Advanced Oxide Material Systems for 1650 °C Thermal/Environmental Barrier Coating Applications

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Summary

Advanced thermal and environmental barrier coatings (TEBCs) are being developed for low-emission SiC/SiC ceramic matrix composite (CMC) combustor and vane applications to extend the CMC liner and vane temperature capability to 1650 °C (3000 °F) in oxidizing and water-vapor-containing combustion environments. The advanced 1650 °C TEBC system is required to have a better high-temperature stability, lower thermal conductivity, and more resistance to sintering and thermal stress than current coating systems under engine high-heat-flux and severe thermal cycling conditions. In this report, the thermal conductivity and water vapor stability of selected candidate hafnia-, pyrochlore-, and magnetoplumbite-based TEBC materials are evaluated. The effects of dopants on the materials’ properties are also discussed. The test results have been used to downselect the TEBC materials and help demonstrate the feasibility of advanced 1650 °C coatings with long-term thermal cycling durability.

Introduction

Thermal and environmental barrier coatings (TEBCs) will play a crucial role in advanced gas turbine engine systems because of their ability to significantly increase engine operating temperature and reduce cooling requirements, thus greatly help to achieve engine low emission and high efficiency goals. Under the NASA Ultra-Efficient Engine Technology (UEET) Program, advanced TEBC systems are being developed to provide vital thermal and environmental protection for Si-based ceramic components at gas temperatures exceeding 1760 °C (3200 °F) in harsh combustion environments. The TEBC system is required to have good phase stability, low lattice and radiation thermal conductivity, and high resistance to sintering and thermal stress under the engine high-heat-flux and severe thermal cycling conditions. Advanced heat-flux testing approaches (refs. 1 to 8) have also been established for the 1650 °C coating development. A simulated combustion environment with water vapor has also been incorporated into the heat-flux test capabilities (ref. 3).

In this report, thermal conductivity and water vapor stability of selected HfO₂, pyrochlore, and magnetoplumbite oxide-based materials are evaluated at temperatures up to 1650 °C using a steady-state laser heat-flux technique, and water vapor thermogravimetric analysis (TGA), respectively. Sintering behavior and thermal cycling durability of the plasma-sprayed coatings were determined by monitoring the thermal conductivity changes during the laser heat-flux testing.
Materials and Experimental Methods

Materials

The test specimens of hafnia (HfO₂), pyrochlore (A₂B₂O₇), and magnetoplumbite (AMgAl₁₁O₁₉) oxide materials (where A and B refer to rare earths and zirconium or hafnium, respectively, see table I) were either hot-pressed disks (25.4 mm in diameter, 2 to 4 mm in thickness) or plasma-sprayed coatings (254 to 400 µm in thickness). Spray-dried oxide powders were hot pressed at 1500 °C for an hour under 30 MPa pressure primarily in a graphite die. Sol-gel-derived pyrochlore and magnetoplumbite powders were also used to make hot-pressed specimens.

<table>
<thead>
<tr>
<th>TABLE I.—OXIDE MATERIALS INVESTIGATED FOR ADVANCED THERMAL AND ENVIRONMENTAL BARRIER COATING SYSTEMS</th>
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<tbody>
<tr>
<td>Hafnia-based ceramics (HfO₂-A₂O₃)</td>
</tr>
<tr>
<td>HfO₂-5 mol% Y₂O₃   (5YSHf)</td>
</tr>
<tr>
<td>HfO₂-10 mol% Y₂O₃  (10YSHf)</td>
</tr>
<tr>
<td>HfO₂-15 mol% Y₂O₃  (15YSHf)</td>
</tr>
<tr>
<td>HfO₂-20 mol% Y₂O₃  (20YSHf)</td>
</tr>
<tr>
<td>HfO₂-25 mol% Y₂O₃  (25YSHf)</td>
</tr>
<tr>
<td>HfO₂-18 mol% (Y,Gd,Yb)₂O₃ (Multicomponent)</td>
</tr>
<tr>
<td>Pyrochlores (A₂B₂O₇)</td>
</tr>
<tr>
<td>La₂Hf₂O₇</td>
</tr>
<tr>
<td>La₂Zr₂O₇</td>
</tr>
<tr>
<td>(La,Gd)₂Zr₂O₇</td>
</tr>
<tr>
<td>(La,Yb)₂Zr₂O₇</td>
</tr>
<tr>
<td>(La,Gd,Yb)₂Zr₂O₇</td>
</tr>
<tr>
<td>Magnetoplumbites (AMgAl₁₁O₁₉)</td>
</tr>
<tr>
<td>LaMgAl₁₁O₁₉</td>
</tr>
<tr>
<td>SmMgAl₁₁O₁₉</td>
</tr>
<tr>
<td>GdMgAl₁₁O₁₉</td>
</tr>
<tr>
<td>(Gd,Yb)MgAl₁₁O₁₉</td>
</tr>
</tbody>
</table>

The coating specimens were prepared by plasma spraying the spray-dried, and plasma-reacted powders on either metallic, SiC Hexoloy (Saint-Gobain Ceramics, Niagara Fall, NY), and/or melt infiltrated (MI) SiC/SiC ceramic matrix composite (CMC) substrates (GE Power Systems, NY). For thermal conductivity measurements, the ceramic coating specimens with the low-pressure-plasma-sprayed NiCrAlY bond-coated René N5 (General Electric Company, Fairfield, CT) nickel-base superalloy substrates (25.4 mm in diameter and 3.2 mm in thickness) were used. On the other hand, for 1650 °C sintering and thermal cycling durability testing, complete TEBC coating systems—consisting of layers of the top oxide coating and then either mullite or a mullite-barium strontium aluminosilicate (BSAS) mixture on a silicon coating—were prepared with either the MI SiC/SiC CMC (25.4 mm in diameter, 2.2 mm in thickness) or Hexoloy SiC (25.4 mm in diameter, 3.17 mm in thickness) substrates. The phase structures of the coating materials were examined using x-ray diffraction.

Thermal Conductivity and Thermal Gradient Cyclic Testing

Thermal conductivity testing of hafnia, pyrochlore, and magnetoplumbite hot-pressed and coating specimens was carried out using a 3.5 kW CO₂ laser (wavelength 10.6 µm) high-heat-flux rig. The general test approaches have been described elsewhere (refs. 1 to 4). In this steady-state laser heat-flux thermal conductivity test, the specimen surface heating was provided by the laser beam, and backside air cooling was used to maintain desired specimen temperatures. A uniform laser heat flux was obtained over the 23.9-mm-diameter aperture region of the specimen surface using a beam integrating ZnSe lens with either specimen or lens rotation. Platinum wire flat coils (wire diameter 0.38 mm) were used to form
thin air gaps between the top aluminum aperture plate and stainless steel back plate to minimize the specimen heat losses through the fixture. The thermal conductivities of the hot-pressed and coating specimens were determined from the pass-through heat flux and measured temperature difference through the ceramic specimen (or the ceramic coating) thickness under the steady-state laser heating or thermal cycling conditions by a one-dimensional heat transfer model.

Thermal gradient cyclic testing was conducted for selected HfO2-based coating systems to evaluate coating durability. As in the laser thermal conductivity test, the uniformly distributed laser heat flux was delivered to the coating specimen surface to provide the specimen heating. The required specimen temperatures and thermal gradients were achieved by controlling the delivered laser heat flux and backside air cooling. In the present study, the surface temperature was controlled at 1650 °C and the interface temperature at approximately 1316 °C, and 30-min heating and 3-min cooling cycles were used for the thermal cycling. Thermal conductivity of the coating systems was measured in situ as a function of cycle time to monitor the coating cyclic response.

**Water Vapor Stability Testing**

The water-vapor stability of these oxide materials was investigated using thermogravimetric analysis (TGA) at 1650 °C, in a 50-50 percent flowing H2O-O2 environment. Samples were suspended on sapphire hangers inside a 2.5-cm one-dimensional vertical alumina furnace tube (998A, Vesuvius McDanel, Beaver Falls, PA). Water-vapor-laden oxygen was introduced into the furnace tube using an apparatus described elsewhere (ref. 9). Weight change was continuously monitored with a recording microbalance (C–1000, Cahn Instruments, Cerritos, CA), and specific weight gain and loss (mg/cm²) were measured as a function of time. The linear specific weight change rate constants were obtained from the specific weight change curves of the materials after 100 h of testing.

**Results and Discussion**

**Thermal Conductivity of Hot-Pressed Specimens**

Figure 1 shows the thermal conductivity measurement results of the HfO2-Y2O3 hot-pressed specimens. As shown in figure 1(a), the HfO2 materials generally showed a conductivity decrease with an increase in temperature. A previous study showed that thermal conductivity typically showed less temperature dependence with a higher Y2O3 dopant content (ref. 8). The conductivity increases with temperature in the high-temperature regime can be attributed to the increased radiation heat flux, which will result in the increased apparent thermal conductivity. Figure 1(b) shows measured density and thermal conductivity at 1400 °C of the HfO2 hot-pressed specimens as a function of Y2O3 concentration. The density of the HfO2 specimens was relatively low (i.e., the porosity was relatively high) due to the relatively large particle size powder used. The conductivity data scatter observed was due to the variation in porosity in these hot-processed specimens, with the lower density specimens having lower measured conductivity. Nevertheless, the specimen thermal conductivity showed a general trend to decrease with increase in the yttria dopant concentration. The multicomponent HfO2-18 mol% (Y,Gd,Yb)2O3 coatings specimen showed lower thermal conductivity as compared to the HfO2-Y2O3 coatings at a given total dopant concentration.

Figure 2(a) shows thermal conductivity of La2Zr2O7 (pyrochlore A2B2O7 structure) hot-pressed specimens as a function of surface test temperature. The La2Zr2O7 specimens had low porosity due to the relatively large particle size powder used. The conductivity data scatter observed was due to the variation in porosity in these hot-processed specimens, with the lower density specimens having lower measured conductivity. Nevertheless, the specimen thermal conductivity showed a general trend to decrease with increase in the yttria dopant concentration. The multicomponent HfO2-18 mol% (Y,Gd,Yb)2O3 coatings specimen showed lower thermal conductivity as compared to the HfO2-Y2O3 coatings at a given total dopant concentration.
specimens showed significant thermal conductivity increases starting at 900 °C because of the increased radiation contribution with increasing temperature. The small amount of microporosity in the spray-dried powder-processed specimen did not affect the lattice thermal conductivity dramatically. However, the microporosity in the specimen significantly reduced the radiation conductivity as compared to the almost pore-free, sol-gel powder-processed specimens. The conductivity increased by more than 100 percent for the very dense specimens because of the increased radiation heat transfer under thermal gradient conditions. Figure 2(b) shows that the rare earth-oxide-doped pyrochlores La$_{1.7}$Gd$_{0.3}$Zr$_2$O$_7$, La$_{1.7}$Yb$_{0.3}$Zr$_2$O$_7$, and La$_{1.7}$Gd$_{0.15}$Yb$_{0.15}$Zr$_2$O$_7$ had lower thermal conductivity than the undoped La$_2$Zr$_2$O$_7$. The Gd$_2$O$_3$ and Yb$_2$O$_3$ co-doped materials showed the lowest thermal conductivity.

Figure 3 shows thermal conductivity of hot-pressed magnetoplumbite-type oxide specimens as a function of surface test temperature. The material conductivity exhibited little temperature dependence. It also seemed that GdMgAl$_{11}$O$_{19}$ and SmMgAl$_{11}$O$_{19}$ had lower thermal conductivity than LaMgAl$_{11}$O$_{19}$, as shown in figure 3(a). In addition, similar to the HfO$_2$ and pyrochlore oxides, the rare earth-doped Gd$_{0.7}$Yb$_{0.3}$MgAl$_{11}$O$_{19}$ had the lowest thermal conductivity, as shown in figure 3(b).
**Thermal Conductivity of Plasma-Sprayed Coatings**

Figure 4 shows the thermal conductivity change kinetics of plasma-sprayed HfO$_2$-Y$_2$O$_3$ coatings, coated on SiC hexoloy substrate, tested at 1650 °C with the pass-through heat flux in the range of 95 to 100 W/cm$^2$. It can be seen that HfO$_2$-5 mol% Y$_2$O$_3$ (5YSHf) had a significant conductivity increase upon the 1650 °C thermal exposure even after only a couple of hours testing. On the other hand, the HfO$_2$-15 mol% Y$_2$O$_3$ (15YSHf) and HfO$_2$-25 mol% Y$_2$O$_3$ (25YSHf) coatings showed lower initial and 20-h sintered thermal conductivity, indicating the better temperature stability of the higher dopant coatings.

The x-ray diffraction results showed that the as-sprayed 5YSHf coating initially had a partially stabilized tetragonal phase structure with a small amount of the monoclinic phase (2 to 3 mol%). The as-sprayed 15YSHf and 25YSHf had a stabilized cubic structure. The monoclinic phase content in the 5YSHf coating increased to 10 to 12 mol% after the 1650 °C testing. Therefore, the conductivity increase for the 5YSHf coating is not only due to the significant sintering of the coating, but also to the increased amount of the higher conductivity monoclinic phase in the coating. Advanced multicomponent HfO$_2$ coatings (containing multiple rare earth dopants) have been developed that have achieved even lower thermal conductivity and better thermal stability (refs. 8 and 10).

Figure 5 shows thermal conductivity change kinetics of plasma-sprayed zirconate and/or hafnate (pyrochlore oxide) and magnetoplumbite coatings tested at 1600 to 1630 °C (with the pass-through heat flux of 100 W/cm$^2$). The zirconate and/or hafnate coatings showed significantly lower thermal conductivity than the magnetoplumbite oxide coatings. The development of advanced pyrochlore coatings is also in progress to further improve the coating toughness, thermal stress resistance and overall performance.

Figure 6 shows the 1650 °C sintering and cyclic behavior of the HfO$_2$-18 mol% (Y,Gd,Yb)$_2$O$_3$ coating compared with 5YSHf and 15YSHf coatings. The advanced multicomponent HfO$_2$-based coating had a relatively low conductivity increase during the first 20 hr of steady-state testing. It also showed essentially no cracking and delamination during subsequent testing for 100 30-min cycles at 1650 °C, indicating excellent sintering resistance and cyclic durability. In contrast, the HfO$_2$ baseline coatings showed significant conductivity increases during the initial 20-hr steady-state sintering test and then conductivity reductions during thermal cycling because the coating had cracked and delaminated. The 5YSHf showed severe spallation partially because of the large amount of monoclinic phase formation (>25 mol%) and phase destabilization (ref. 3).
Figure 7 illustrates the long-term durability exhibited by the multicomponent HfO$_2$-18 mol\% (Y,Gd,Yb)$_2$O$_3$ coating system coated on mullite/mullite+20\%BSAS/Si during 1650 °C thermal cycling. It can be seen that the multicomponent HfO$_2$-18 mol\% (Y,Gd,Yb)$_2$O$_3$/mullite-based thermal and environmental barrier coating systems demonstrated 300-hr long-term 1650 °C sintering and cyclic durability on SiC/SiC ceramic matrix composites under the thermal gradient cyclic testing conditions. Further advanced coating development is underway to further improve the coating temperature capability and durability under simulated engine combustion environments.
Water Vapor Stability

Figure 8 shows the water vapor stability of selected HfO₂-based and pyrochlore oxides, determined by TGA in a 50-50 percent flowing water vapor-oxygen environment at 1650 °C. It can be seen that the HfO₂ oxides showed very good water vapor resistance without weight loss and only a slight weight gain after the 100-h TGA water vapor testing. X-ray diffraction also showed no phase change or other phase contaminations after the testing. The minor weight gain of the HfO₂ was attributed to some possible OH⁻ incorporation into the oxide system, as was later confirmed from the increased oxygen concentration (reduced oxygen deficiencies) within the oxides by scanning electron microscopy-energy dispersive spectroscopy (SEM/EDS) analyses. The pyrochlore oxides Sm₂Zr₂O₇, Gd₂Zr₂O₇, and La₂Hf₂O₇ seemed to be stable and showed some weight gains after the water vapor testing. The La₂Zr₂O₇ and Nd₂Zr₂O₇ had initial weight losses in the first 10 to 20 h of testing, suggesting the water vapor attack vulnerability at this temperature. The large weight gains of these pyrochlore oxides in the late stage of the tests are found to be related to some reaction products formed when the specimens reacted with the environments. The alumina furnace tube likely reacts with water vapor to form Al(OH)₃ (ref. 11), which effects sample weight gain (e.g., postexposure x-ray diffraction of La₂Zr₂O₇ also shows LaAlO₃).

The water vapor TGA test for one of the magnetoplumbite oxides (LaMnAl₁₁O₁₉) showed a significant weight loss (–0.037 mg/cm²·h) even at 1500 °C, indicating the poor water vapor stability of the oxide material. Further studies may be necessary to investigate the water vapor stability of other rare earth-doped magnetoplumbite oxides.

Conclusions

Advanced HfO₂, pyrochlore, and magnetoplumbite oxides are being developed for 1650 °C (3000 °F) thermal and environmental barrier coatings for low-emission SiC/SiC ceramic matrix composite (CMC) combustor and vane applications. Rare earth doping and composition optimization have demonstrated an effective approach for reducing material thermal conductivity as well as improving thermal and water vapor stability. Multicomponent, co-doped oxide systems generally showed better performance. HfO₂ and certain pyrochlore oxides are promising candidate materials for the 1650 °C coatings because of their low thermal conductivity and good high-temperature stability in oxidizing and water-vapor-containing combustion environments. Further studies are needed to investigate magnetoplumbite materials for the
high-temperature coating applications. The thermal gradient cyclic tests also demonstrated the 1650 °C coating feasibility and capability for the potential higher temperature SiC/SiC CMC engine component applications.

References

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