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Effect of rare-earth dopant (Sm) concentration on total hemispherical emissivity and ablation resistance of ZrB_2/SiC coatings

Winnie Tan[c], Mitchell Adducci[a], Christopher Petorak[b], Anneliese E. Brenner[a], Rodney W. Trice[a,*]

[a] Purdue University, West Lafayette, IN 47907, USA
[b] Praxair Surface Technologies Inc., Indianapolis, IN 46222, USA
[c] Siemens Energy Inc., Charlotte, NC 28273, USA

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ABSTRACT

The temperature of leading edges during hypersonic flight can be reduced by maximizing the emissivity of their surface. In this study, the concentration of a known emissivity modifier (Sm) has been varied (3, 5, and 8 mol% Sm in ZrB_2/SiC coatings) and the total hemispherical emissivity and ablation resistance of the coatings has been evaluated. Maximum emissivity was observed to occur for the 5 mol% Sm ZrB_2/SiC coating, with a value of 0.9 measured at 1600 °C. All the ablated Sm-doped coatings have an oxide scale consisting of m-ZrO_2 and c_1-$Sm_{0.2}Zr_{0.9}O_{1.9}$ and/or $Sm_2Zr_2O_7$ depending on the Sm concentration. Large amounts of porosity were observed in the oxide scale of the ablated 8 mol% Sm ZrB_2/SiC coating. This was attributed to viscosity reduction of the B_2O_3 and SiO_2 glassy phases by the Sm^{3+} and their subsequent vaporization. The 5 mol% Sm-doped ZrB_2/SiC demonstrated the optimal emissivity properties and dense oxide scale formation.

1. Introduction

The stagnation region of nose cones and leading edges of hypersonic vehicles have a large heat flux impinging their structure that leads to surface temperatures approaching 2000 °C [1]. Zirconium diboride (ZrB_2), with 20–30 vol% SiC additions, is being considered for hypersonic applications because of its relative resistance to these extreme environments. The operating temperature of ZrB_2 with SiC additions, however, is still limited by the active evaporation of SiO_2 at 1600 °C [2,3].

There are at least two heat transfer strategies to mitigate the temperature extremes that occur on the leading edges. These strategies point to a specific properties of the leading edge material to optimize. First, a high thermal conductivity lead edge material is desired to mitigate the effect of local hot spots and improve thermal shock resistance via conduction of the heat to thicker regions of the leading edge. The thermal conductivity of 30 vol% SiC/ZrB_2 has been reported as ranges between 44–64 W/m/K at 400–1200 °C [4]. Second, the emissivity of the surface should be maximized to be as close to that of a black body, $\varepsilon \approx 1$, as possible. The radiation component of heat transfer has been shown to significantly cool the surface during hypersonic flight via re-radiation of the absorbed heat [2,5].

Previous studies by Guazzoni and McMahon et al. demonstrated the unique high emissivity properties of several rare-earth oxides, including Sm_2O_3 and Tm_2O_3 [6,7]. The unique optical properties of Sm_2O_3 arise from the strongly localized *f*-shell states of the samarium, which is independent of the details of the chemical bonding between the samarium and oxygen [8]. Based on Wien's Displacement Law, at 1500°–2000 °C the maximum spectral emissivity occurs between 0.76–0.97 eV (1.27–1.62 μm). The absorption spectrum of Sm^{3+} [Xe]4*f* [5] is localized at 0.74–1.24 eV.

Preliminary work has indicated that emissivity modification is possible by doping samarium into ZrB_2/SiC coatings via a chemical infiltration approach [9–11]. At 1200 °C, the total hemispherical emissivity increased from 0.8 to 0.93 when 10.3 mol% Sm was incorporated into the ZrB_2/SiC coating [9]. Furthermore, the ablation product of the samarium-doped ZrB_2/SiC coatings was c_1-$Sm_{0.2}Zr_{0.8}O_{1.9}$. This oxide has a melting temperature exceeding 2000 °C [10], and remained protective after a 60 s exposure to a 2000 °C oxyacetylene torch [12]. As maintaining sharp leading edges is crucial for performing flight maneuvers, the samarium-

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[*] Corresponding author at: 701 West Stadium Avenue, West Lafayette, IN 47907, USA.
E-mail address: rtrice@purdue.edu (R.W. Trice).

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modified ZrB_2/SiC system shows promise as a potential extreme condition coating for hypersonic flight.

The purpose of the current work was to determine the optimum concentration of samarium dopant required for ZrB_2/SiC coatings to maximize total hemispherical emissivity at temperatures up to 1500 °C. In addition, the effect of the amount of samarium on the microstructural development of the oxide ablation scale was studied. Thus, ZrB_2/SiC coatings were doped with 3, 5, and 8 mol% Sm as emissivity modifiers. The as-sprayed microstructure and phase analysis were investigated using several techniques including transmission electron microscopy (TEM).

2. Experimental procedure

2.1. Powder preparation and formulation

Spray-dried powders were prepared from a suspension with 58% powder loading. The suspension consisted of 80 vol% ZrB_2 (3–5 μm, Grade A, HC Starck, Munich, Germany), 20 vol% α-SiC (1.4 μm, Grade UF-05, HC Starck, Munich, Germany), 0.4 wt.% dispersant (Darvan 821A, R.T. Vanderbilt Company, Inc., Norwalk, USA), 2 wt.% PVA binder (Celvol 203, Celanese Corporation, Dallas, USA) and DI water. The average spray dried particle size was approximately 38 μm.

Samarium dopant was added to the spray dried ZrB_2/SiC powders via a chemical infiltration method [9,13]. In this process, 5, 10, and 15 mol% samarium nitrate hexahydrate (99.9% pure $Sm(NO_3)_3 \cdot 6H_2O$, Sigma-Aldrich, St. Louis, USA) were dissolved into 200-proof ethanol and the resulting solution was then infiltrated into the porous spray-dried ZrB_2/SiC powder. Next, the solvent was removed via a rotary evaporator (BM 200, Yamato Scientific America Inc., Santa Clara, USA) at 100 °C. This powder was heated at 400 °C in air for an hour to remove residual moisture and nitrates. Subsequently, the dried mixture was sieved using a 60-mesh (250 μm aperture) to eliminate large agglomerates. Fumed silica (0.02 wt.%, Cab-O-Sil®, Cabot Corporation, Boston, USA) was added to all the powders as a flowing agent for feeding the powders during the plasma spray process. The four different coatings studied are listed in Table 1.

The amount of samarium and silicon incorporated into the coatings was measured by mass spectroscopy on pulverized coatings (NSL Analytical Services Inc., Cleveland, USA). The actual concentrations of samarium in each coating are listed in Table 1. To help simplify discussion, the naming convention based on the *actual* samarium molar concentration will be used. For instance, the 3SmZBS coating contains ~3 mol% Sm in the ZrB_2/SiC matrix.

2.2. Plasma spray process

The coatings were prepared at Praxair Surface Technologies (Indianapolis, USA) using a shrouded plasma spray process, which limits oxidation of ZrB_2 and SiC [14]. Specifically, the shroud is flooded with argon during spraying. The coatings were sprayed on aluminum panels, ~99% dense sintered ZrB_2/SiC substrates, and tungsten rods for coating analysis, ablation testing, and total hemispherical emissivity testing, respectively. The average coating thickness ranged between 50–350 μm, depending on the test geometry. Stand-alone coatings were obtained by dissolving the coated aluminum panels in 5 M NaOH at 70 °C for 1 h.

2.3. Microstructural and phase analysis

The density of each coating, off the substrate, was determined using Archimedes' methodology as described in the ASTM C373-88 standard [15]. The theoretical density was calculated using the rule of mixtures based on final coating compositions, where the density of ZrB_2, SiC, and Sm are 6.09 g/cm^3, 3.21 g/cm^3, and 7.52 g/cm^3, respectively. The surface roughness (R_a) of the coatings was quantified with a profilometer (AS0200 AlphaStep, Tencor Corporation, Milpitas, USA) at a scan speed of 10 μm/second. A total length of 300 μm was measured for each coating.

X-ray diffraction (XRD) using CuKα radiation (D8 Focus, Bruker Corporation, Billerica, USA) was performed on as-sprayed and oxidized coatings over 2θ values of 20–70°. A step size of 0.05° and a scan rate of 5°/min were used. Coating topography, cross section, and element analysis were observed using a scanning electron microscope (SEM) equipped with energy dispersive x-ray spectroscopy (EDS) (Phillips XL-40, FEI Co., Hillsboro, USA). The non-conductive ceramic coatings were coated with a thin layer of Au/Pd prior to imaging. All post-ablative test samples were stored in a desiccator and the polishing process was performed with non-aqueous solutions.

TEM specimens were prepared with a focused ion beam (FIB) equipped with a gallium ion beam (FEI Quanta 3D FEG, Oregon, USA). Using a manipulator, the FIB specimens were lifted out and attached to a copper grid. Bright field (BF) images, electron energy loss spectroscopy (EELS), and EDS were acquire using a FEI Titan Environmental Electron Microscope (Oregon, USA).

2.4. Total hemispherical emissivity

Emissivity tests were performed by TPRL Inc. (West Lafayette, IN, USA) using the ASTM C835-06 standard as a guide [16]. A ~20 μm thick coating of ZrB_2/SiC was applied on the electrically conductive tungsten rod (3.8 mm outer diameter) before applying 50 μm of one of the samarium-doped ZrB_2/SiC coatings currently investigated. Prior to the start of the emissivity test, two pairs of type-K thermocouples and a pair of platinum electrodes were spot welded onto the center region of the sample to obtain temperature and voltage readings, respectively. The emissivity as a function of temperature, $\varepsilon(T)$, was calculated according to Stefan-Boltzmann law:

$$\varepsilon(T) = \frac{i\Delta V}{PL\sigma(T^4 - T_o^4)} \quad (1)$$

where i is the electric current in amperes, ΔV is the voltage drop measured across the rod in volts, P and L are the perimeter and length of the rod, respectively, in meters, σ is the Stefan-Boltzmann constant (W/m^{2}K^4), and T and T_o are the sample and ambient temperatures, respectively, in Kelvin. This test was performed in a vacuum (<1.3 mPa) to ensure radiation was the sole heat transfer mechanism. All emissivity values reported and discussed in this study are total hemispherical emissivity.

2.5. Oxyacetylene ablation test

The ablation resistance of the coatings in high heat flux conditions was evaluated by an oxyacetylene torch rig. The oxyacetylene ablative test setup was constructed using the ASTM 285-08 [17] standard as a guide. A two-color pyrometer (OS3750, Omega Engineering Inc., Stamford, CT, USA) was used to measure the front sample face temperatures and was connected to a data logger to record real time temperatures as a function of time. The coatings were deposited on sintered ZrB_2/SiC substrates and sectioned into 12 mm by 12 mm square samples. Each sample was held in place by a graphite fixture during testing. The ablation torch (Victor Technologies, St. Louis, USA) had a 3 mm orifice and the separation distance between the sample surface and torch was held constant at 20 mm. An oxygen-rich flame with a 10:12 slpm acetylene to oxygen ratio was used to simulate the oxidizing operating environment. Specimens were tested for 60 s, starting from when the

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