Thermodynamic analysis and growth of ZrO₂ by chloride chemical vapor deposition

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Abstract

Equilibrium calculations were used to optimize conditions for the chemical vapor deposition (CVD) of zirconia. The results showed zirconia formation would occur at high oxygen to zirconium atomic ratios (>4), low hydrogen to carbon ratios (<10), low pressures (<105 Pa) and high temperatures (>800 °C). Using these calculations as a guide, single-phase monoclinic zirconia coatings were deposited onto 2-cm diameter α-alumina substrates. The maximum growth rate achieved was 2.46 mg cm⁻² h⁻¹.

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1. Introduction

Zirconia films and coatings are used in many applications, such as semiconductor gate dielectrics and yttria-stabilized zirconia (YSZ) thermal barrier coatings (TBCs) for gas turbine blades. Zirconia thin films (<1 μm thickness) have a high dielectric constant (about four times that of silica), which is desired for limiting high leakage currents and electron tunneling in semiconductor devices [1,2]. As a TBC, zirconia is doped (6–8 wt.%) with yttria, which is used to reduce metallic blade component temperatures in the gas turbine environment [3,4].

For turbine blades, YSZ is typically fabricated by electron-beam physical vapor deposition (EB-PVD) or plasma spray [5,6], which are high-cost and low throughput methods, or result in lower quality coatings, respectively. Alternatively, chemical vapor deposition (CVD) offers a potential lower cost, high quality, and higher throughput coating fabrication method [7]. It uses inexpensive reagent delivery routes (e.g., in situ metal chlorination [8]), control of the reaction through supplying H₂O for oxidizing the metal chloride using the reverse water gas shift reaction [9–12], and simple chamber designs (e.g., vertical, cold-wall, axisymmetric chamber) to deposit single-phase coatings.

To promote relatively uniform and thick coating growth in CVD a stagnation plane flow injector can be used. A stagnation plane flow injector (for vertical, cold-wall CVD chambers) minimizes the radial and tangential components of the gas flow [13–16] and localizes c-axis coating growth on the substrate. This type of injector may also reduce gas flow recirculation [17,18] that leads to undesirable homogeneous nucleation and/or reactor wall deposition. For example, Holstein [17] demonstrated that at high flow rates (4000 cm³/min), a stagnation plane flow profile prevented gas flow recirculation (indicated by the lack of rolling contours in the gas flow profile above the substrate) in a computational hydrodynamic model. Despite these advantages, the CVD method is limited by the possibility of secondary-phase formation [10,19,20] and homogeneous nucleation [11].
In the current work, a stagnation plane flow injector was used to ensure efficient reagent delivery to the substrate and promote uniform and thick coating growth in the CVD of zirconia from a chloride precursor. The approach includes: (1) using a thermodynamic analysis to identify deposition conditions (i.e., atomic ratios, temperature, and pressure) and (2) demonstrating deposition of zirconia in an experimental CVD reactor. In the thermodynamic analysis, the updated phase diagram for the Zr–O system of Liang, et al. [21] was used to describe phase equilibria. Favorable conditions determined from the thermodynamic analysis were used to guide experimental zirconia growth on α-alumina substrates in a vertical, cold-wall CVD system.

2. Thermochemical properties and calculations

The thermochemical properties for the Zr–O–C–H–Cl–Inert system were obtained from several sources [21–24]. The assessment by Liang et al. [21] represented several phases with different models. These included (1) the ideal gas phase, (2) the monoclinic (α–ZrO2), tetragonal (β–ZrO2), and face-centered cubic (γ–ZrO2) zirconia phases as line compounds, and (3) the α–Zr hexagonal close packed (hcp) and β-Zr dodecahedron (bdc) zirconium phases containing dissolved oxygen with the two-sublattice model. The Zr–O phase diagram was re-computed to confirm the thermodynamic values for the phases, and it compared very well with the experimental phase diagram for the Zr–O system of Ondik and McMurdie [25]. Note that Liang et al. included additional phases within the α–Zr region (0.15–0.28 atom fraction O, 300–770 °C) [21]; however, Ondik and McMurdie did not include these phases in their diagram. The above suggests these phases may be metastable and thus were excluded from our calculations.

The overall reaction for the chloride CVD of zirconia assumed the reaction of ZrCl4 with water generated in the reverse water gas shift reaction:

\[ \text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O} \]  

(1)

\[ \text{ZrCl}_4 + 2\text{H}_2\text{O} = \text{ZrO}_2 + 4\text{HCl} \]  

(2)

Thermochemical equilibrium diagrams were generated using inlet compositions and variables [20,26] of the proposed experimental system. The restrictions \( n_{\text{Cl}} - 4n_{\text{Zr}} = 0 \) and \( 2n_{\text{C}} - n_{\text{O}} = 0 \), where \( n \) is the number of gram-atoms of a component, were imposed on the reacting system since ZrCl4 and CO2 are reagents. A basis of \( n_{\text{O}} + 2n_{\text{Zr}} = 0.001 \) for the calculations was also used. Thus, the variables explored included the substrate temperature (800–1400 °C), reactor pressure (103–105 Pa) and the input gram-atom ratios,

\[ n_{\text{H}}/n_{\text{C}} \]  

(3)

\[ n_{\text{H}}/n_{\text{Cl}} \]  

(4)

\[ n_{\text{inert}}/(n_{\text{Zr}} + n_{\text{O}} + n_{\text{H}} + n_{\text{Cl}} + n_{\text{C}}) \]  

(5)

Tauber, et al. [27] investigated the deposition of zirconia using ZrCl4 carried in hydrogen, thus any added benefit that would be gained by using hydrogen carrier gas was investigated such that variable (4) from above is replaced with,

\[ n_{\text{H}}/(n_{\text{Zr}} + n_{\text{O}} + n_{\text{inert}} + n_{\text{Cl}} + n_{\text{C}}) \].

(6)

3. Experimental details

3.1. Materials

The reagents were Ar, H2, CO2, and HCl (UHP grade, Air Liquide, Oak Ridge, TN) and zirconium chips (crystal bar turnings of 99.5% purity, Strem Chemicals Inc., Newburyport, MA). The substrates used were α-alumina (0.05 cm thick, 2 cm diameter, 99.6% purity, Coors Inc., Oak Ridge, TN). The susceptor for heating the substrates was composed of an aluminum-rich nickel-based super-alloy [28].

3.2. Apparatus

Schematics of the CVD fused silica chamber and overall CVD system are given in Figs. 1 and 2, respectively. Sample substrates were placed in a recess in the susceptor in the CVD reactor, and the fused silica reactor chamber was sealed with stainless steel compression fittings. The chamber pressure was maintained by a dry vacuum pump (Model SD 40 V2, Kashiyama Industry Co., Ltd., Nagano, Japan). The pressure was controlled using a capacitance manometer (MK622 series, MKS Instruments, Livermore, CA) linked to a pressure controller (MK561 series, MKS Instruments) and a pressure control valve (model no. QBV15DSQF40, MKS Instruments).

The susceptor was heated by a radio frequency (RF) generator (10 kW, Lepel, Inc., Maspeth, NY) The susceptor temperature was measured by a thermocouple, (K-type Omega, Stanford, CT), the output of which controlled the temperature via the RF generator, positioned in a fused silica thimble in the bottom of the fused silica susceptor holder that extended into a hole in the susceptor. The susceptor temperature was also measured with optical pyrometers (Ultimax UX10, 900–3000 °C, and Ultimax UX 50P, 300–900 °C, Ircon, Niles, IL) as long as the quartz chamber wall remained clear. The optical pyrometer was also used to measure the substrate temperature, and the difference was noted as a correction to the thermocouple temperature.

A cooling oil recirculator (model A-01262-09, Cole Parmer Instruments Company Vernon Hills, IL) was used to control the gas injector temperature. Heating tape was used to maintain the chamber wall at 500 °C and to heat the gas inlet lines.

3.3. Procedure

During deposition the ZrCl4 precursor was formed by the reaction of zirconium chips with HCl gas and carried into the CVD chamber by Ar (20 cm3/min through the chlorinator and 1480 cm3/min through the Ar preheater). It was assumed that all the HCl reacted to form ZrCl4, and this was verified by measuring weight change in the zirconium bed after several deposition runs. Coating experiments were two hours in length.
After coating, samples were calcined for 4 h at 1000 °C in an air furnace (series II, NEY Furnace, Tacoma, CA) to remove residual carbon, if any, from the films. This calcine step was added because of the observed carbon formation by Minet et al. [10] in coatings deposited in the Zr–O–C–H–Cl–Ar system between 800 °C and 1000 °C.

3.4. Characterization

A Scintag PADV room-temperature x-ray diffractometer (RT-XRD) with a vertical θ/2θ goniometer provided for phase identification. It used a Cu Kα source (45 kV, 40 mA) and a Peltier-cooled solid state Si (Li) detector with a radius of 220 mm. The high energy discrimination of the Si (Li) detector eliminated the need for a Ni-foil beta filter. Data were collected from 5° to 90° 2θ with increments of 0.02°, at a scanning rate of 1.0° min⁻¹. The instrument slit settings were: 1 mm divergence, 2 mm anti-scatter, 0.5 mm receiving anti-scatter, and 0.3 mm receiving. The software package JADE was used to analyze the X-ray data [29,30].

The coating thickness and uniformity were determined using scanning electron microscopy (SEM) (S4700, Hitachi, Inc., Japan) of polished sample cross-sections at five evenly spaced regions (20 measurements per position).

4. Results

4.1. Thermodynamic analysis

Single-phase formation of zirconia, α–ZrO₂ or β–ZrO₂ depending on temperature, was predicted to occur at all n_O/n_Zr ratios.
ratios and also all substrate temperatures explored. In addition, the thermochemical calculations indicated deposition was efficient (Fig. 3), utilizing essentially all the ZrCl₄ at inlet $n_{O}/n_{Zr}$ ratios greater than 4 to form single-phase zirconia.

Given the carbon in the CO₂ provided to the reactor, there were conditions where carbon was calculated to co-deposit with zirconia. The results of equilibrium calculations shown in Figs. 4–6 indicate boundaries within which carbon formed with zirconia. These boundaries were calculated at $n_{H}/n_{C}$ ratios of 3, 5, and 10 and at pressures over the range $10^{3}$–$10^{5}$ Pa as a function of temperature and $n_{O}/n_{Zr}$ ratio.

Under low oxygen and high hydrogen conditions, ZrC formation was also possible. In Fig. 5, it can be seen that at $10^{3}$ Pa, formation of ZrC occurred at $T>1050^\circ{C}$, $n_{H}/n_{C}=10$, and $n_{O}/n_{Zr}<2$.

Replacement of the inert carrier gas with hydrogen did not result in single-phase formation of zirconia for $n_{O}/n_{Zr}$ ratios < 4.
but instead caused the formation of metallic Zr phases (α-Zr and β-Zr). For example, at 1100 °C and \( n_\text{O}/n_\text{Zr} \) ratio of \( 4 \times 10^{-4} \), ZrC and β-Zr containing 1.96 at.% oxygen were predicted to form. Single-phase formation of zirconia still occurred, however, at all substrate temperatures for \( n_\text{O}/n_\text{Zr} < 4 \) (Fig. 7) with complete ZrCl\(_4\) utilization (Fig. 8).

### 4.2. Zirconia CVD

Results of the CVD experiments are summarized in Table 1. The CVD variables were explored by increasing flow rate (Q), increasing the CO\(_2\) or H\(_2\) content, and reducing the pressure. Significant gas-phase nucleation occurred and substantial deposition on the reactor wall was observed. The poor deposition rate on the substrate was reflected in the observed growth efficiency. The deposited coatings appeared off-white in color and no observable weight change occurred after calcination; thus, it was presumed that minimal or no carbon (or carbides) co-deposited with the oxide.

Coatings analyzed by XRD showed strong characteristic peaks (28° and 31.5° 2θ) for monoclinic zirconia with (−1 1 1) structure. Coatings analyzed by SEM showed characteristic microstructure consistent with the ZrO\(_2\) phase.

![Fig. 9. XRD result showing monoclinic zirconia (baddeleyite, syn – ZrO\(_2\), PDF card # 37-1484) and the α-alumina (corundum — Al\(_2\)O\(_3\), PDF card # 74-1081) substrate (run 4 in Table 1). Lower intensity peak patterns consistent with tetragonal zirconia (ZrO\(_2\), Zirconium Oxide, PDF card # 50-1089) were also seen.](image)

![Fig. 10. Scanning electron micrographs of zirconia layers as-deposited (run 4, Table 1) a) at low and b) high magnification.](image)
and (111) texturing (Fig. 9). (Relatively low-intensity peaks of tetragonal zirconia were also observed and were too low-intensity for further analysis). The thickest, polycrystalline monoclinic zirconia coating (run 4, Table 1) was determined to be 10.9±2.19 μm as seen in SEM images (Fig. 10). The coatings appeared to adhere to the alumina substrate; however, the large variation in coating thickness indicated that the stagnation plane flow injector did not provide sufficiently uniform gas flow distribution over the substrate surface.

5. Discussion

The equilibrium analysis predicted formation of single-phase monoclinic zirconia using the conditions: \( n_{O} / n_{Zr} > 4, 10^3 < P \) (Pa)<10^5, \( T < 1205 \) °C, and \( n_{H}/n_{C} < 3 \). The use of conditions suggested by the thermochemical analysis led to the deposition of zirconia coatings. However, high coating rates were not achieved, and the overall efficiency was <1%.

The thermochemical prediction of undesirable carbon co-deposition could be avoided by decreasing the \( n_{H}/n_{C} \) ratio and total pressure, resulting in a shift of the carbon boundary to lower temperatures. Similarly, increasing the temperature and \( n_{O}/n_{Zr} \) resulted in decreased carbon formation because of carbon oxidation to form CO and CO₂ at high temperature (Fig. 3).

The likelihood of carbon formation was also reflected in the deposition efficiency of carbon. It was computed that as much as 22% of the inlet carbon would be deposited as graphite at low oxygen content (\( n_{O}/n_{Zr} = 1 \)), relatively high pressure (10^5 Pa), and moderate temperatures (800 °C) (Fig. 6).

The results of the thermodynamic analysis are reflected in earlier thermochemical calculations on the deposition of YSZ [20]. High system oxygen (\( n_{O}/n_{Zr} > 4 \)) fulfills the stoichiometric need to fully oxidize zirconia, as has been demonstrated in the work of Varanasi et al. [20] and Minet et al. [31]. Similarly, the presence of excess hydrogen promotes the reduction of CO₂ and CO to form carbon and water vapor [10,20].

The variable that most influenced computed carbon deposition was the \( n_{H}/n_{C} \) ratio (Fig. 4). When the \( n_{H}/n_{C} \) ratio was low, increasing pressure did not result in carbon formation. Carbon formation was only likely if the \( n_{H}/n_{C} \) ratio was sufficiently high such that an increase in pressure (Figs. 5 and 6) or decrease in temperature (\( n_{O}/n_{Zr} < 4 \); Figs. 4 and 5) increased its stability. Carbon formation was not observed under any of the experimental conditions.

A previously unreported result of equilibrium analyses was the formation of ZrC in the presence of excess hydrogen. This occurred under conditions of high temperature (\( T > 800 \) °C), low pressure (10^5 Pa), and low system oxygen content (\( n_{O}/n_{Zr} < 4 \)) (Figs. 5 and 7). Intentional ZrC deposition from hydrogen and chloride precursors without the presence of oxygen has been reported [32,33]. In their equilibrium analysis of the Zr–Cl–H (ZrCl₄–CH₄–H₂) system, Ducarroir et al. [34] found that high temperature (\( T > 1200 \) °C) and high hydrogen content resulted in ZrC formation. In the experimental work conducted by Reynolds et al. [32,33], they suggested that the reaction to form ZrC from ZrCl₄ and CH₄ could not occur without hydrogen.

In the efforts reported here the low growth rates and efficiency for ZrO₂ were attributed to hydrodynamic factors. In comparing the results of this work (runs 1 and 2, Table 1) with that of Minet et al. [10] and Sipp et al. [11], it can be seen that higher growth rates were achieved by using reduced pressure, which enhances reagent diffusion from the gas-phase to the substrate [35,36] as does higher ZrCl₄ reagent concentration.

The use of a stagnation plane flow injector at a relatively low flow rate may have also contributed to poor deposition efficiency and uniformity. Evidence of significant chamber wall deposition both above and below the near-substrate region indicated that recirculation of the gas flow occurred. Recirculation in CVD is known to be a balance between convective reagent transport, reflected in the Reynolds number \( Re \), and natural convection away from a hot surface due to thermal buoyancy, reflected in the Grashof number \( Gr \). This balance is quantified in the following relationship [17,18]:

\[
\frac{Gr}{Re^2} = \frac{A^2gL}{Q^2T_M} \left( \frac{T_{substrate} - T_{inlet}}{T_{inlet}} \right)
\]

where \( g \) is the gravitational constant, \( L \) is the characteristic length scale (distance between gas inlet and the substrate surface), \( T_{substrate} \) is the substrate temperature, \( T_{inlet} \) is the inlet gas temperature, \( Q \) is the inlet gas flow rate, \( A \) is the cross sectional area of the inlet gas flow tube, and \( T_M \) is the mean gas temperature at the substrate-gas phase interface (\( T_{substrate} \) and the inlet gas temperature \( T_{inlet} \)). In this equation, it is easily seen that when there is a 2.3-fold increase in \( Q \) (from 1500 cm^3/min in this work to 4000 cm^3/min of Holstein [17]), a resulting 5.3-fold decrease occurs in \( Gr/Re^2 \), which illustrates the strong relationship between gas velocity and recirculation. Therefore, if the gas flow rate is increased, stagnation flow can be established and potentially result in more efficient and uniform coating growth.

Another issue is the close proximity of the injector to the substrate and the poor cooling of the end of the injector, which may have allowed the reactant gas to reach too high a temperature, resulting in homogeneous nucleation. This may have caused the observed deposition on and within the screens and the end of the injector.

6. Conclusions

Thermodynamic analysis can be a useful tool for determining the conditions for experimental growth of single-phase zirconia. Zirconia formation was predicted at high system oxygen (\( n_{O}/n_{Zr} > 4 \)), high substrate temperatures (\( T > 800 \) °C), low pressures (\( P < 10^5 \) Pa), and low system hydrogen (\( n_{H}/n_{C} < 10 \)).

Single-phase monoclinic zirconia was experimentally deposited, with the highest growth rate of 10.9±2.19 μm h⁻¹ and growth efficiency of less than 1%. The poor growth rate and efficiency are attributed to chamber wall deposition because indications are that the stagnation plane flow injector did not prevent recirculation of gas flow due to the relatively low flow rate. In addition, deposition occurred on the injector due to heating of the reagents within an insufficiently cooled nozzle.
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