Reactive vapor deposition of metal oxide coatings


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Abstract

The reactive deposition of metal oxide coatings has been achieved using an electron beam directed vapor deposition (DVD) approach. In this approach, a transonic helium carrier gas jet has been combined with electron beam evaporation to create and efficiently transport metal vapor to a substrate. Metal oxide coatings were then produced by adding oxygen to the carrier gas. The synthesis of multi-component oxide coatings could be achieved using either an alloy source or by simultaneous evaporation of metals from two or more sources. In the latter, the reactive carrier gas jet was used to facilitate vapor phase mixing of the evaporated fluxes. The preferred approach was found to be dependent on the vapor pressures of the individual source components. When large differences between the component vapor pressures exist, multi-source evaporation is preferred. Results are reported for the reactive deposition of zirconia from a single metal source and reactive deposition of yttria stabilized zirconia from two metal sources (Y and Zr). The phase and morphology are similar to those found in similar coating compositions created by the evaporation of a pre-compounded oxide. Very good compositional uniformity in the binary metal oxide films has been observed. Vapor transport modeling is used to explore the origin of the composition uniformity. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electron beam physical vapor deposition (EB-PVD) is used for the deposition of binary metal oxide thermal barrier coatings [1]. There is also an interest in extending its use to other applications including the fabrication of anode/cathode solid oxide fuel cell structures [2], and perhaps, thin film batteries [3]. Single metal oxides can be synthesized either by evaporating directly from the pre-compounded metal oxide source [4] or by evaporating the corresponding metal in an oxidizing environment [5]. Efforts to extend these approaches to multi-component metal oxides directly can be challenging because the vapor cloud is not of the same composition as the source when the vapor pressures of the components differ by more than a factor of 1000 at the surface temperature of the vapor emitting surface [6]. In such cases, the composition of the resulting coatings can differ greatly from that of the source and varies with deposition time [7]. It is also important to note that thermodynamic and kinetic processes govern the oxidation state of the vapor species deposited from either a pre-compounded oxide or reactive source. Under conventional EB-PVD conditions, films evaporated from oxide sources are often deficient in oxygen and it is necessary to add oxygen to the deposition process [8].

In material systems where large vapor pressure differences exist between the pre-compounded oxide source components (for example Y2O3–CeO2; see Table 1), multiple source evaporation from individual metal oxide sources is required to deposit a coating with the desired composition. In these cases, reactive deposition from a metal alloy source can sometimes provide an alternative to pre-compounded oxide evaporation since the vapor pressure differences between metallic alloy components can be significantly different than that of their oxides. For example, Table 1 shows only a factor of 3 difference in the vapor pressures of Ce and Y at 2500°C. In such

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cases, multi-component oxide coatings can be produced using a binary alloy which is stoichiometrically evaporated. In principle, this enables one to avoid multiple source evaporation and can expand the range of the complex oxides which can be deposited using EB-PVC techniques.

In conventional (high vacuum) EB-PVD processes, vapor phase collisions are rare. When reactive deposition is employed, the vapor components are absorbed onto the substrate before the gas phase reactions occur. Under these conditions, Ritter [9] has shown that the ratio of the number of substrate collisions of the reactive gas to the evaporated material, $V_a/V_b$, must be high (i.e. $>10^3$) in order to obtain a non-reduced film. Thus, the partial pressure of the reactive gas must increase with the deposition rate to maintain an adequate impingement of oxygen onto the substrate. As a result, the chamber pressure must increase with deposition rate. However, conventional EB guns need to operate in a high vacuum to successfully generate and maintain a high-density electron beam and this constrains the deposition rate of the process. This problem can be partially overcome either by using a high-pressure EB-PVD process or employing plasma activation. Increased chamber pressure not only allows for a high oxygen/metal ratio, but also controls vapor phase collisions. At increased pressures, the reaction can occur both during vapor transport and at the substrate. In plasma activation, ionization of the reactive and metal vapor increases the collisional cross section of the reactants to promote vapor phase collisions and reactions without increasing the chamber pressure [7].

Recently, a high pressure electron beam directed vapor deposition (DVD) process has been developed, Fig. 1 [10]. It combines high rate, low vacuum electron beam evaporation with a rarefied gas jet to entrain the vapor and transport it to a substrate. The approach uses a combination of a continuously operating, high voltage (60 kV) e-beam gun [modified to function in a low vacuum (13.3–665 Pa) environment] and a He carrier gas jet. The transonic jet is produced by maintaining a high-pressure stream of the jet nozzle opening that is at least twice that of the downstream chamber pressure. During operation, a source material is vaporized and the carrier gas jet collides (at high velocity) with the vapor, entraining and directing it towards the substrate. Binary collisions in the flow cause the vapor to be scattered toward the substrate where it condenses. By entraining all the vapor in a small (~3 cm) diameter jet, a high fraction of the evaporated flux can be deposited and high local deposition rates are achievable, even with moderately low power (10 kW) electron beam guns [11]. By adding oxygen to the gas flow and manipulating the pressures, the flux of reactive gas atoms entering the chamber can be controlled. This allows the metal vapor/carrier gas mean free path to be altered and thus the vapor–oxygen collision frequency can be controlled. The process has been used successfully to create zirconia and yttria-stabilized zirconia coatings from pre-compounded oxide sources [12].

A variety of metal sources (such as Zr, Al, Y, etc.) can also be evaporated. If oxygen is present in the carrier gas, the evaporated metal atoms have an opportunity to react with the reactive component of the carrier gas flow (either in the vapor phase or at the substrate) to create an oxide coating. The process might be superior to conventional EB-PVD for reactive deposition in several ways. First, the low vacuum environment increases the vapor phase collision rate and is likely to promote reactions during vapor transport. The process

Table 1
Vapor pressures of various materials at 2500°C

<table>
<thead>
<tr>
<th>Material</th>
<th>Vapor pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>932.2</td>
</tr>
<tr>
<td>Zr</td>
<td>7.7</td>
</tr>
<tr>
<td>Y</td>
<td>2837.1</td>
</tr>
<tr>
<td>CeO₂</td>
<td>2026.5</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>4.1</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic illustration of the directed vapor deposition system used for reactive deposition. In this arrangement, an electron beam gun located directly above the source is used to vaporize a metal. By introducing a large pressure ratio (2.2) between the upstream and downstream of the nozzle opening and adding oxygen to the carrier gas, a high speed reactive gas jet can be created. This jet directs the vapor efficiently onto the substrate.
Fig. 2. Schematic illustration showing the use of a two-crucible arrangement for alloy deposition by using conventional electron beam evaporation. Note that the deposit in this case is not compositionally uniform. When $s$ is similar to $h$, only a small fraction of the evaporated material can be utilized to create an alloy of a desired composition.

also allows a sufficient supply of reactive gas for high rate deposition. Secondly, carrier gas/vapor atom interactions with the electron beam result in higher fractions of ionized species which further increases the reaction probability. Thirdly, the high kinetic energy of the carrier gas and vapor atoms (a result of the supersonic expansion of the carrier gas) may assist reaction barrier activation [11]. These factors are anticipated to enhance the reaction probability between the reactants and lead to a more favorable environment for reactive deposition. One objective of the work described here is to explore the utility of the DVD process for creating a simple (single) metal oxide from a metal source. Multi-component oxides could then be made using a single alloy source provided the vapor pressure constraints above apply.

When they do not, materials must be evaporated from two or more sources using either a single or multiple electron beam gun arrangement. In a conventional EB-PVD configuration, Fig. 2, the film composition is strongly dependent on the position of the sources and the substrate. The compositional uniformity and region of vapor mixing can be maximized when the source spacing, $s$, is small and the source-to-substrate distance, $h$, is large. However, such a configuration is often not advantageous, as large source-to-substrate distances lower the materials utilization efficiency (MUE, the ratio of mass deposited to mass evaporated) and the use of a small source size leads to reduced evaporation rates. This is not conducive to high rate deposition and is significantly more costly than single source evaporation [7]. Improved multi-source deposition approaches, which yield compositionally uniform vapor fluxes and a high process efficiency are, therefore, desired.

We note that in DVD vapor phase mixing can be attempted by aligning two (or potentially more) sources in line with a carrier gas flow and using electron beam scanning to uniformly heat both sources (Fig. 3). The use of the carrier gas jet in this case not only scatters the vapor flux toward the substrate, leading to a potentially high MUE (and high deposition rates), but also randomizes the vapor trajectory, possibly facilitating vapor phase mixing of the two fluxes. A high MUE...
Fig. 4. XRD pattern of reactively deposited zirconia coatings. Also shown are the peak positions for monoclinic zirconia.

Table 2

Relative peak intensities for a reactively deposited zirconia coating and a randomly orientated zirconia sample

<table>
<thead>
<tr>
<th>Plane</th>
<th>DVD Coating</th>
<th>Random orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I{111}</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>I{200}</td>
<td>6.38</td>
<td>0.45</td>
</tr>
<tr>
<td>I{220}</td>
<td>1.10</td>
<td>0.46</td>
</tr>
<tr>
<td>I{311}</td>
<td>0.47</td>
<td>0.25</td>
</tr>
<tr>
<td>I{400}</td>
<td>0.50</td>
<td>0.04</td>
</tr>
</tbody>
</table>

would allow for the use of small diameter metal source materials which could be spaced closely together to further improve the compositional uniformity of the coating while still achieving a high rate of deposition. The composition of the deposited layer could be systematically controlled by altering the electron beam scan pattern to change the surface temperature (and thus the evaporation rate) of each source material.

We report initial investigations of reactive deposition of metal oxides from both single and two metal sources using the DVD approach. The evaporation of zirconium metal and co-evaporation of yttrium and zirconium in a reactive environment are investigated. The ZrO₂–Y₂O₃ system was chosen due to the wide vapor pressure difference between Y and Zr metals and the technological importance of yttria stabilized zirconia coatings in a variety of applications [1,2].

2. Experimental set-up

Using the DVD approach, zirconia layers were reactively deposited onto a stationary substrate aligned perpendicular to the vapor flux. The evaporation source consisted of a 12.7-mm diameter 99.999% zirconium ingot. A 3.5-kW electron beam with a 3.0-mm spot size and a 10-Hz scan rate was used for evaporation. The chamber pressure was 13.3 Pa. The evaporated flux was entrained in a 5.0-standard liter per minute (slm) helium–5.0 vol.% oxygen gas flow. A pressure ratio of 10.0 was used. The vapor was deposited on a 2.54-cm diameter coupon of Inconel alloy 600 at a deposition rate of 5.0 μm/min. The substrate was positioned 10.0 cm from the nozzle, 8.49 cm from the zirconium source and 6.71 cm from the yttrium source. Energy dispersive spectroscopy (EDS) was used to investigate the compositional uniformity. EDS spectra were obtained using a voltage of 20 keV and the coating composition was determined from the intensity of the zirconium Kα₁ peak (15.78 keV) and the yttrium Kα peak (14.93 keV).

3. Single metal reactive deposition

An XRD pattern for the coating deposited using a single zirconium source is given in Fig. 4. In Table 2,
Table 3
Relative peak intensities for a reactively deposited yttria stabilized zirconia coating and a randomly orientated yttria stabilized zirconia sample

<table>
<thead>
<tr>
<th>Plane</th>
<th>DVD coating</th>
<th>Random orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I{111}</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>I{200}</td>
<td>4.24</td>
<td>0.20</td>
</tr>
<tr>
<td>I{220}</td>
<td>0.26</td>
<td>0.56</td>
</tr>
<tr>
<td>I{311}</td>
<td>0.23</td>
<td>0.38</td>
</tr>
<tr>
<td>I{400}</td>
<td>1.12</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Fig. 5. SEM micrographs showing the cross section (a) and the top surface (b,c) of reactively deposited zirconia using a deposition rate of 10.0 μm/min., a chamber pressure of 13.3 Pa, a pressure ratio of 10.0 and a substrate temperature of 1080°C. Note the columnar grains and the surface facets.

Fig. 6. XRD pattern for a reactively deposited yttria stabilized zirconia system. The addition of yttria results in the formation of a tetragonal crystal structure.

the peak intensities found in the coating and the expected peak intensities for monoclinic zirconia are shown. All the peaks could be assigned to monoclinic zirconia, indicating that the stable phase of zirconia was formed during deposition. By comparing the peak intensities of the coating with that of a randomly orientated sample, the texture in the coating could be estimated. By noting the strong intensity in the {200} and {400} type peaks (Table 3) it can be seen that the coatings had a large fraction of {200} type planes aligned parallel to the substrate surface. Highly textured coatings of this type are typical of zirconia oxide evaporated coatings created using EB-PVD approaches [13]. The zirconia coatings were found to have a dense, columnar morphology (Fig. 5). The columns had a diameter of between 0.25 and 0.50 μm and had a faceted surface. Such a structure was typical of a zone II type morphology from structure zone diagrams [14] and is consistent with the morphology of coatings deposited from pre-compounded zirconia sources using similar deposition conditions [15]. However, it is distinctly different from zirconia layers reactively deposited using DVD at higher chamber pressures (93 Pa). These coatings were found to have porous, columnar morphologies with distinct intercolumnar porosity [12]. The porosity in these coatings was due to an increased probability of oblique vapor atom arrivals which resulted from the higher chamber pressure [15].

4. Two metal source reactive deposition

An XRD pattern for a coating produced using two source (Zr and Y) evaporation is shown in Fig. 6. The
coating had a tetragonal structure consistent with the incorporation of yttrium into the film. Zirconia transforms from a monoclinic to tetragonal and then cubic structure with increasing yttria content [16]. The c/a ratio also changes monotonically with yttria content [17]. The tetragonal structure observed here had a c/a ratio of 1.006. By comparing the lattice parameters found in the coating to data provided by Scott [17] and Lefevre [18], the overall composition of the coating was estimated to be \( \sim 13.0 \text{ mol.\% YO}_{1.5} \). The compositional uniformity of the coating was investigated using EDS. The yttria content was found to vary less to 2.0 at.\% across the substrate area. A high intensity (200) peak was again present (Table 3) consistent with a strong (200) texture in the coating. The morphology of the coating was similar to that of the reactive zirconia coating (Fig. 5).

5. Vapor transport analysis

The spatial uniformity of a coating created by a multi-source evaporation process is governed by diffusion of the vapor during its transport to the substrate. To explore the utility of multi-source DVD evaporation as a deposition concept for depositing compositionally uniform coatings, a direct simulation Monte Carlo (DSMC) approach has been combined with binary collision theory (BCT) to track the propagation of representative vapor species.

DSMC modeling is a well established method for the analysis of rarefied gas flows [19]. The basic premise of this approach is that the motion of simulated molecules can be decoupled from their collisions over a time step set by the collisional mean free path [20]. During

Fig. 7. (a) A DSMC simulation shows the carrier gas speed in the x-direction as a function of position. The crucible position is included for reference. (b) BCT predicted atom trajectories are shown for both zirconium and yttrium atoms. Note that the zirconium atoms are more efficiently turned towards the substrate since the gas speed above the Zr crucible is higher than above the Y crucible. Also note that near the substrate the carrier gas speed is low resulting in increased adatom diffusion in the y-direction.

Fig. 8. An x-y plot showing the impact position of zirconium and yttrium atoms on the substrate. Note that the atoms are well intermixed. The point \( x, y=0 \) defines the center of the nozzle.
the motion phase atoms, molecules or ions are assumed to move in free flight along a path determined by their starting velocity and the forces acting on them. During the collision phase, collision pairs are randomly selected from within an individual cell (into which the geometry is divided). The cell size is typically chosen to be smaller than the mean free path [21]. A variable hard sphere (VHS) molecular model [22] is used to determine the scattering angles and momentum transfer of collision events. This modeling approach has been found to reproduce well the transport properties of gas phase materials in both equilibrium and non-equilibrium (e.g. supersonic expansion of a gas) situations [23].

The simulation of vapor transport in a reactive flow is complicated. Elastic collisions occur between inert gas atoms and O₂ molecules. Either elastic or inelastic collisions occur between both carrier gas species and the evaporated atoms and between all ‘reactant’ species and the molecular species created by metal/metal oxide–O reactions in the gas phase. These reactions create ‘hot’ reaction products which promote the diffusion of molecular species, but the simulation of their trajectories is complex. As a result, we ignore this interaction and analyze the simpler elastic collisions between the carrier gas and the metal atoms. The resulting compositional profiles are expected to overestimate the compositional gradients. We have adapted the implementation of Groves et al. [11] to simulate metal atom transport within a helium carrier gas supersonic...
expansion and its subsequent interaction with a flat substrate. This approach produced results which effectively reproduced the observed flow characteristics in the helium gas (i.e. shock characteristics) and gave good approximations of the adatom energy, adatom angle of incidence and deposition efficiency of metal atoms in the dilute limit [11].

The DSMC approach was used to determine the speed distribution of carrier gas atoms during supersonic expansion from a choked nozzle. The horizontal component of this flow field for the deposition conditions used for this work is shown in Fig. 7. Note the existence of a high-speed region near the nozzle which results from the supersonic expansion of the carrier gas. This speed steadily decreases with distance from the nozzle. Also note that the x-direction speed directly above the crucible varies from 1365 m/s above the zirconium source to 1022 m/s above the yttrium source. A wall jet near the substrate resulted in a moderate y-component speed (not shown).

The transport of Zr and Y atoms in the carrier gas jet flow was simulated using a stochastic biatomic collision theory (BCT) model. Using the BCT code, the trajectories of individual atoms were determined by binary collisions. Zirconium atoms were introduced from a source located 4.309 cm away from the nozzle exit and 0.635 cm below its centerline. Yttrium atoms were introduced from a source located 4.309 cm away from the nozzle exit and 0.635 cm below its centerline. The VHS parameters for yttrium and zirconium were estimated using a method previously described [15]. A total of 40,000 atoms were introduced from each source. Examples of a few atom trajectories from each source are given in Fig. 7.

Several aspects of the vapor transport can be observed. The high x-speed carrier gas atoms near the nozzle rapidly turn the vapor atoms so that their trajectory quickly becomes similar to the streamlines of the carrier gas flux. The vapor atoms remain in this trajectory until the x-direction speed decreases near the substrate. The combination of the low x-direction speed near the substrate and the development of a y-speed component resulting from the wall jet leads to multidirectional scattering, which promotes vapor atom diffusion. It is this diffusive phase that results in most of the mixing of the vapor from the two sources.

The impact probability in the y-direction exhibited a slightly larger variation between the two sources. This variation resulted from the lower x-component speed above the yttrium source as the yttrium vapor atoms were not as efficiently turned into the flow streamlines. Thus, the average y-position for yttrium atom impacts was 0.01361 m compared to 0.01066 m for zirconium. This variation leads to a slightly larger composition variation in the y-direction. As a result, the composition changed from 53 at.% Zr to 47 at.% Zr across the 2.54-cm diameter substrate. The experimentally observed uniformity was better than predicted by vapor transport modeling which did not account for the beneficial effects of thermally induced diffusion on the substrate.

6. Conclusion

A modified electron beam-directed vapor deposition process has been explored as a means for synthesizing single and two component oxide coatings. Coatings have been produced using reactive deposition and either single or dual vapor sources. The results have indicated that DVD can deposit oxide coatings at high rate (at least 5.0 μm/min) even when the source components have widely varying vapor pressures. The coatings had microstructures similar to that of conventional EB-PVD processes. When dual evaporation sources were used, good compositional uniformity across the substrate was obtained. Future work will focus on altering the nozzle/source geometry and the process conditions to optimize the materials utilization efficiency of the process while still retaining a uniform composition.

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References