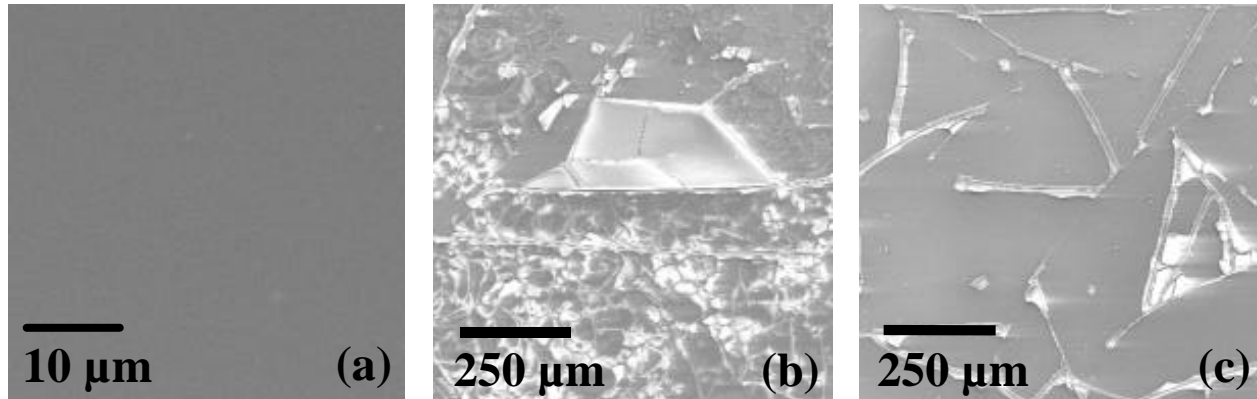


Figure 2. Al_2O_3 deposited on Si: (a) as prepared, (b) annealed at 800°C showing partial spallation, and (c) annealed at 1200°C showing severe spallation.

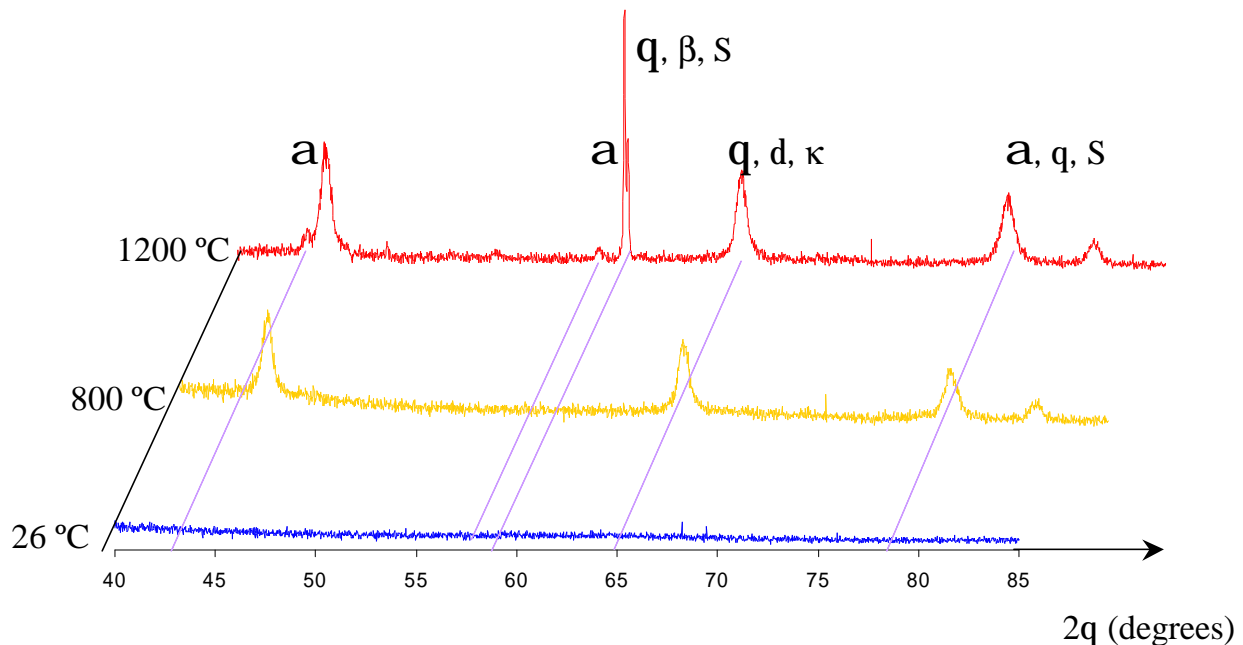


Figure 3. XRD patterns of the Al_2O_3 coating after annealing at 800°C and 1200°C (α = α - Al_2O_3 , S = $\text{Al}_2\text{Si}_4\text{O}_{10}$).

The Al_2O_3 coating deposited on the CSZ-coated cast iron and free-standing CSZ substrates exhibited a nodular surface morphology, as shown in Figure 4a. Annealing of these coating specimens resulted in extensive microcracking, but no spallation of the coating (see Figures 4 and 5). No major difference was observed between the Al_2O_3 coating deposited on the CSZ-coated cast iron *versus* free-standing CSZ substrates. In general, the degree of microcracking increased with annealing temperature. Also, the samples annealed at 1000 and 1100°C showed the presence of secondary features such as pores and what appear to be grain boundaries (Figure 5c).

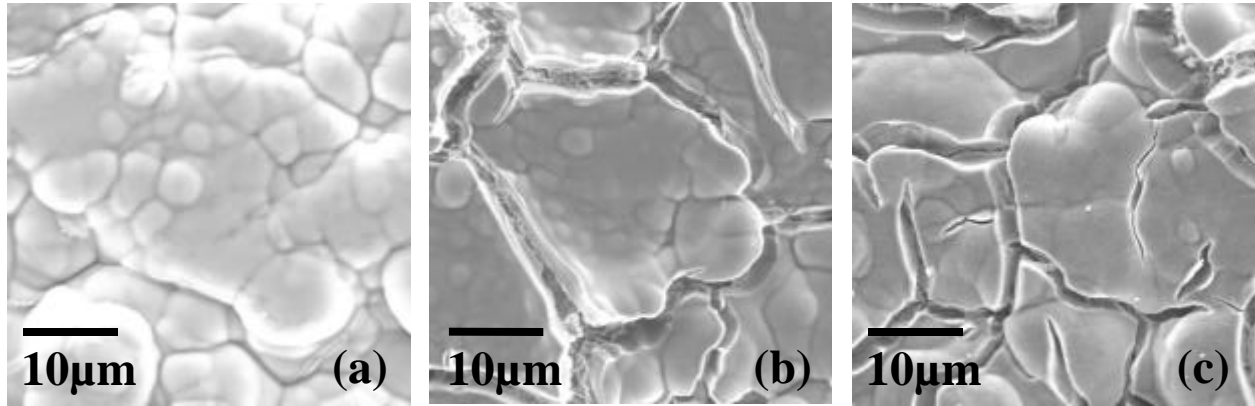


Figure 4. Al_2O_3 deposited on CSZ-coated cast iron: (a) as prepared, (b) annealed at 700°C, and (c) annealed at 1000°C.

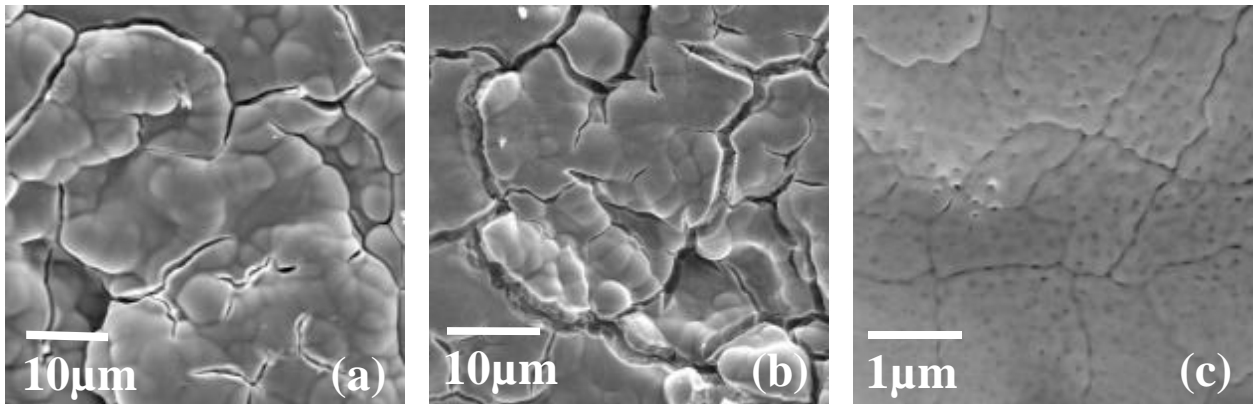


Figure 5. Al_2O_3 deposited on free-standing CSZ: (a) annealed at 700°C, (b) and (c) annealed at 1100°C.

The Al_2O_3 coating on Si exhibited considerable spallation due to both CTE mismatch strains ($\sim +0.5\%$) and the volume shrinkage associated with crystallization of the amorphous coating ($> -9\%$). In contrast, the Al_2O_3 coating on the CSZ surface, whether free-standing or on cast iron, did adhere well to the substrate, although it microcracked extensively. The adhesion of the coating on the CSZ surface was attributed to: (1) mechanical interlocking at the Al_2O_3 -CSZ interface and, (2) lower residual stresses at the interface due to the lower CTE mismatch between Al_2O_3 and CSZ. Nevertheless, the Al_2O_3 coating on the CSZ surface is expected to be inadequate for sealing the porous CSZ surface because of the observed microcracking of the coating upon annealing.

CONCLUSIONS

A uniform, amorphous Al₂O₃ coating was prepared on the porous CSZ substrate surface using Al(acac)₃ and water vapor as precursors at ~500°C. Thermal annealing of the Al₂O₃-coated CSZ substrates resulted in significant microcracking of the coating, mainly because of the volume shrinkage induced by the crystallization of the amorphous coating to metastable- and α-Al₂O₃ phases. The crystallization occurred at temperatures as low as 700°C within 20 hours. These observations suggest that the amorphous Al₂O₃ coating, although it can be prepared at ~500°C as a conformal and uniform coating, would not be useful as a seal coating for the CSZ-TBC coating application. This study demonstrates Al₂O₃ must be deposited as a crystalline coating (preferably in the thermodynamically stable α-Al₂O₃ phase) to mitigate the adverse effects of volume shrinkage caused by crystallization.

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