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Rare-earth modified zirconium diboride high emissivity coatings for hypersonic applications

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Abstract

Sharp features of hypersonic vehicles increases heat transfer to the surface during flight. This thermal energy can be reduced via increasing the radiation and conduction heat transfer away from the surface. In this study, an emissivity modifier was incorporated into an ultra-high-temperature-ceramic coating system (ZrB_2/SiC) to increase its surface radiation heat transfer rate by increasing the emissivity of the surface. The rare-earth were incorporated into the coatings via mechanical mixing Sm_2O_3 or Tm_2O_3 with ZrB_2/SiC or chemically infiltrating $Sm(NO_3)_3$/ethanol solution into ZrB_2/SiC. Coatings were fabricated using shrouded air plasma spray. Total hemispherical emissivity results show that the $Sm(NO_3)_3$ infiltrated ZrB_2/SiC coating had a higher emissivity compared to the baseline ZrB_2/SiC coatings up to 1200 °C. The thermal conductivity of all coatings presently studied was below 12 W/m/K. The presence of rare-earth in the boria-rich surface glasses formed during oxidation increases the glass evaporation rate of the coatings compared to the ZrB_2/SiC coating.

Keywords: Thermal protection systems; Emissivity; Rare-earth oxides; Zirconium diboride; Plasma spray

1. Introduction

In next generation hypersonic vehicles, blunt leading edges will be replaced with sharp profiles to reduce aerodynamic drag and improve performance. As a consequence of this design change, their aerodynamic heating rate is also drastically increased,[1] with leading edge materials required to withstand very high temperatures for extended times. Ultra high temperature ceramics (UHTCs), such as ZrB_2 and HfB_2, are explored for this application because of their oxidation and ablation resistant properties.[2] Studies have shown that ZrB_2 with an additional 20–30 vol.% SiC secondary phase has the best oxidation performance, where the SiC forms a protective silicon oxide glass on the surface upon oxidation to extend the maximum operating temperature.[3]

During high-speed flight, a large amount of energy is being transferred into the system from the surface via convection and chemical heating.[4] Convection heating arises from the high enthalpy bow shock layer surrounding the sharp structures. At speeds of Mach 5 and above, the diatoms in the air such as N_2 and O_2 will dissociate into ions. These ions will recombine on the hot structure to release energy; hence chemically heating the surface.[4] Thermal energy can be removed from the surface via two mechanisms. A leading edge with high thermal conductivity is desirable because it reduces the thermal gradient within the system and mitigates the effect of local hot spots.[5] While thermal conduction helps to distribute the heat in the leading edge, radiation heat transfer has the ability to re-radiate the heat away from the system, resulting in a lower surface temperature on the leading edge.

The material property that determines the amount of radiation heat transfer is emissivity, ε. A high emissivity is desired to maximize the amount of heat radiated from the surface. Van Wei et al. developed a radiation equilibrium approach to calculate the wall temperature of a hypersonic vehicle surface. In their study, they demonstrated the importance of having a high emissivity surface on the leading edge to reduce its temperature. For example, at a pressure of 0.24 atm and a speed of Mach 10, surfaces with an emissivity of 0.5 and 1.0 have a surface temperature of

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2400 °C and 2100 °C, respectively.[1] Furthermore, Guazzoni and Alfano et al. state that radiation heat transfer is the only method for heating and cooling in outer space applications.[6,7] Clearly, optimizing radiation heat transfer can make a significant difference in reducing leading edge temperature, but few studies have been performed to understand the radiation properties of high temperature materials.[8]

An ideal material system for hypersonic applications requires a melting temperature of 1500 °C and above, high thermal conductivity, high emissivity, and low chemical reactivity.[7,8] Rare-earth oxides (REO) meet the above criteria. Not only do they have melting temperatures greater than 2200 °C, they also have low chemical reactivity with the environment. High emissivity over a broad temperature range is desirable because the system is able to redistribute heat, reduce surface temperature, and chemical reaction rates.[7] Studies indicate that Sm_2O_3, Er_2O_3, Tm_2O_3, and Nd_2O_3 have high average emittance values overoptical and infrared wavelengths (0.5–5.0 μm).[6,9] In particular, samarium and thulium oxides have similar f-shell absorption bands, causing the two to have similar optical performance.[10] Total hemispherical emissivity, where emittance is integrated over all wavelengths and all directions, is the best indicator to quantify surface emissivity. While the REOs mentioned have the requisite high emissivity, they also possess coefficient of thermal expansions that are 20–30% larger than ZrB_2/SiC.[11,12] Thus, a composite coating containing ZrB_2/SiC and REO is an attractive approach as the majority phase of the coating is the same as the underlying ZrB_2/SiC structure.

Finally, conventional air plasma spray is not an acceptable fabrication method to prepare ZrB_2/SiC coatings. Preliminary x-ray diffraction studies of ZrB_2 prepared by conventional air plasma spray revealed that all ZrB_2 powder oxidized to *m*-ZrO_2. Tului et al. patented an inert gas plasma spray process to create ZrB_2/SiC coatings, which also demonstrated that the oxidation behavior of such coatings is very similar to the sintered ZrB_2-SiC system, despite their very different microstructures.[13,14] The major plasma spray technique used in this project is the shrouded air plasma spray (APS) using a proprietary process developed by Praxair Surface Technologies. This spraying technique provides a faster process time and reduces production cost compared to vacuum or inert gas plasma spray.[15]

In the work reported currently we have modified the emissivity of ZrB_2/SiC coatings via the addition of rare-earth additives using two approaches. In the first approach, 23 vol.% (10 mol.%) of either Sm_2O_3 or Tm_2O_3 powders were added to spray-dried ZrB_2 powders. In the second approach, 20 mol% $Sm(NO_3)_3$ dissolved in ethanol was infiltrated into the porous spray-dried ZrB_2 powders and the solvent was evaporated. In both approaches, 20 vol.% SiC was added to the spray-dried mixtures prior to shrouded air plasma spraying. The microstructure and physical properties of these coatings, including total hemispherical emissivity, thermal conductivity and oxidation resistance are described in this paper.

2. Experimental procedure

2.1. Powder preparation and formulation

A lab spray dryer (APV Anhydro Model S1, Anhydro Inc, Soeborg, Denmark) was used to produce powder agglomerate from a liquid feed. (Aero-Instant Spraying Service, Brunswick, USA) The suspension consisted of 50 vol.% ZrB_2(Grade B, HC Starck, Munich, Germany), DI water, 0.15 wt% dispersant (Darvan 821 A, R. T. Vanderbilt Company, Inc., Norwalk, USA) and 2 wt% PVA binder (Celvol 203, Celanese Corporation, Dallas, USA). The suspension was fed into the drying chamber via a spraying nozzle, where the air was heated to 200 °C. A rotary atomizer spun at ~30,000 rpm to atomize the suspension into controlled-size droplets. The temperature at the outlet was approximately 105 °C. The average particle size of the spray-dried powder was analyzed by a Malvern Mastersizer 2000(Malvern Instrument Ltd., Worcestershire, UK), and was approximately 38 μm using a reflective index of 1.92.

Two types of rare-earth elements and two mixing approaches were investigated. In the first approach, spray dried ZrB_2, SiC (Grade UF-10, HC Starck, Munich, Germany), and either Sm_2O_3 or Tm_2O_3 powders (99.9% pure, American Elements, Los Angeles, USA), were dry-mixed (DM) in the desired proportions and roller milled to ensure homogeneous mixing. The chemical compositions of the two types of DM coatings are shown in Table 1.

In the second approach, the rare-earth dopant was added via a chemical-doping (DOP) approach by dissolving 20 mol% samarium nitrate, $Sm(NO_3)_3$ (99.9% pure, Sigma–Aldrich, St. Louis, USA) into 200-proof ethanol. The solution was then infiltrated into the spray-dried ZrB_2 powder and roller milled for 24 hours to ensure homogenous mixing. The mixture was next dried using a RotoVap (BM 200, Yamato Scientific America Inc., Santa Clara, USA) at 100 °C to remove the solvent. This powder was heat treated at 500 °C for 1 h to remove residual moisture and nitrates. The dried mixture was then sieved using a 325-mesh (44 μm) sieve to eliminate large agglomerates, and 20 vol.% SiC powders were added and mechanically mixed. The formulation of the DOP powder is listed in Table 1.

All coatings prepared currently contain the baseline materials, which were ZrB_2/20vol.% SiC, and are identified currently

Table 1
Chemical formulations of coatings prepared via shrouded air plasma spray.

vol% (mol%)	SiC	ZrB_2	Sm_2O_3	Tm_2O_3	$Sm(NO_3)_3{\cdot}6H_2O$
ZBS	20 (27.06)	80 (72.84)	–	–	–
SmZBS-DM	16.7 (24.35)	60.1 (65.65)	23.2 (10.00)	–	–
TmZBS-DM	16.8 (24.35)	60.5 (65.65)	–	22.7 (10)	–
SmZBS-DOP	20 (24.35)	80 (55.65)	–	–	(20)