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Final Report to AFOSR

Award No. FA9550-10-1-0189

Performance Period: 15 May-2010 - 14-May-2013

Principal Investigator: Erica L. Corral, The University of Arizona, Tucson, AZ

Title: (YIP-10) Enabling Dynamic Oxidation Mechanisms in Reverse Infiltrated Ultra-High Temperature Ceramic Coated C-C Composites for Application in Hypersonics

### **Project Overview**

The goal of this young investigator research plan is to establish a comprehensive research program that will advance the fundamental understanding of high-temperature oxidation mechanisms in novel reverse infiltrated multilayer ultra-high temperature ceramic (UHTC) coated carbon-carbon (C-C) composites that will provide oxidation for future hypersonic vehicles. C-C composites provide high strength and low density for their use in hypersonics, but they oxidize in air at temperatures  $>500$  °C, and need thermal protection system (TPS) materials in order to survive aerothermal heating in excess of 2800 °C.

This approach represents a radical departure from conventional ablative TPS materials because the oxidation protection materials are thoughtfully designed throughout the bulk of the C-C composite as fully infiltrated UHTC multilayer coatings. The formal hypothesis statement for this proposed research is: "A fully infiltrated multilayer UHTC coated C-C composite will enable dynamic oxidation mechanisms when tested at temperatures above 2000 °C that will be superior to conventional UHTC coated C-C composites that are not fully infiltrated." The proposed hypothesis driven research will result in a new fundamental understanding of dynamic high-temperature oxidation mechanisms for fully infiltrated C-C composites with UHTC filler systems, which are strongly dependent on specific precursor microstructure, and composition.

The specific outcomes of the project are:

- (1) rapid chemical synthesis of sol-gel precursors to  $ZrB_2$  and  $HfB_2$  with identification of new conversion mechanisms employed during the high temperature carbothermal reduction of the precursors to ceramic powders;
- (2) created novel reverse infiltrated UHTC filler systems within C-C composites using powder filled precursors (PFPs) of  $HfB_2$ ,  $ZrB_2$ , and SiC with a range of compositions and precursor ;
- (3) high-temperature oxidation kinetics of novel filler systems as a function of composition, and microstructure using static and rapid heating tests reveal new mechanisms for oxidation formation within UHTC composites and filler systems that result in a self healing coating; and
- (4) developed two novel high temperature oxidation testing methods, dynamic non-equilibrium thermal gravimetric analysis, and ultra-high temperature oxyacetylene torch testing in high heat flux and oxygen rich environments.

The details for these project outcomes are to be published in the *Journal of the American Ceramic Society* and the *International Journal of Applied Ceramic Technology*, at the time this report was due. Therefore, an executive summary of the outcomes is provided here.

### Executive Summary for Outcome 1

Sol-gel precursors to  $\text{HfB}_2$  and  $\text{ZrB}_2$  are processed by high-energy ultrasonication of Hf,Zr oxychloride hydrates, triethyl borate, and phenolic resin to form precipitate free sols that turn into stable gels with no catalyst addition. Both precursor concentration and structure (a sol or a gel) are found to influence the synthesis of the diboride phase at high temperature. Decreasing sol concentration increases powder surface area from, 3.6 to 6.8  $\text{m}^2/\text{g}$ , while heat-treating a gel leads to residual oxides and carbides. Figure 1 shows the X-Ray diffraction spectra for  $\text{HfB}_2$  (a) and  $\text{ZrB}_2$  (b) precursor conversion upon increasing heat treatment with presence of residual oxides and carbides. Particles are either, fine rounded particles, unique elongated rods, and/or platelets indicating localized particle growth with directional coarsening. Investigating the conversion process to  $\text{ZrB}_2$  indicates a multistep reaction is likely taking place with: 1)  $\text{ZrC}$  formation, 2)  $\text{ZrC}$  reacts with  $\text{B}_2\text{O}_3$  or 3)  $\text{ZrC}$  reacts with  $\text{B}_2\text{O}_3$  and  $\text{C}$  to form  $\text{ZrB}_2$ . At low temperatures  $\text{ZrC}$  formation is limiting, while at higher temperatures the reaction of  $\text{ZrC}$  to  $\text{ZrB}_2$  becomes limiting.  $\text{ZrC}$  is found to be a direct reducing agent for  $\text{B}_2\text{O}_3$  at low temperature to form  $\text{ZrB}_2$  and  $\text{ZrO}_2$ , at high temperatures it reacts with  $\text{B}_2\text{O}_3$  and  $\text{C}$  to form pure  $\text{ZrB}_2$ . Both  $\text{HfB}_2$  and  $\text{ZrB}_2$  can be processed using these techniques and optimizing the chemistry, processing, and heat treatment conditions can result in the desired final ceramic product.

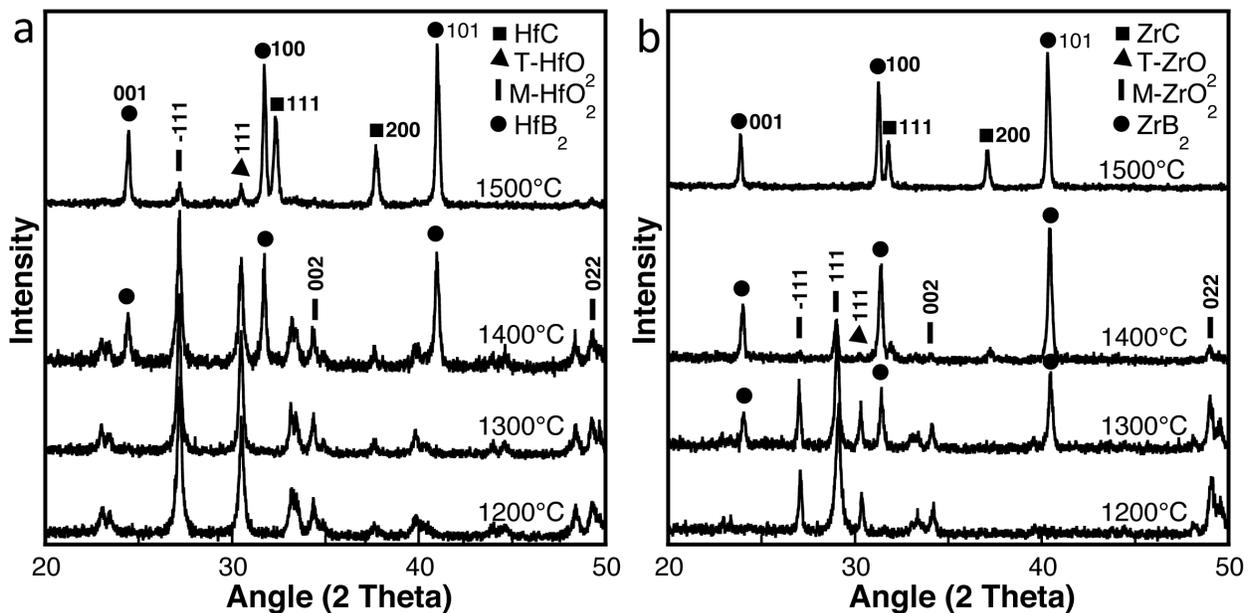


Figure 1. X-Ray diffraction spectra for sol-gel precursor conversion to crystalline (a)  $\text{HfB}_2$  and (b)  $\text{ZrB}_2$  powders, as a function of heat treatment temperature.

### Executive Summary for Outcome 2, 3 and 4

Ultra high temperature ceramics (UHTCs) form protective surface oxide layers that inhibit oxygen diffusion at high temperature and are candidate coating materials. Oxidation protection for C-C can be achieved by duplicating the surface oxide chemistry of bulk UHTCs formed by a “composite effect” between  $\text{ZrB}_2$  and  $\text{SiC}$ . Dynamic non-equilibrium (DNE) TGA

is used to evaluate the oxidation properties isothermally at 1600°C using in-situ mass changes. Pure SiC coatings are ineffective at protecting the C-C while ZrB<sub>2</sub>-SiC containing composite coatings retained up to 90% of the initial mass. Excessive B<sub>2</sub>O<sub>3</sub> in the SiO<sub>2</sub> oxide scale reduces viscosity allowing the oxide layer to spread out across the surface of the C-C forming a protective oxide layer. Figure 2a shows a cross section of a C-C composite filled with UHTC composite containing SiC precursor material and 100% ZrB<sub>2</sub> powder fill after pyrolysis and before high temperature oxidation. Figure 2b shows the cross section of C-C composite after oxidation using DNE-TGA at 1600 °C for 15 minutes, shows the glass-ceramic coating (that formed a shell upon cooling) was generated from within the UHTC filled C-C composite. Notice, in Figure 2a that there is no coating formed after pyrolysis, which means that in Figure 2b the only way the coating formed was from the dynamic self generation of the coating during high temperature exposure to oxygen. The formation of a ZrO<sub>2</sub>-SiO<sub>2</sub> glass-ceramic coating on the C-C composite is believed to be responsible for the enhanced oxidation protection and is directly compared to bulk monolithic ZrB<sub>2</sub>-SiC ceramics tested using DNE-TGA in the same conditions where a comparable glass-ceramic surface layer forms to prevent oxygen diffusion.

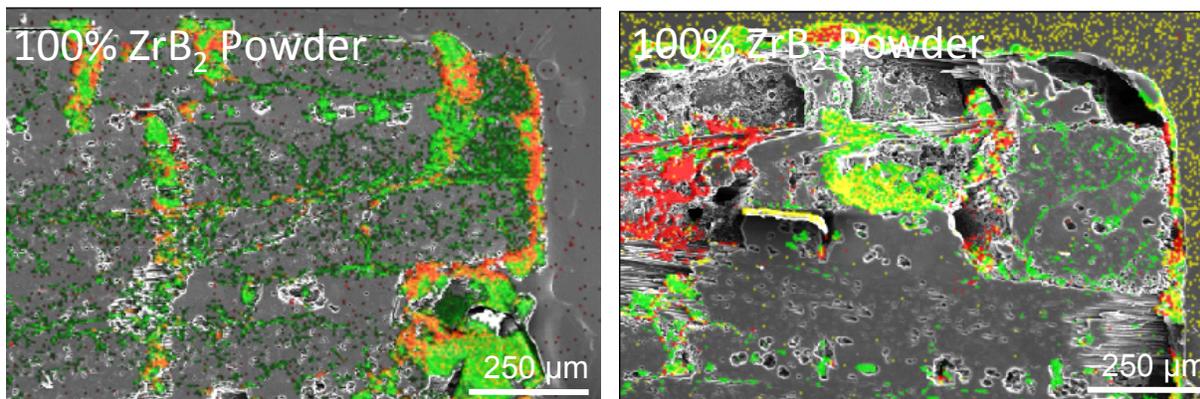


Figure 2. Scanning electron micrographs for cross-sections prepared (a) after pyrolysis and (b) after high temperature oxidation testing, for 100% ZrB<sub>2</sub> powder filled SiC precursor filler system.

#### Executive Summary of Outcome 4

The oxyacetylene torch is a facility capable of replicating many of the factors for testing UHTCs oxidation behavior. It is inexpensive and easy to operate. However, careful attention to the specific test environment must be made. The bulk flame chemistry dictates the range of tests available to the operator. The local flame chemistry can be chosen to meet a number of criteria. The most consistent way to compare oxidation tests between various materials is to fix local oxygen content and/or heat flux and compare the rates noting that different temperatures are measured.

An oxyacetylene torch is used for testing oxidation behavior of carbon and ceramic materials at high temperatures (>1500°C), oxygen rich environments (up to pO<sub>2</sub> of 12 kPa), and fast heating rates (1000°C/min) under flowing gases (200 m/s). The testing facility consists of a welding tip (1.8 mm orifice) connected to oxygen and acetylene supply tanks. Ratios of oxygen

to acetylene are adjusted with mass flow controllers. Samples are exposed to the torch by sliding the sample mount to the desired test position on rails. Sample geometry with face and stub discs is designed to minimize temperature gradients across the sample and prevent the flame from removing the sample from its mount.

The oxyacetylene torch testing environment is well characterized in order to understand how materials will respond in this environment. An oxygen sensor, optical pyrometer, and heat flux gauge are used to characterize important variables of the torch environment including oxygen partial pressure, total pressure, temperature, and heat flux, respectively. Oxygen sensor measurements were performed to determine the relationship between local oxygen content from the oxygen sensor and partial pressure of oxygen using oxygen and argon as the gases. A pressure sensor was used to measure the total pressure in the flame in order to calculate partial pressures of oxygen.  $ZrO_2$  discs for temperature measurements were prepared using spark plasma sintering, and graphite samples for temperature and oxidation measurements were machined with front and stub discs. Experimental results show that as position from torch tip increases, temperature decreases, local oxygen content increases, and local heat flux decreases. As bulk flame chemistry (VFR) increases, local oxygen content increases and flame length decreases. Changing sample position in flame will alter the temperature and local oxygen content. Changing the bulk flame chemistry (ratios of oxygen to acetylene) will alter adiabatic flame temperature and therefore, the heat flux of samples. These variables are shown in Figure 3. Oxidation rate of graphite increases with increasing local oxygen content at constant heat flux, heat flux at constant local oxygen content, and front face temperature at constant local oxygen content.

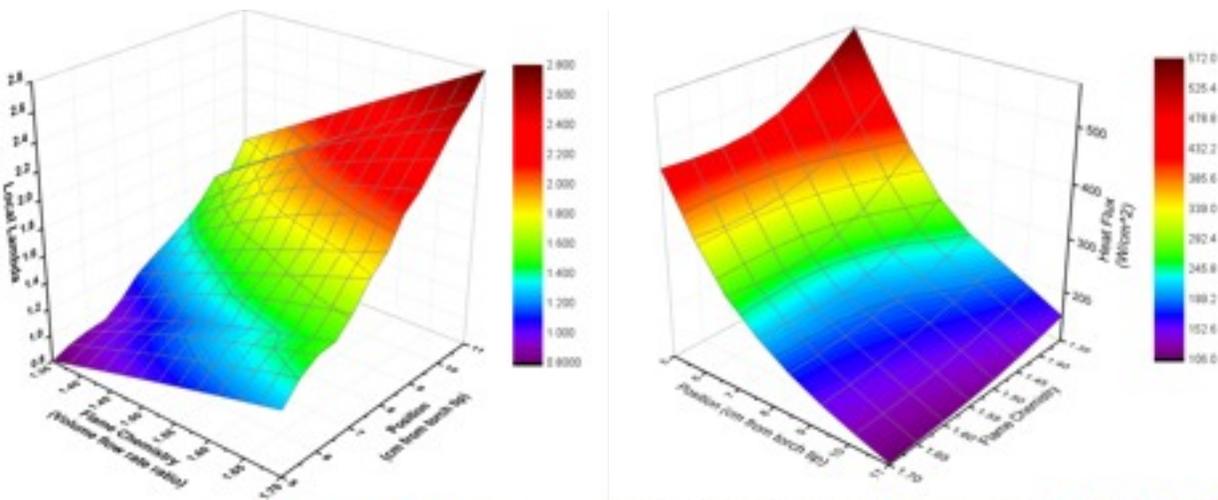


Figure 3. Characterization of the critical variables used during high temperature ablation testing using an oxyacetylene torch test facility show that (a) oxygen content within the flame and (b) heat flux generated by the flame are independently varied as a function of distance from specimen to torch tip and flame chemistry (air to fuel ratio).