



# Oxidation of Ultra High Temperature Ceramics in Water Vapor

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# OXIDATION OF ULTRA HIGH TEMPERATURE CERAMICS IN WATER VAPOR

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## ABSTRACT

Ultra High Temperature Ceramics (UHTCs) including  $\text{HfB}_2 + 20\% \text{ SiC}$  (**HS**),  $\text{ZrB}_2 + 20\% \text{ SiC}$  (**ZS**), and  $\text{ZrB}_2 + 30\% \text{ C} + 14\% \text{ SiC}$  (**ZCS**) have been investigated for use as potential aeropropulsion engine materials. These materials were oxidized in water vapor (90%) using a cyclic vertical furnace at 1 atm. The total exposure time was 10 hours at temperatures of 1200, 1300, and 1400°C. CVD SiC was also evaluated as a baseline for comparison. Weight change, X-ray diffraction analyses, surface and cross-sectional SEM and EDS were performed. These results are compared with tests conducted in a stagnant air furnace at temperatures of 1327°C for 100 minutes, and with high pressure burner rig (HPBR) results at 1100 and 1300°C at 6 atm for 50 h. Low velocity water vapor does not contribute significantly to the oxidation rates of UHTCs when compared to stagnant air. The parabolic rate constants at 1300°C, range from 0.29 – 16.0  $\text{mg}^2\text{cm}^4/\text{h}$  for HS and ZCS respectively, with ZS results between these two values. Comparison of results for UHTCs tested in the furnace in 90% water vapor with HPBR results was difficult due to significant sample loss caused by spallation in the increased velocity of the HPBR. Total recession measurements are also reported for the two test environments.

## INTRODUCTION

### Background

Ultra-High Temperature Ceramics (UHTCs) have historically been evaluated as reusable thermal protection systems for hypersonic vehicles, e.g., Bull and Rasky [1-2]. Re-entry conditions include high temperatures (up to 2000°C) and velocities, low air pressures (0.005 - 0.010 atm), and short times (~15 minutes/re-entry).

Recently, Levine et al. [3] studied UHTCs for aeropropulsion applications including cyclic oxidation in air. Due to their high temperature capabilities, UHTCs have been evaluated

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in this study for their environmental durability in propulsion applications under the Ultra Efficient Engine Technology (UEET) Program at NASA Glenn Research Center. Combustion conditions include: high temperatures (900-1500°C) and gas velocities, high pressures (10-100 atm), long time (thousands of hours), and hydrocarbon fuel combustion products ( $N_2$ ,  $O_2$ ,  $CO_x$ , and  $H_2O$ ).

## Objective

The objective of this study was to evaluate the effect of water vapor on the oxidation of UHTC materials. Three compositions of UHTCs ( $HfB_2 + 20\% SiC$ ,  $ZrB_2 + 20\% SiC$ , and  $ZrB_2 + 30\% C + 14\% SiC$ ) were evaluated in this study along with CVD SiC as a control. For ease of describing the three compositions mentioned above, they will be referred to as HS, ZS and ZCS, respectively. All three compositions contain metal diboride as the major constituent and a significant amount of silicon carbide. Refractory metal boride and carbides, as well as the oxides formed on high temperature exposure in air, have very high melting points. The melting points of  $HfB_2$  and  $ZrB_2$  are 3300 and 3200°C, respectively [4]. SiC decomposes at a temperature of 2800°C [4]. The oxide melting points of  $HfO_2$ ,  $ZrO_2$  and  $SiO_2$  are 2900, 2700, and 1700°C, respectively [5]. Boria ( $B_2O_3$ ) is one of the oxides resulting from the oxidation of UHTCs. Boria has a low melting point of 410-450°C [6,7]. At high temperatures (<1100°C) in water vapor,  $HBO_2(g)$  will be the primary volatile species formed by  $B_2O_3(l)$  [6]. SiC was included as a control for several reasons. First, it has been extensively studied in water vapor environments and reported in the literature by Opila [8]. It is known that a protective  $SiO_2$  scale will form from the oxide of SiC in water vapor at high temperature.  $SiO_2$  will in turn react with water vapor to form the volatile species  $Si(OH)_4(g)$  [8]. Second, SiC has been considered for applications in combustion environments and is therefore a fair comparison for UHTCs in propulsion applications. Finally, SiC is of interest since it is a component of all three UHTC compositions studied here.

Typical combustion environments contain oxygen, water vapor and carbon dioxide. This study will evaluate UHTCs in a water vapor environment and compare their performance to oxidation in stagnant air and high velocity environments produced in the high pressure burner rig (HPBR).

## **EXPERIMENTAL**

Three compositions of UHTC mentioned above and designated as HS, ZS, and ZCS were manufactured by Materials and Machines, Inc. (Tucson, AZ), and have been evaluated for their durability in 90% water vapor and 10% oxygen in a vertical cyclic furnace. From this point onward, the test environment will be referred to as simply 90% water vapor. All UHTC materials were provided by NASA Ames Research Center and machined at Southern Research Institute (Birmingham, AL). Typical sample size is 2.54 x 1.28 x 0.32 cm with a 0.32 cm diameter hole, giving an average surface area of 9.1 cm<sup>2</sup>. The average starting sample weights are 9.7 g for HS, 5.5 g for ZS, and 4.6 g for ZCS. CVD SiC samples were tested simultaneously as controls. The typical sample size of CVD SiC is 3.00 x 1.50 x 0.30 cm with a 0.32 cm diameter hole results in an average surface area of 11.84 cm<sup>2</sup>. The average starting weight is

4.25 g. All samples were ultrasonically cleaned successively in a concentrated cleaning solution, de-ionized water, acetone and alcohol prior to exposure.

A vertical furnace with molybdenum disilicide heating elements was used with a 5.1 cm diameter alumina ( $\text{Al}_2\text{O}_3$ ) furnace tube as can be seen in Figure 1. A controlled elevator was used to move the furnace and furnace tube up and down during cycling while the sample and platinum hang wire remained in a fixed position. The hot zone is approximately 5 cm long. Alumina beads were used to prevent reaction between the platinum hook and the CVD SiC coupons. A peristaltic pump was used to introduce the water from the top of the furnace tube into a 7.6 cm fused quartz wool plug. Oxygen flows through the plug entraining the water as vapor in the gas stream. Flow rates of deionized water at 80 mL/hr, liquid (equivalent to 1800 ccm vapor) with 200 ccm of oxygen were used, resulting in a total linear gas velocity of 2 cm/sec. Condensed water collected at the bottom of the furnace tube, is then measured to verify the desired liquid flow rate.

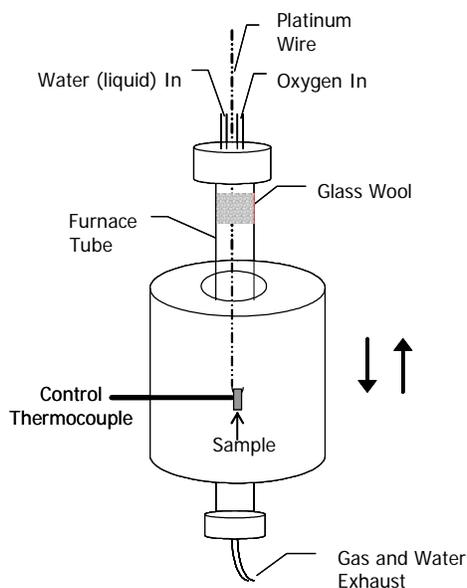


Figure 1. Schematic of cyclic furnace with 90% water vapor and 10% oxygen

The samples were typically exposed for a total of 10 cycles, where each cycle consists of one hour in the hot zone and 20 minutes in the cold section. Two samples from each of the three compositions were evaluated. One test for HS was performed at 1400°C for 26 hours. Each experiment contained one CVD SiC as a control. An average of five pan weight measurements were taken with a Sartorius model 1712 MP8 electronic balance to the nearest  $\pm 0.02$  mg at multiple intervals during each experiment. X-ray diffraction analyses (Phillips XRG 3600) were performed after the final weight was recorded. Scanning electron microscopy (Jeol 840A) was used to evaluate the surface of the sample. Cross-sections were then polished to 1  $\mu\text{m}$  using a non-aqueous cutting and polishing method in order to preserve any boron-containing glass species. Field emission scanning electron microscopy (FE-SEM, Hitachi S-4700) was used to evaluate these cross-sections.

The results from this study were also compared to results obtained in stagnant air and the higher velocity HPBR exposed specimen. Oxidation of UHTCs in stagnant air was previously

reported by Levine et al. [3]. Sample sizes were the same as those listed above, but without the hang hole. Samples were exposed to ten-minute oxidation cycles at 1327°C in a box furnace with molybdenum disilicide heating elements. A maximum exposure time of 100 minutes was used.

The HPBR specimen sample size is 1.3 x 7.6 x 0.3 cm. Test conditions include 6 atm total pressure, approximately 0.6 atm water vapor partial pressure, a gas velocity of 18 meters/sec and the fuel to air ratio is 0.060. Samples were exposed for 50 hours with weight change monitored at intermediate intervals.

## RESULTS AND DISCUSSION

Typical parabolic specific weight changes, as shown in Figure 2, were observed for the UHTCs. The expected paralinear weight changes were observed for SiC.

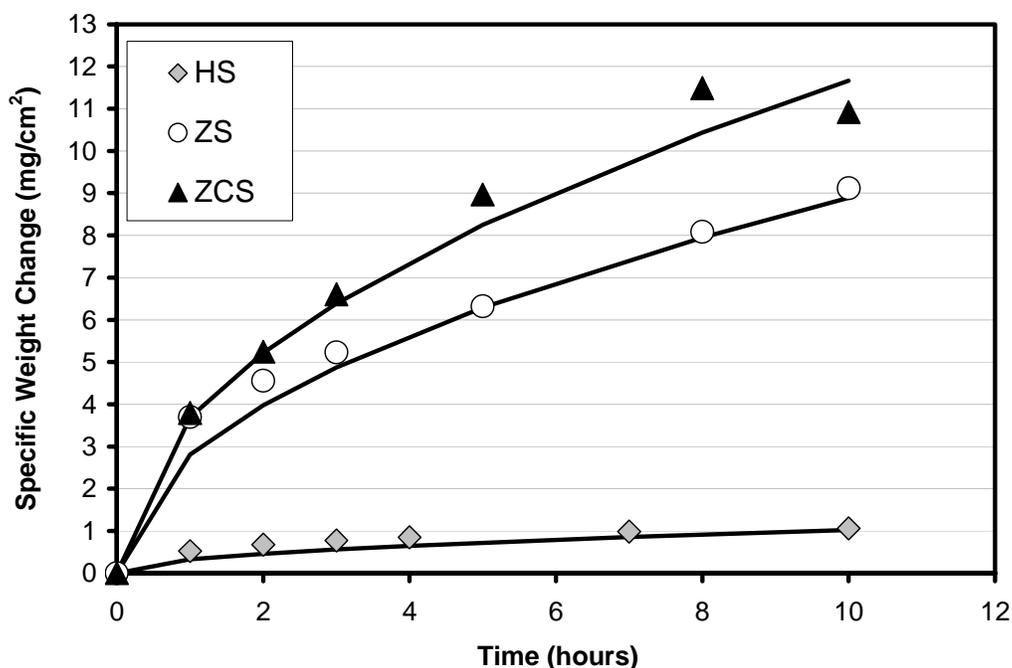


Figure 2. Typical weight change results for UHTCs exposed to 90% water vapor and 10% oxygen cyclic furnace at 1200 °C for 10 hours. Smooth lines represent the parabolic curve fit to the data.

A complete summary of specific weight change data with respect to temperature after 10 hours for all tested materials can be found in Figure 3. The error bars reflect uncertainties in results from two samples for each UHTC and five-six samples for SiC at each temperature. The calculated parabolic oxide growth rates are shown in Table 1. UHTCs parabolic rates were obtained from the slopes of the square of the specific weight change plotted versus time at each temperature. The SiC parabolic oxide growth rates were determined from fits to a paralinear oxidation model, which takes into account the oxide growth and volatility loss [8].

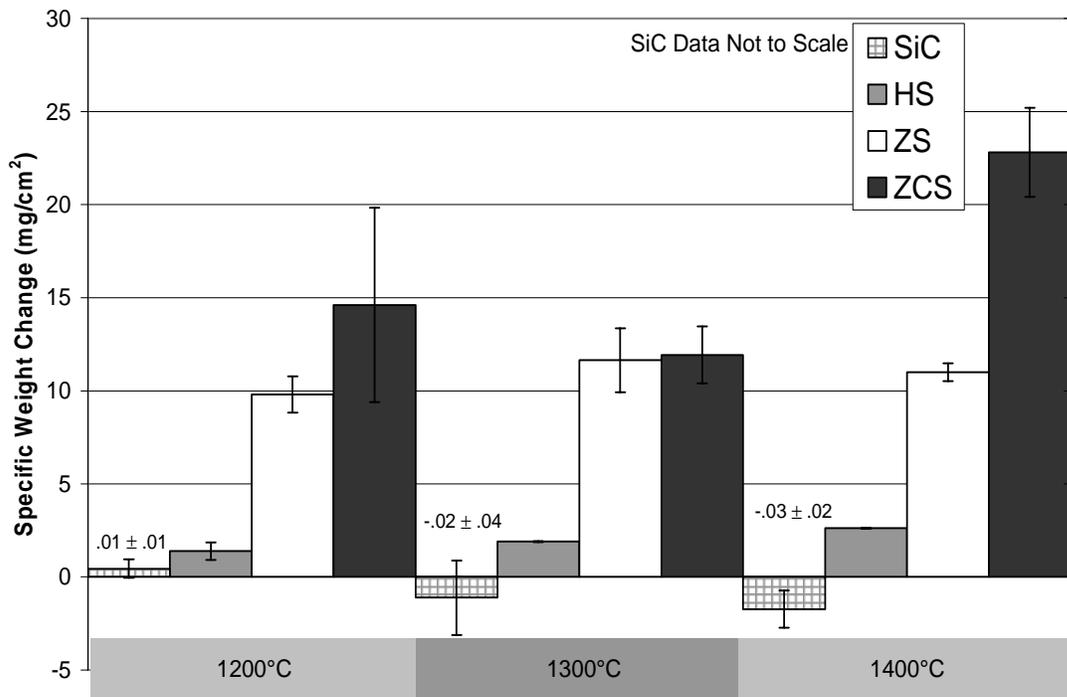


Figure 3. Specific weight change for UHTCs exposed in 90% water vapor and 10% oxygen in a cyclic furnace at 3 temperatures for 10 hours. (Note: SiC not shown on the same scale)

Table 1. Parabolic oxide growth rates ( $\text{mg}^2/\text{cm}^4\text{hr}$ ) for UHTCs exposed in 90% water vapor and 10% oxygen cyclic furnace for 10 hours calculated from the slopes of the square of the specific weight change versus time. SiC results were determined from a fit to the parabolic oxidation model [8].

Sample	1200°C	1300°C	1400°C
HS	$2.90 \times 10^{-1}$	$3.53 \times 10^{-1}$	$6.94 \times 10^{-1}$
HS	$1.05 \times 10^{-1}$	$2.90 \times 10^{-1}$ (11.2 hrs)	$6.56 \times 10^{-1}$
ZS	7.90	15.9	8.92
ZS	10.5	9.89	9.37
ZCS	32.3	16.0	58.5
ZCS	13.6	11.1	42.3
SiC	$7.69 \times 10^{-4}$	$2.62 \times 10^{-3}$	$3.33 \times 10^{-3}$

The oxide formed on the HS material appears visually in tact with minimal physical changes. The ZS material underwent a color change at the 1200 and 1300°C temperatures. Some glass formation is visible at 1300°, followed by a complete glass encapsulated coating at 1400°C. The ZCS oxide formation at all three temperatures changed to a white color in appearance with a non-continuous oxide scale. The scale for this material is visually non-adherent and some limited oxide spalled. X-ray diffraction for HS at 1200 and 1300°C detected HfO<sub>2</sub> as the major scale constituent and HfSiO<sub>4</sub> as a minor constituent. The opposite is seen at 1400°C for HS. ZrO<sub>2</sub> peaks are predominant for the ZS material at all three temperatures. However, at 1200°C, ZrSiO<sub>4</sub> can be seen as a minor constituent. There are no visible ZrSiO<sub>4</sub> peaks at 1300 and 1400°C for this class of UHTCs. Finally, the ZCS series of UHTCs has major peaks for ZrSiO<sub>4</sub> and minor peaks for ZrO<sub>2</sub> at all test temperatures.

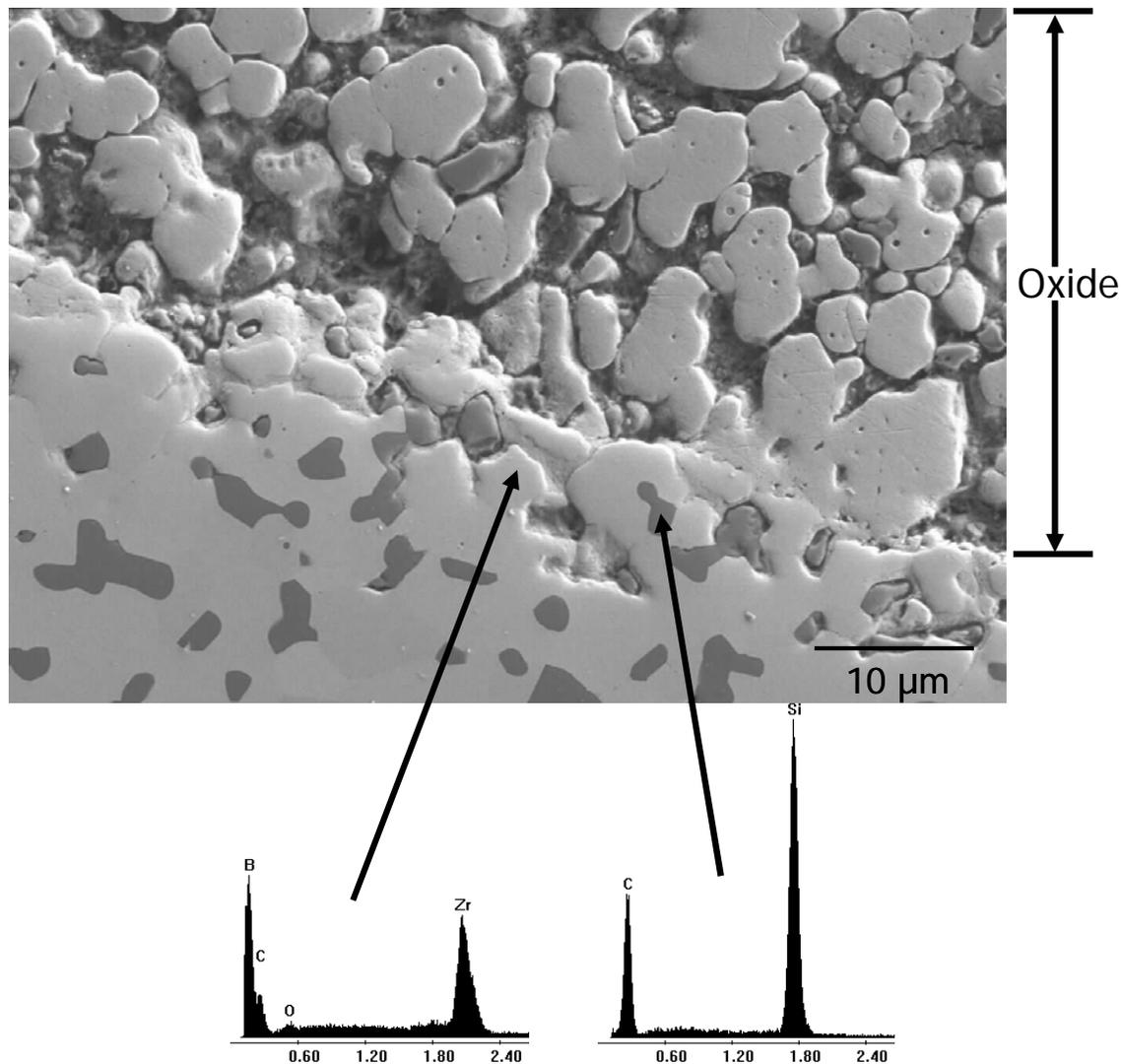
Cross-section FE-SEM analyses were obtained along with EDS results. For all three compositions of UHTCs, there is a differentiation between the oxidized and unoxidized areas of the material which can be clearly seen by FE-SEM as shown in Figure 4. When oxidized hafnium diboride and zirconium diboride with silicon carbide additions are polished, the transition from the unaffected area to the oxide is clearly apparent due to the pullout and edge rounding found in the oxide phase. Evidence of partially oxidized silicon carbide particles remain in the oxidized regions. Boron is readily detected in the unoxidized ZrB<sub>2</sub> or HfB<sub>2</sub> by the EDS detector. However, Mα-zirconium and Kα-boron peaks substantially overlapped at 0.177 and 0.185 keV, respectively. Kα-silicon and Mα-hafnium also suffer from the similar close overlap at 1.740 and 1.645 keV, respectively. These overlaps make it difficult to differentiate boron-containing glass species for the ZS and ZCS material. The hafnium and silicon peak overlap also makes it difficult to identify the presence of hafnium silicate species in the oxide areas. Three areas of phase contrast at the surface of the scale were observed for the oxide layer on HS samples as shown in Figure 5. EDS analysis of the dark phase shows Si and O peaks consistent with SiO<sub>2</sub>. This phase always contained Al, which could have been the result of contamination due to the use of alumina furnace tubes. EDS analysis of the bright phase shows Hf and O peaks consistent with HfO<sub>2</sub>. The medium contrast phase also shows Hf and O peaks by EDS. A shoulder on the Hf peak may indicate the presence of Si which would be consistent with HfSiO<sub>4</sub>. At the highest test temperature of 1400°C, no trace of boron was detectable in the silica. However, at 1200 and 1300°C, silica phases show traces of boron.

EDS of the oxide layer on ZS showed results consistent with zirconia and silica for all test temperatures. Trace amounts of boron was detected in the SiO<sub>2</sub> phase at all temperatures as well. ZCS at 1400°C had no detectable boron peaks. At 1200 and 1300°C, boron traces were found only in the silica phases. Zirconia and silica are apparent through out the oxide scale at all three temperatures.

The ZCS composition tested at 1400°C showed the poorest oxidation behavior of the UHTCs studied in this paper. The recession rate is high and can easily be measured. Recession, Δx, is defined here as:

$$\Delta x = \frac{1}{2}(t_i - t_f)$$

where  $t_i$  is the initial sample thickness and  $t_f$  is the final thickness of the unoxidized portion of the sample after test.



*Figure 4. Typical cross-section for all UHTC materials at the interface area where the oxidized and unoxidized region meets. The sample shown is ZS in 90% water vapor at 1300°C for after 10 hours.*

The ZCS composition showed a 1 mm loss of the original matrix after 10 hours as seen in Figure 6.

Recession measurements were made for all three UHTC compositions oxidized in 90% water vapor at the highest test temperature of 1400°C. These results can be seen in Table 2 and compared to the measured weight change. HS showed the least amount of weight gain 3 mg/cm<sup>2</sup>, while ZCS gained the most weight, 22.8 mg/cm<sup>2</sup>, after ten hours of exposure. Since HS showed the least amount of weight gain at the highest temperature of 1400°C, the furnace exposure time was extended to 26 hours. HS continued to yield the least amount of recession (35μm per side after 26 hours at 1400°C), as compared to that of ZS and ZCS (87 and 535μm per side, respectively, after only 10 hour exposures).

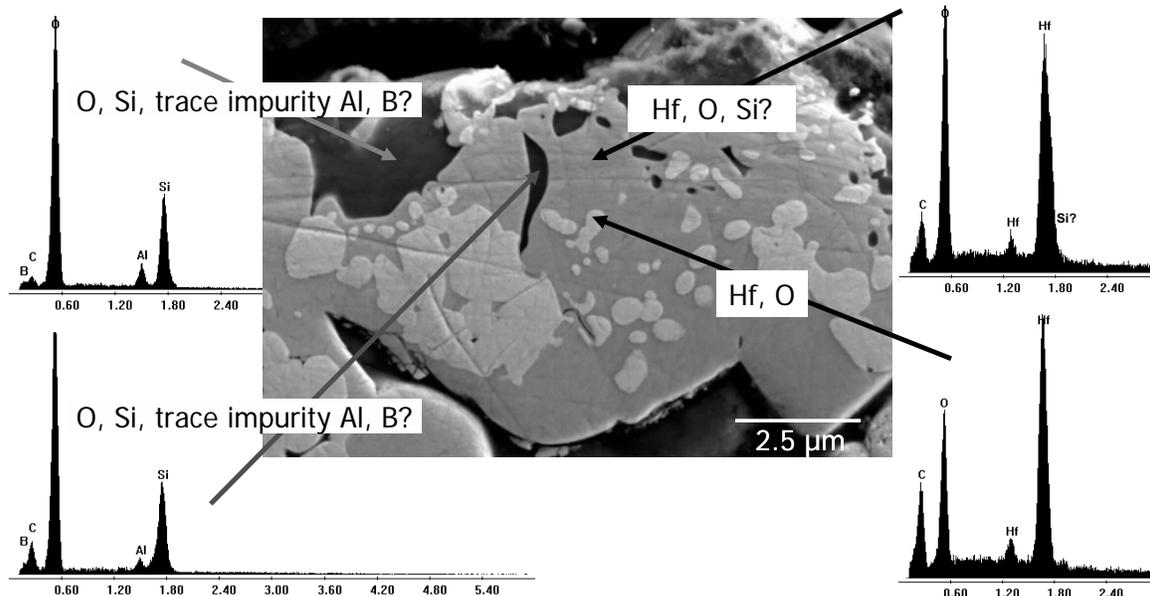


Figure 5. Cross-section FEM and EDS analysis of HS in 90% water vapor at 1300 °C after 10 hours

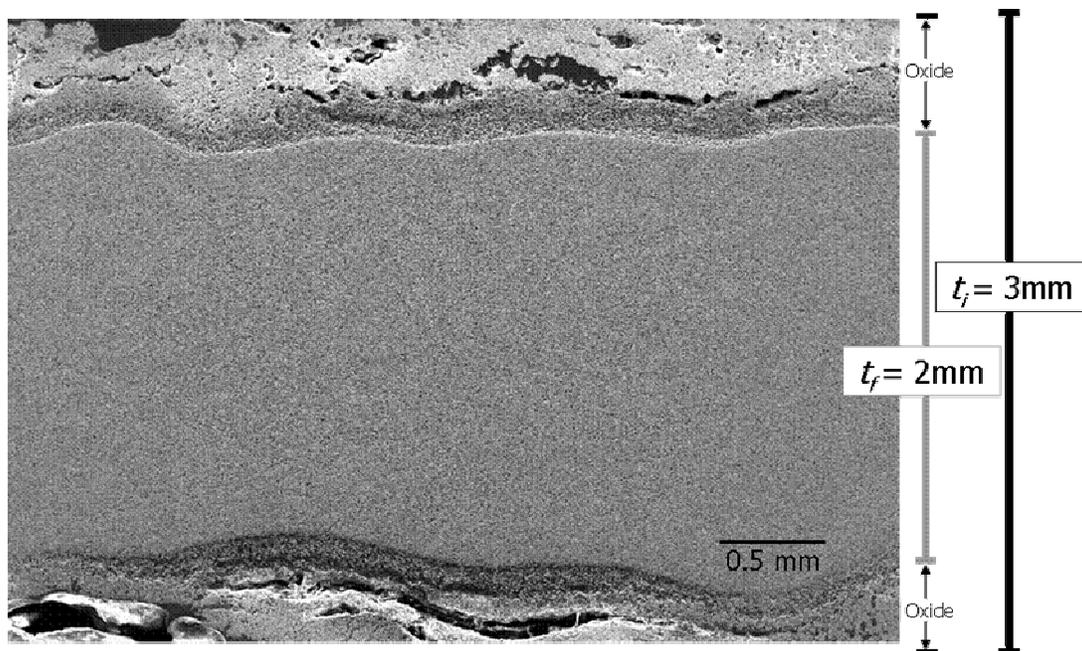


Figure 6. ZCS cross-section recession after exposure in 90% water vapor at 1400 °C for 10 hours. The original sample thickness was 3mm. The 2mm marker indicates the final thickness of the unoxidized portion of the sample.

Table 2. *Recession and weight change after exposure to 90% water vapor and 10% oxygen at 1400 °C for 10 hours*

	<b>Total Recession (<math>\mu\text{m}</math> per side)</b>	<b>Specific Weight Change (<math>\text{mg}/\text{cm}^2</math>)</b>
<b>HS</b>	$35.0 \pm 0.01$ (26 hrs)	3.0
<b>ZS</b>	$86.5 \pm 0.03$	11.0
<b>ZCS</b>	$535.0 \pm 0.10$	22.8

Table 3. *Oxidation comparison for 90% water vapor and 10% oxygen to box furnace tests in stagnant air*

	<b>1300°C in 90% H<sub>2</sub>O (<math>\text{mg}^2\text{cm}^4/\text{h}</math>)</b>	<b>1327°C in Air (<math>\text{mg}^2\text{cm}^4/\text{h}</math>)</b>
<b>HS</b>	0.35	0.48 <sup>[9]</sup>
<b>HS</b>	0.29	----
<b>ZS</b>	16.56	4.94 <sup>[3]</sup>
<b>ZS</b>	10.19	6.29 <sup>[3]</sup>
<b>ZCS</b>	15.40	17.2 <sup>[3]</sup>
<b>ZCS</b>	11.03	----

Results obtained for UHTCs oxidized in a box furnace in stagnant air are reported in Table 3. These results have been previously reported by Levine et al. [3] for ZS and ZCS compositions. The HS result has not yet been published [9]. There is no significant difference between the oxidation rates in low velocity water vapor and air.

Results of the 90% water vapor samples were also compared to tests ran in the HPBR. Figure 7 visually shows all three UHTC compositions after 50 hours exposure in the HPBR at 1300°C. The oxide scales found on these materials are not uniform or consistently adherent. The HS sample turned primarily white in most areas. Both ZS and ZCS scales were flaky and brittle to the touch. The ZS material had glass-like blisters and the ZCS material was most fragile and susceptible to flaking by routine handling. Weight change results for UHTCs and SiC exposed in the HPBR can be found in Figure 8. The UHTCs were tested at 1100 and 1300°C. Results for SiC tested at 1315°C are also plotted on the same chart for comparison of weight change versus time after 50 hours. At 1100°C, only ZS and ZCS were evaluated. At this temperature the ZS composition had 1% to weight loss after 50 hours performed better than ZCS. At 1300°C, all three compositions of UHTCs were evaluated and can be compared to SiC at 1315°C in 5 atm. At this temperature there is no significant difference between the ZS and the ZCS compositions. They both show the typical parabolic weight loss of approximately 225 mg/cm<sup>2</sup>, which results in 42% weight loss after 50 hours. HS is the most oxidation resistant of the three UHTCs compositions evaluated in the HPBR. HS shows a weight loss of 3% after 50 hours. This is consistent with results obtained in both furnace studies previously discussed. SiC weight loss is 0.4% after 52 hours of exposure time. Specific weight change data and total recession rate measurement for HPBR samples are summarized in Table 4. While the water vapor partial pressure in the HPBR is slightly less than the furnace (0.6 atm vs. 0.9 atm respectively), the gas velocity is almost three orders of magnitude higher. This high gas velocity must therefore be responsible for the differences in oxidation behavior observed between the furnace test and the HPBR. The high gas velocity can increase both silica volatility and oxide spallation. It has been shown that SiO<sub>2</sub> volatility in the HPBR is proportional to the square root of the gas velocity [10]. Comparison of the results for SiC in the HPBR to those for UHTCs, show that the weight loss rate is much higher than observed for silica volatilization alone. However volatilization of the silica on the UHTCs may contribute to the fast spallation of the underlying HfO<sub>2</sub> and ZrO<sub>2</sub>. The micrographs in Figures 4 and 5 show that the (HfO<sub>2</sub> and ZrO<sub>2</sub>) particles are surrounded by a continuous silica rich phase. If this continuous phase is removed by a volatilization process the HfO<sub>2</sub>/ZrO<sub>2</sub> phase would become non-adherent and spall. It is therefore not possible to separate volatilization/spallation effects in the HPBR exposures. It should be emphasized that the intent of this study is to evaluate the oxidation resistance of UHTCs in combustion environments. Whether the observed weight loss is due to volatility or spallation, the low durability of these materials in the HPBR demonstrates the unsuitability of these materials for propulsion applications.

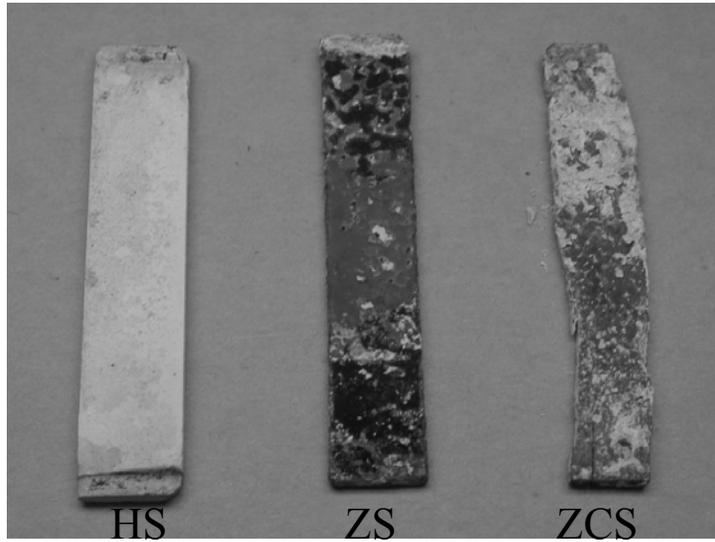


Figure 7. HPBR macrograph of UHTC at 1300°C after 50 hours at 6 atm

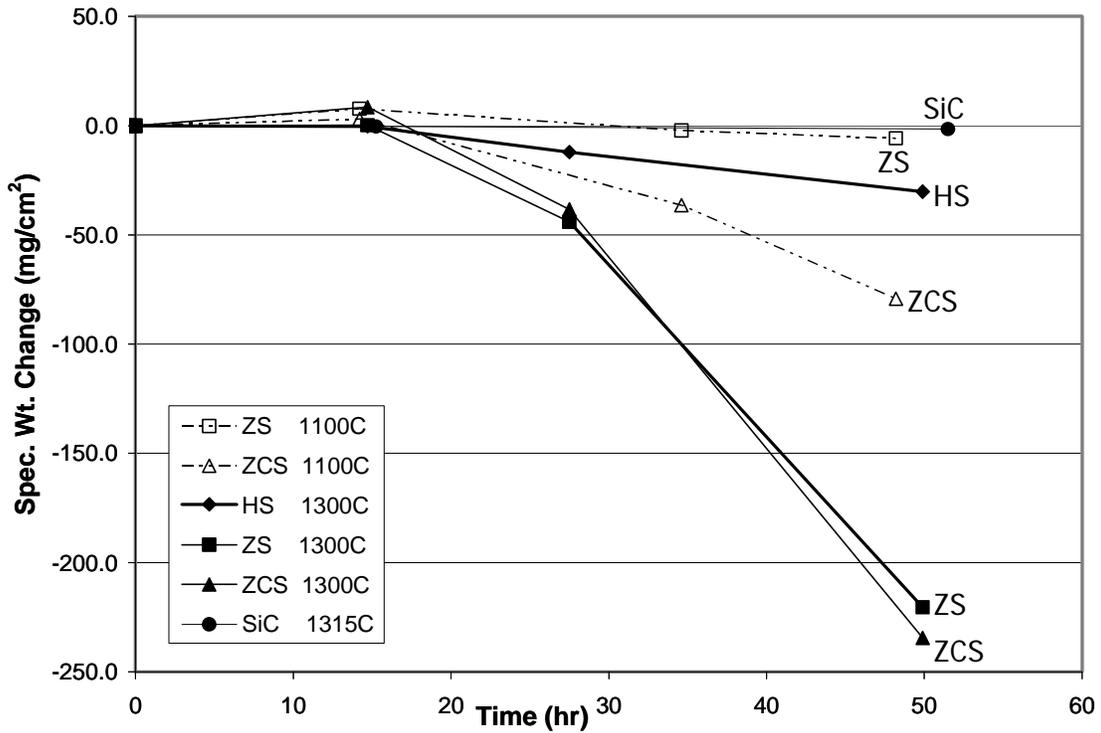


Figure 8. HPBR specific weight change for UHTCs at 6 and SiC at 5 atm

Table 4. HPBR weight change and recession measurements for UHTCs at 6 atm

	HPBR Specific Weight Change (mg/cm <sup>2</sup> )		HPBR Total Recession (µm per side)	
	1100°C 48h	1300°C 50h	1100°C 48h	1300°C 50h
<b>HS</b>	+2.2	-30.2	----	145 ± 18
<b>ZS</b>	-6.1	-220.5	178 ± 14	635 ± 63
<b>ZCS</b>	-79.3	-234.5	469 ± 8	645 ± 51

## CONCLUSION

The environmental durability of three compositions of UHTCs was evaluated for potential use in propulsion applications. These materials were exposed to a 90% water vapor and 10% oxygen environment at temperatures of 1200, 1300 and 1400°C at 1 atm. The results were compared with tests conducted in a stagnant air furnace and with HPBR results. Low velocity water vapor does not have a significant effect on the oxidation rates as compared to stagnant air. Gas velocity is an important contributor to volatility, spallation and accelerated recession of UHTC materials. These UHTC materials are inappropriate for long term aer propulsion applications because of rapid oxidation and material recession rates in combustion environments.

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<b>13. ABSTRACT</b> ( <i>Maximum 200 words</i> )  Ultra High Temperature Ceramics (UHTCs) including $\text{HfB}_2 + 20\% \text{SiC}$ ( <b>HS</b> ), $\text{ZrB}_2 + 20\% \text{SiC}$ ( <b>ZS</b> ), and $\text{ZrB}_2 + 30\% \text{C} + 14\% \text{SiC}$ ( <b>ZCS</b> ) have been investigated for use as potential aer propulsion engine materials. These materials were oxidized in water vapor (90 percent) using a cyclic vertical furnace at 1 atm. The total exposure time was 10 h at temperatures of 1200, 1300, and 1400 °C. CVD SiC was also evaluated as a baseline for comparison. Weight change, X-ray diffraction analyses, surface and cross-sectional SEM and EDS were performed. These results are compared with tests ran in a stagnant air furnace at temperatures of 1327 °C for 100 min, and with high pressure burner rig (HPBR) results at 1100 and 1300 °C at 6 atm for 50 h. Low velocity water vapor does not make a significant contribution to the oxidation rates of UHTCs when compared to stagnant air. The parabolic rate constants at 1300 °C, range from 0.29 to 16.0 $\text{mg}^2\text{cm}^4/\text{h}$ for HS and ZCS, respectively, with ZS results between these two values. Comparison of results for UHTCs tested in the furnace in 90 percent water vapor with HPBR results was difficult due to significant sample loss caused by spallation in the increased velocity of the HPBR. Total recession measurements are also reported for the two test environments.			
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