OXIDATION OF ULTRA-HIGH TEMPERATURE CERAMICS IN WATER VAPOR

QuynhGiao N. Nguyen†, Elizabeth J. Opila*, and Raymond C. Robinson&

†NASA Glenn Research Center, Cleveland, OH 44135
*Cleveland State University, Cleveland, OH 44115
&QSS Group Inc., Cleveland, OH 44135

Ultra high temperature ceramics (UHTCs) including HfB_2 + SiC (20% by volume), ZrB_2 + SiC (20% by volume) and ZrB_2 + SiC (14% by volume) + C (30% by volume) have historically been evaluated as reusable thermal protection systems for hypersonic vehicles [1]. This study investigates UHTCs for use as potential combustion and aeropropulsion engine materials. These materials were oxidized in water vapor (90%) using a cyclic vertical furnace at 1atm. The total exposure time was 10 hours at temperatures of 1200, 1300, and 1400°C. CVD SiC was also evaluated as a baseline comparison. Weight change measurements, X-ray diffraction analyses, surface and cross-sectional SEM and EDS were performed. These results will be compared with tests ran in static air at temperatures of 1327, 1627, and 1927°C [2]. Oxidation comparisons will also be made to the study by Tripp [3]. A small number of high pressure burner rig (HPBR) results at 1100 and 1300°C will also be discussed.

Specific weight changes at all three temperatures along with the SiC results are shown in Figure 1. SiC weight change is negligible at such short duration times. HfB_2 + SiC (HS) performed the best out of all the tested UHTCS for all exposure temperatures. ZrB_2 + SiC (ZS) results indicate a slightly lower oxidation rate than that of ZrB_2 + SiC + C (ZCS) at 1200 and 1400°C, but a clear distinction can not be made based on the limited number of tested samples.

Scanning electron micrographs of the cross-sections of all the UHTCs were evaluated. Figure 2 is a representative area for HS at 1400°C for 26 hours, which was the composition with the least amount of oxidation. A continuous SiO_2 scale is present in the outer most edge of the surface. Figure 3 is an image of ZCS at 1400°C for 10 hours, which shows the most degradation of all the compositions studied. Here, the oxide surface is a mixture of $ZrSiO_4$, ZrO_2 and SiO_2.

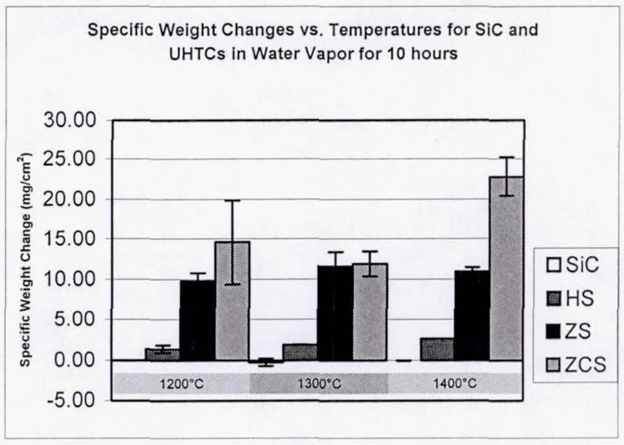


Figure 1. Sample weight change for UHTCs and SiC

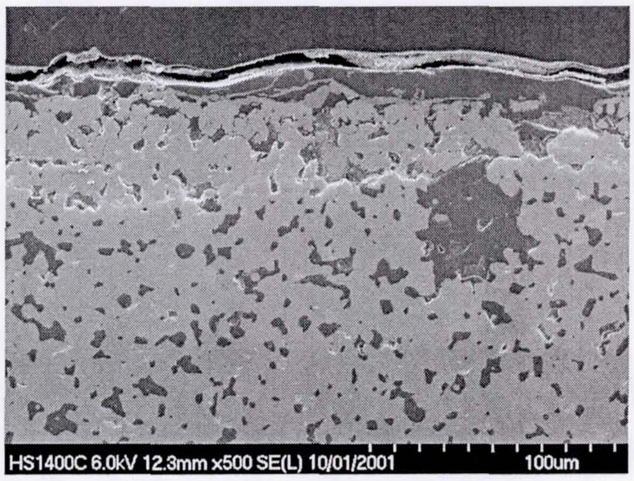


Figure 2. Cross-section image of HS at 1400°C for 26 hours

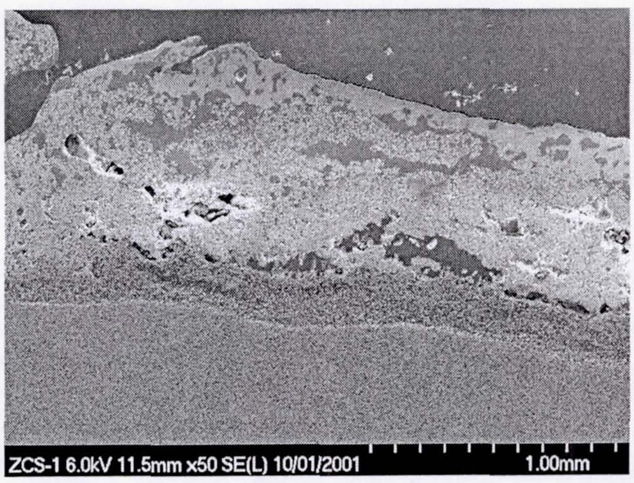


Figure 3. Cross-section image of ZCS at 1400°C for 10 hours

References

1. J.D. Bull, D. J. Rasky, and J. C. Karika, "Stability Characterization of Diboride Composites under High Velocity Atmospheric Flight Conditions," 24th International SAMPE Technical Conference, p. T1092 (1992).

2. S.R. Levine, E.J. Opila, M.C. Halbig, J.D. Kiser, M. Singh, and J.A. Salem, "Evaluation of Ultra-High Temperature Ceramics for Aeropropulsion Use," J. European Cer. Soc., **22**, 2757 (2002).

3. W.C. Tripp, H.H. Davis, and H.C. Graham, "Effect of SiC Addition on the Oxidation of ZrB_2," Cer. Bull., **52**, 8, 612 (1973).

Oxidation of Ultra-High Temperature Ceramics in Water Vapor

QuynhGiao N. Nguyen
Elizabeth J. Opila* and Raymond C. Robinson&
Environmental Durability Branch, NASA Glenn Research Center
Cleveland, Ohio USA

Electrochemical Society Meeting – Paris, France
April 27 – May 2, 2003

*Cleveland State University, Ohio
&QSS Group Inc. – Cleveland, Ohio

Acknowledgements

GLENN RESEARCH CENTER

The Authors Express Their Gratitude to:

Terry R. McCue for Field Emission Microscopy

Ralph G. Garlick for X-ray Diffraction Analyses

Kang N. Lee for Preliminary Vertical Cyclic Furnace Set-Up

James L. Smialek for Technical Discussions

NASA Ultra-Efficient Engine Technology (UEET) Program Office for Funding this Research

NASA Ames Research Center for Providing the UHTC Materials

GLENN RESEARCH CENTER

Outline

- Background and Objective
- Materials and Testing Conditions
- Parabolic Oxidation Rates & X-ray Diffraction Results
- Macro, Micrographs, and Energy Dispersive Spectroscopy (EDS)
- Results of Box Furnace Test (Air) and Parabolic Rate Constants
- Results of High Pressure Burner Rig (HPBR) Results for Weight Changes and Recession Measurements
- Summary/Conclusions

Background

Ultra-High Temperature Ceramics (**UHTCs**)

- Refractory Metal Borides and Carbides –limited by the Melting Point of the Oxide Scale

- High Melting Points (°C)

HfB_2	3100
ZrB_2	3040
SiC	2100

- Oxide Melting Points (°C)

HfO_2	2800
ZrO_2	2700
SiO_2	1730

Possible Applications for UHTCs

- Thermal Protection Systems for Hypersonic Vehicles

Re-entry Conditions:
- **high temperature (to 1727°C) and velocity**
- **low pressures (.005 - .010 atm)**
- **short times (~15 minutes/re-entry)**
- **O_2 and N_2, (shock leads to O, N, ions)**

- Structural Components or Coatings for Aeropropulsion Applications

Combustion Conditions:
- **high temperature (900 – 1500°C) and velocity**
- **high pressures (10 – 100 atm)**
- **long times (1000s hours)**
- **hydrocarbon fuels, exhaust (N_2, O_2, CO_x and H_2O)**

Background

SiC Containing UHTCs Rely on the Formation of a Protective SiO_2 Layer to Increase Oxidation Resistance.

1200 – 1400°C

$$SiO_2(s) + 2H_2O(g) \longrightarrow Si(OH)_4(g)$$

$$B_2O_3(l) + H_2O(g) \longrightarrow 2\,BO_2H(g)$$

GLENN RESEARCH CENTER

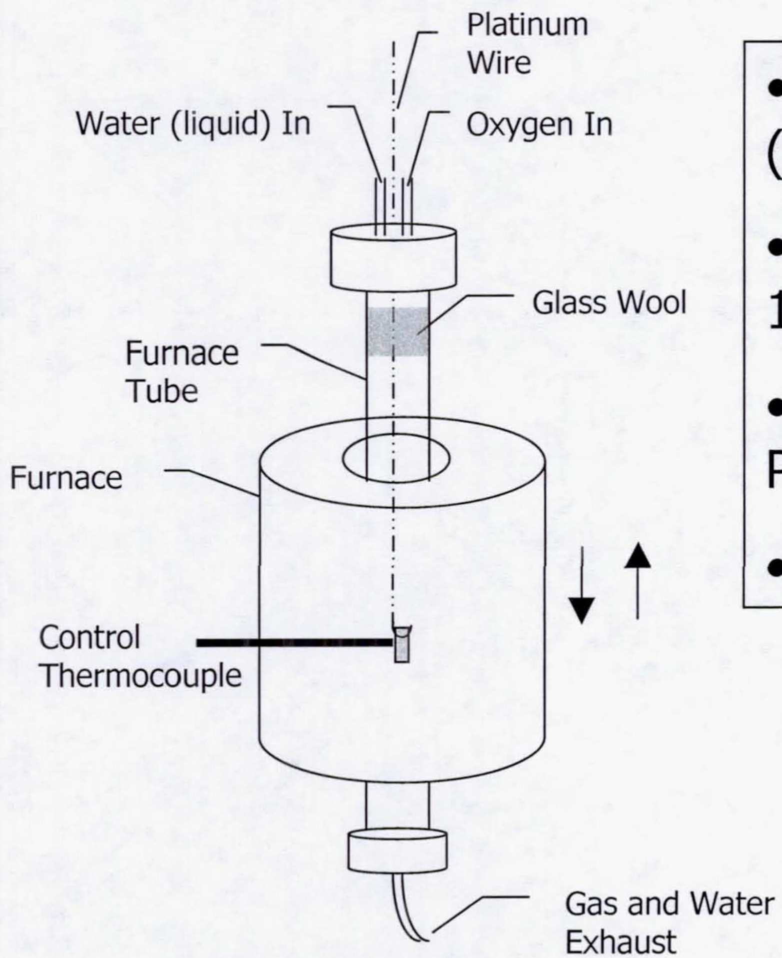
Objective

Evaluate UHTCs (containing 13-20%v SiC) in Model Combustion Environment and see if Water Vapor has a Major Role/Difference in Oxidation as Compared to Stagnant Air

Materials and Test Conditions

- Materials Compositions:
  HS (HfB_2 + 20%v SiC)
  ZS (ZrB_2 + 20%v SiC)
  ZCS (ZrB_2 + 30%v C + 14%v SiC)
- Hot Pressed Billets - Manufactured by Materials & Machine, Machined at Alabama Specialty Products, Inc.
- Sample Size: 2.54 x 1.28 x 0.32 cm & (0.32 cm hole)
- Testing Conditions: Cyclic Furnace
  - vertical furnace tube
  - 90% H_2O and 10% O_2
  - 1 atm
  - 1200, 1300, and 1400°C.
  - 10 hrs (26 hr max)
- CVD SiC was used in each test as a control

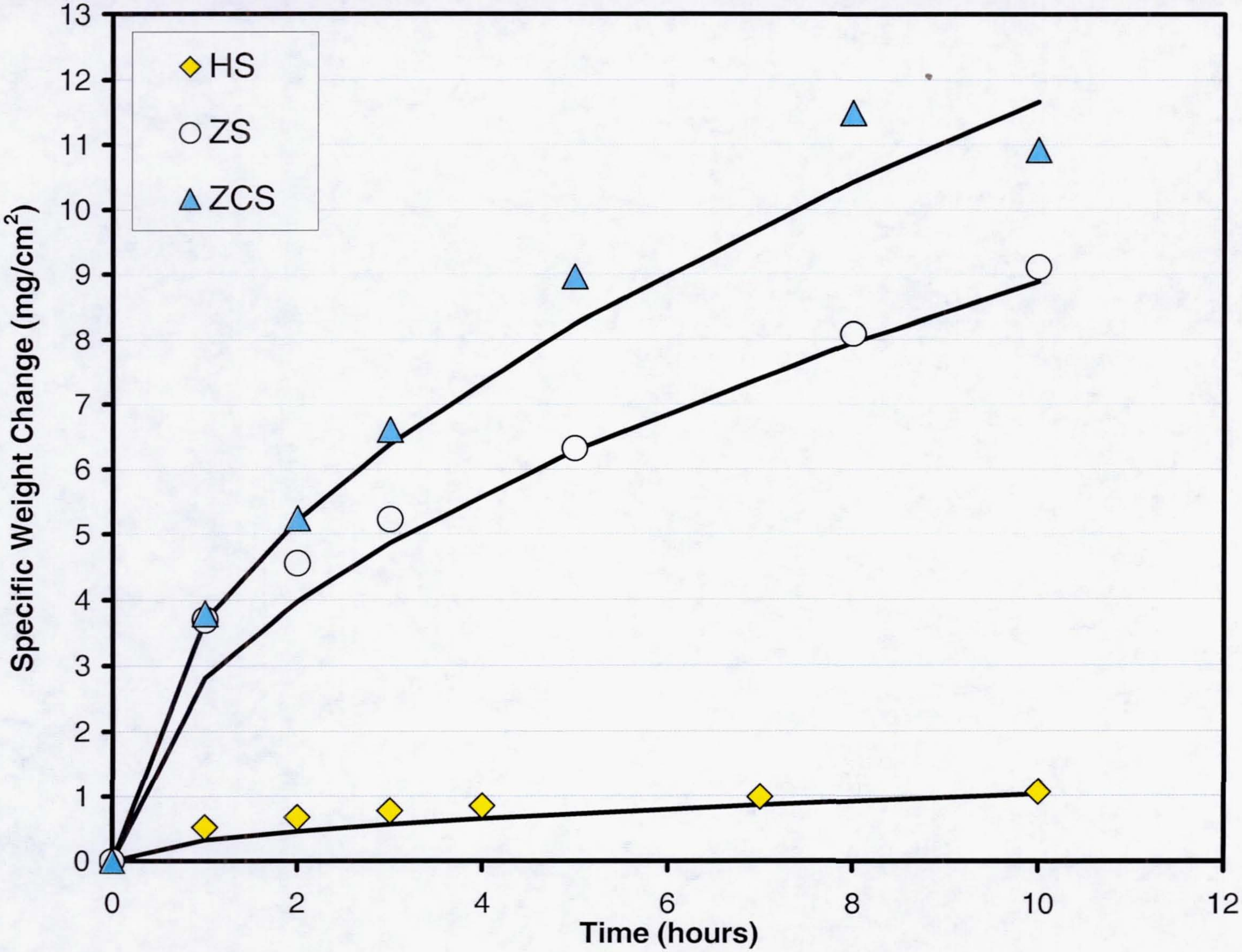
Furnace Schematic



- 90% H_2O and 10% O_2 Cyclic Furnace Test (1-hr cycles), 1 atm
- Total Linear Gas Flow Velocity = 128cm/min
- Alumina Furnace Tube, $MoSi_2$ Elements, Platinum Hanger
- Hot Zone = 5 cm

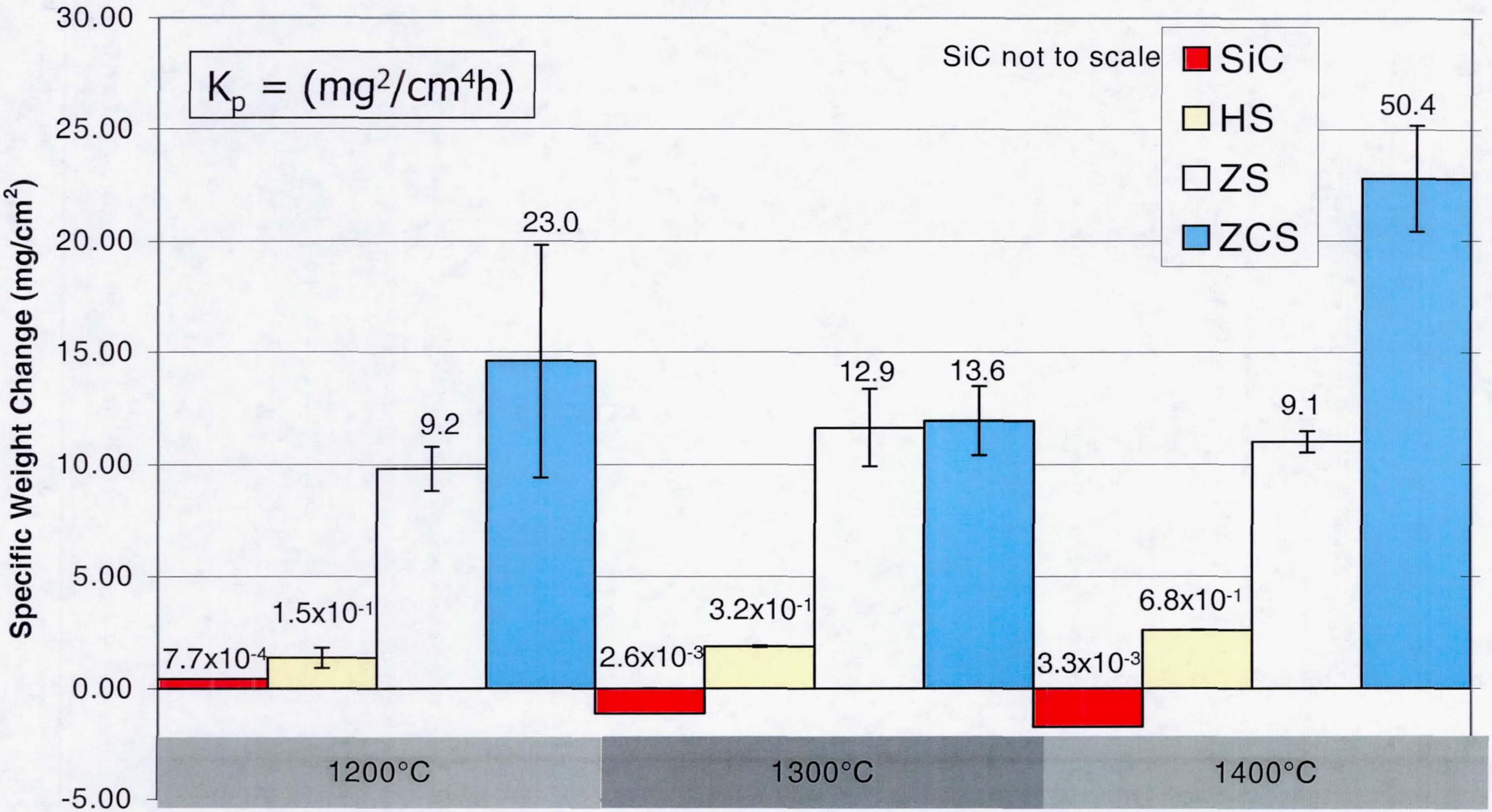
Typical Specific Weight Change in 90% Water Vapor at 1200°C

GLENN RESEARCH CENTER



GLENN RESEARCH CENTER

Complete Specific Weight Change in 90% Water Vapor, 10 hrs



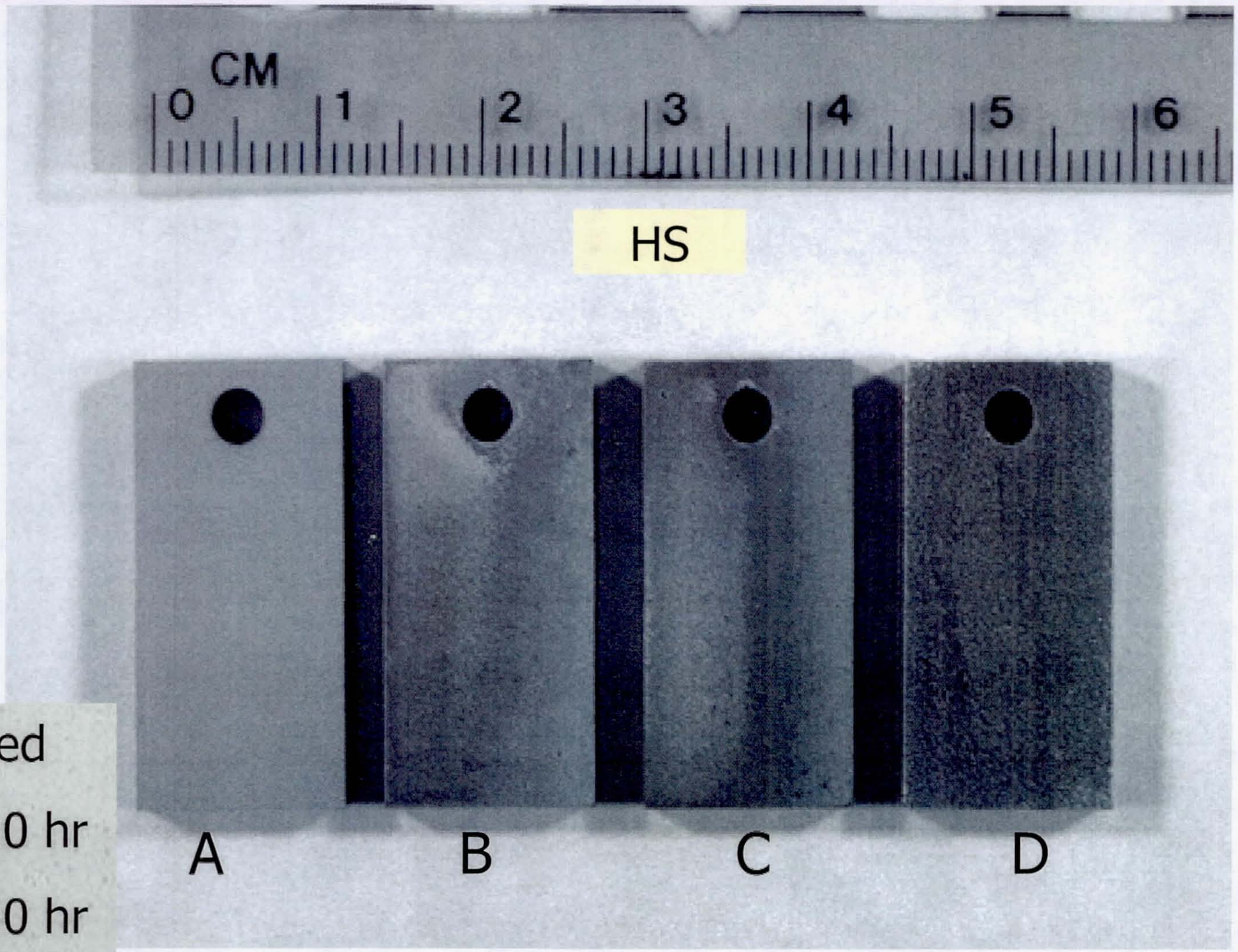
X-Ray Diffraction Results at 10hrs in 90% Water Vapor

90% H_2O and 10% O_2, Cyclic Furnace (1-hr cycles)

	HfB_2/SiC		ZrB_2/SiC		$ZrB_2/C/SiC$	
	Major	Minor	Major	Minor	Major	Minor
1200°C	HfO_2	$HfSiO_4$	ZrO_2	$ZrSiO_4$	$ZrSiO_4$	ZrO_2
1300°C	HfO_2	$HfSiO_4$	ZrO_2	-----	$ZrSiO_4$	ZrO_2
1400°C	$HfSiO_4$	HfO_2	ZrO_2	-----	$ZrSiO_4$	ZrO_2

GLENN RESEARCH CENTER

HS Macrographs in 90% Water Vapor



A: As Received

B: 1200°C, 10 hr

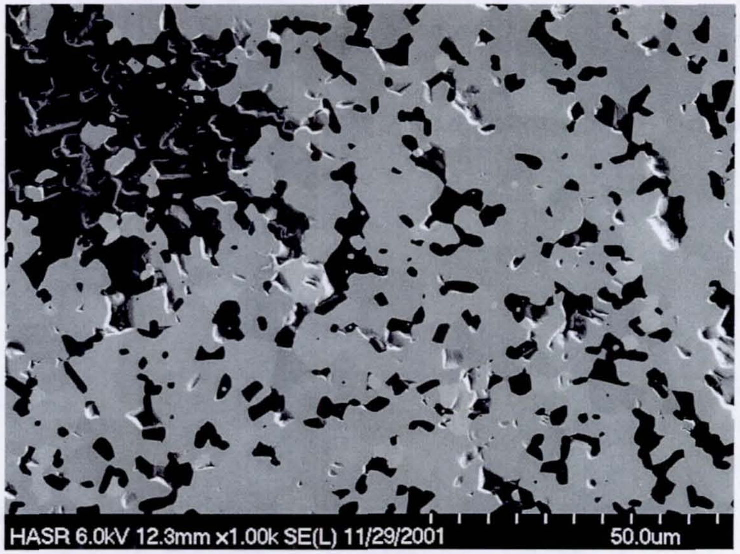
C: 1300°C, 10 hr

D: 1400°C, 26 hr

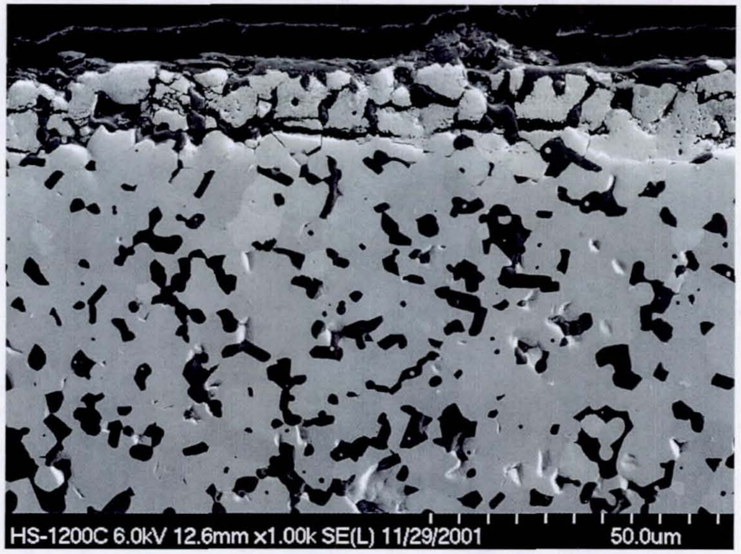
HS SEM Cross-Section in 90% Water Vapor

GLENN RESEARCH CENTER

As Received



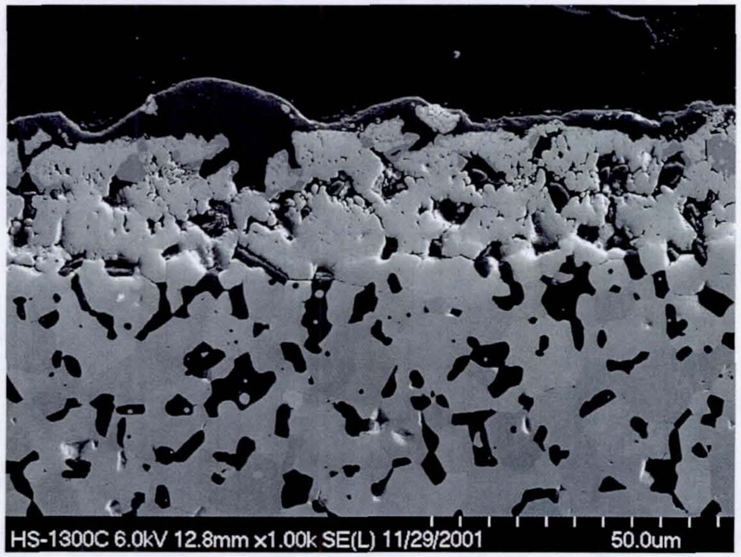
1200°C
10 hrs



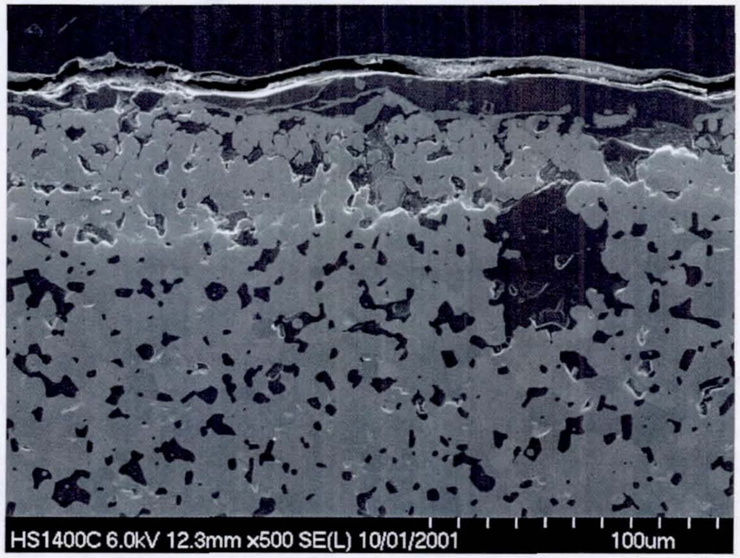
— 10 μm

1300°C
10 hrs

10 μm —



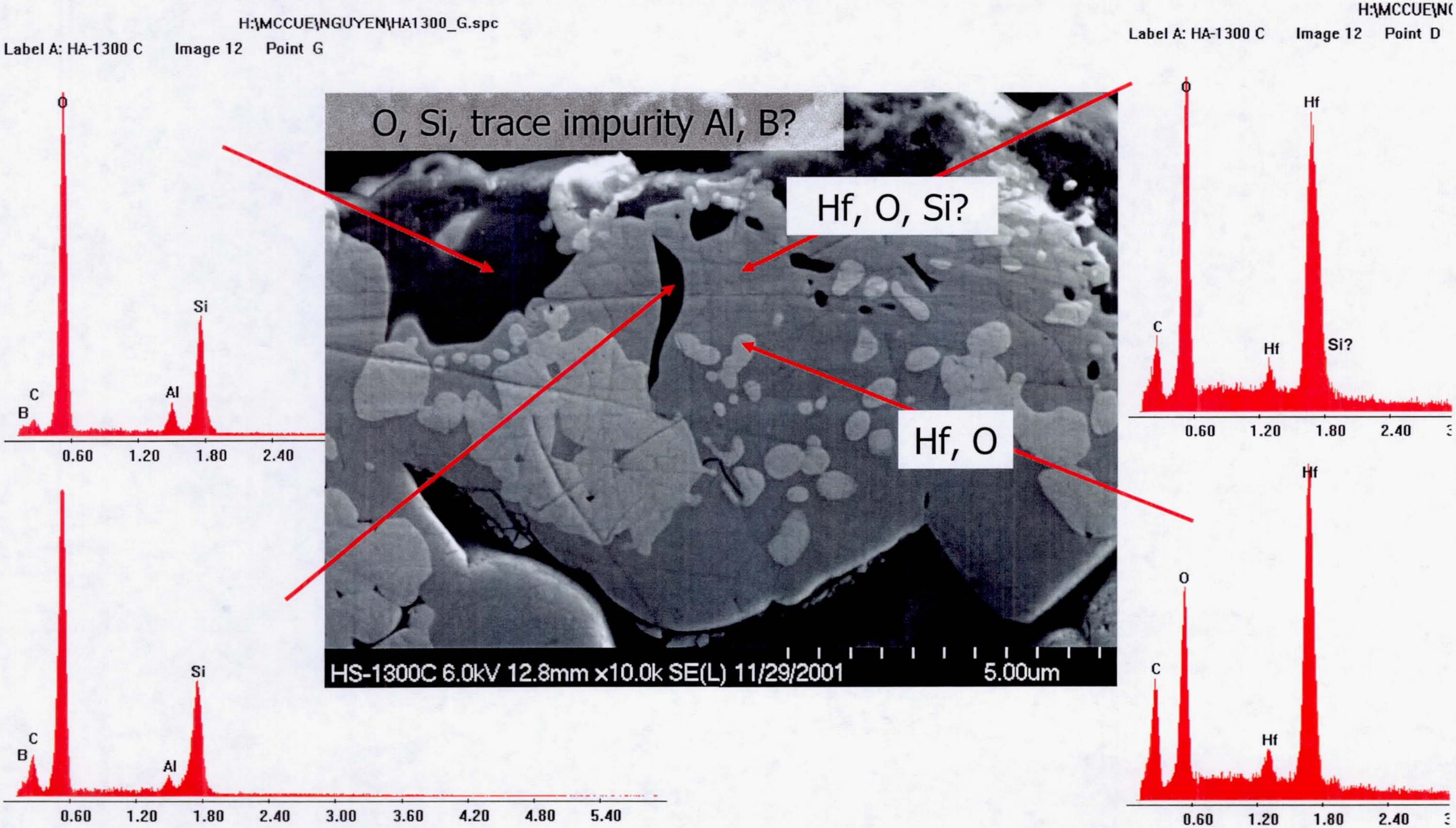
1400°C
24 hrs



— 20 μm

HS EDS Cross-Section at 1300°C in 90% Water Vapor at Edge

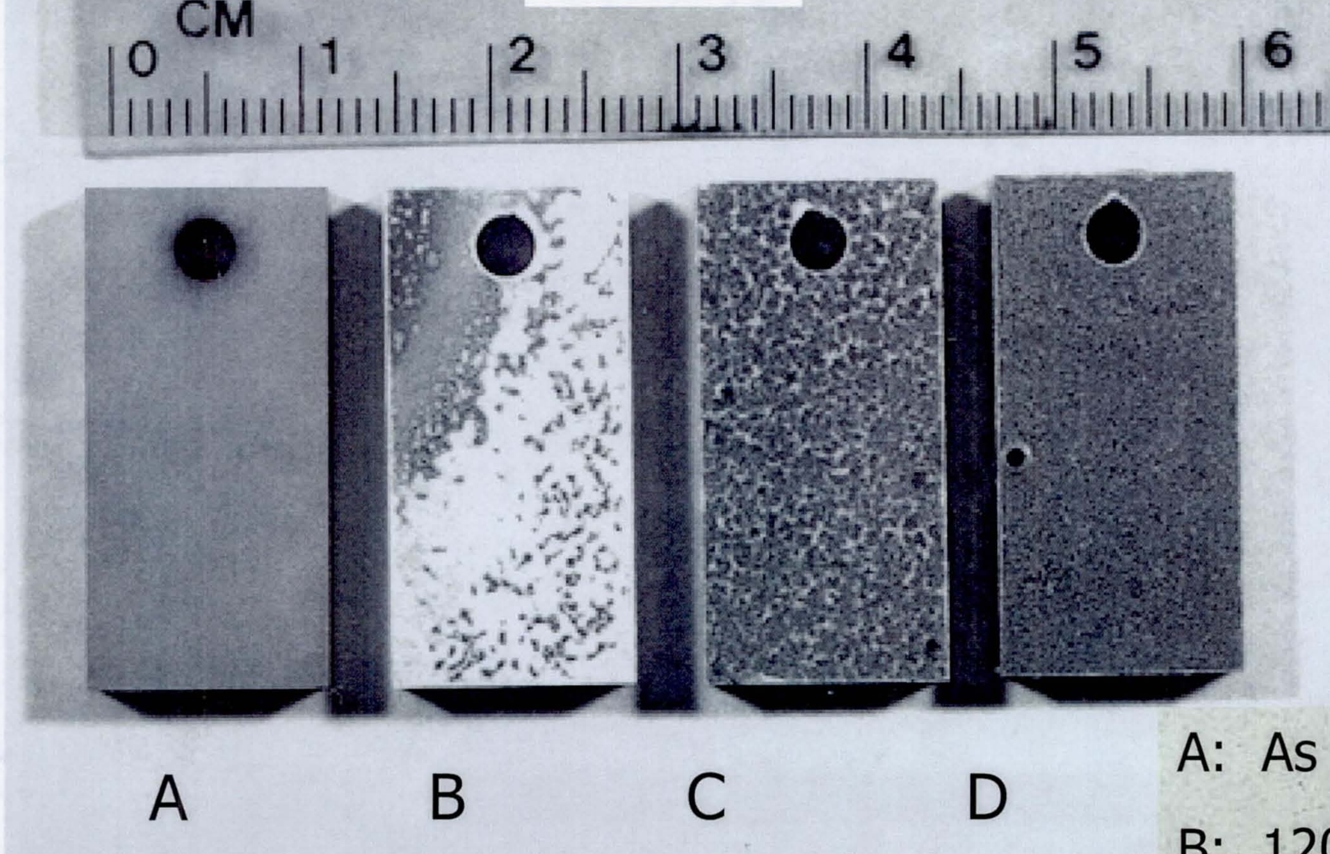
GLENN RESEARCH CENTER



GLENN RESEARCH CENTER

ZS Macrographs in 90% Water Vapor

ZS



A: As Received

B: 1200°C, 10 hr

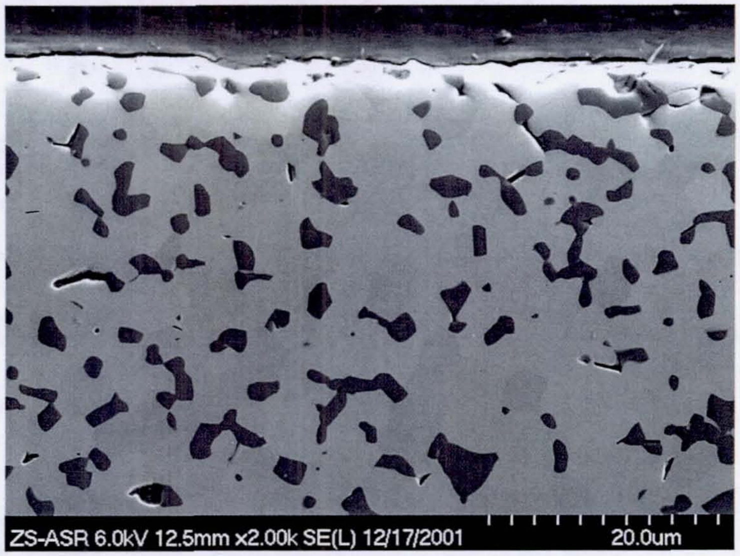
C: 1300°C, 10 hr

D: 1400°C, 10 hr

GLENN RESEARCH CENTER

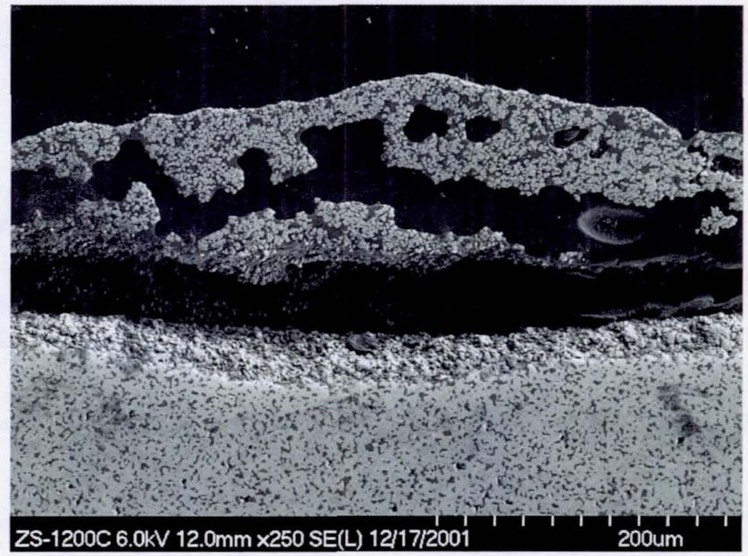
ZS SEM Cross-Section in 90% Water Vapor after 10 hrs

As Received



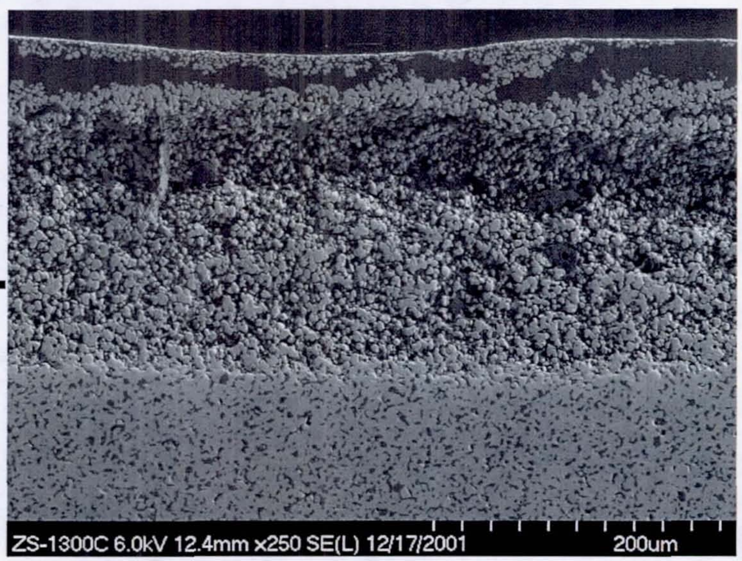
1200°C

40 µm



1300°C

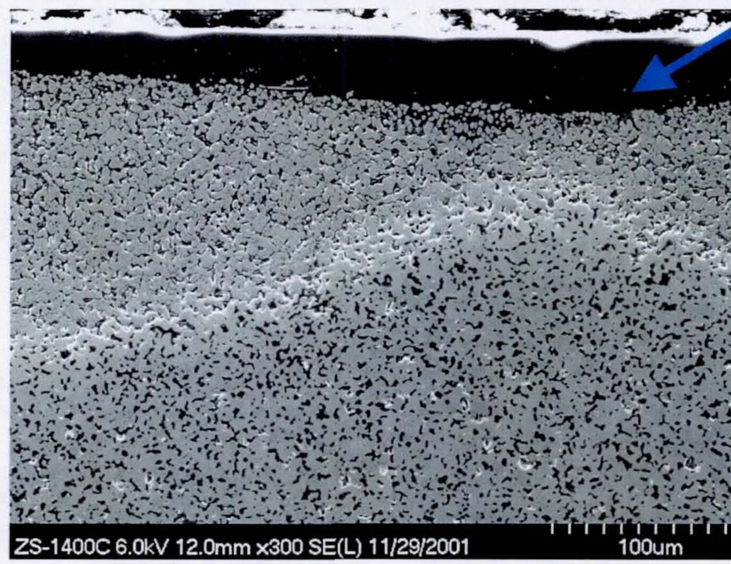
40 µm



SiO_2

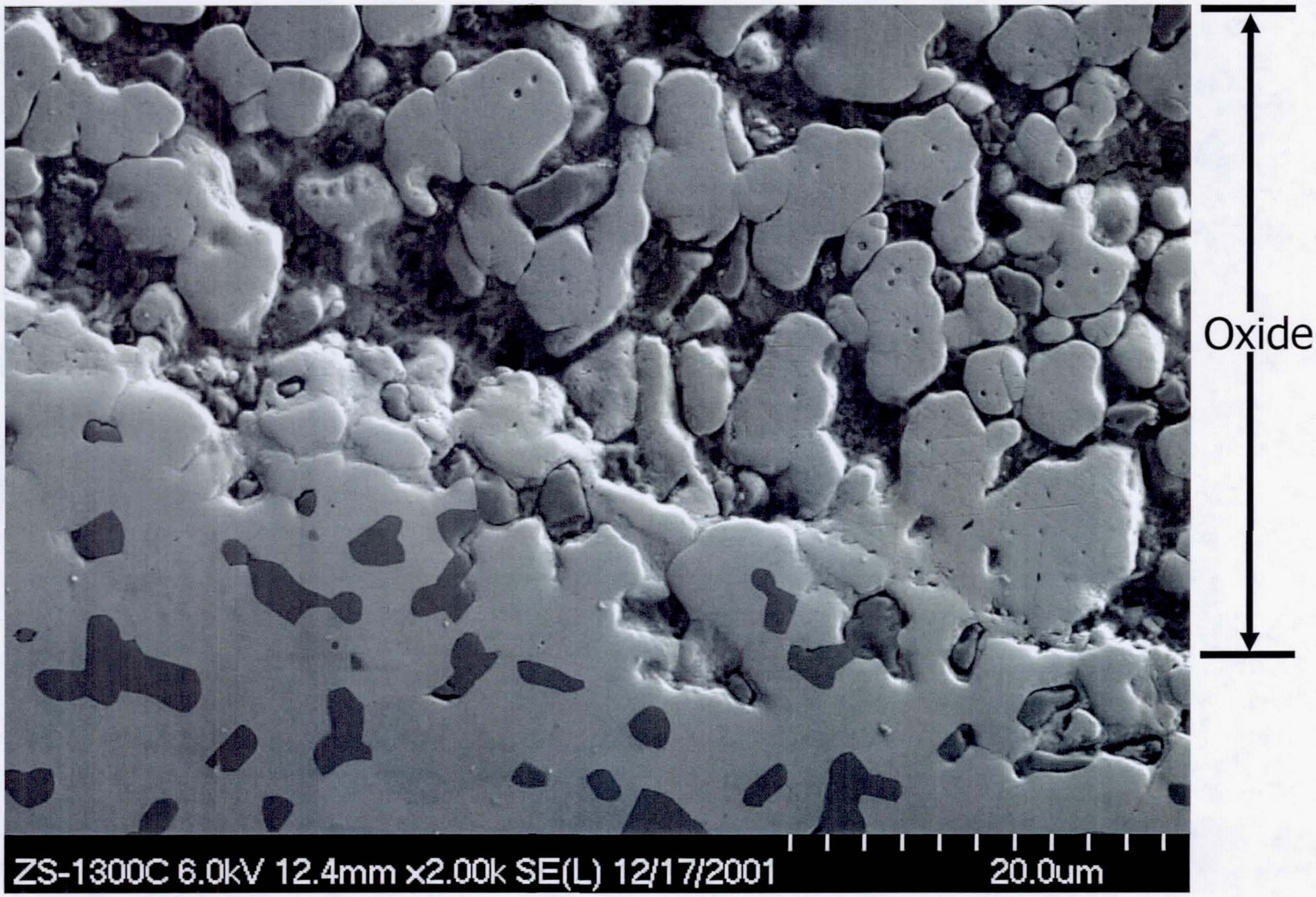
1400°C

40 µm



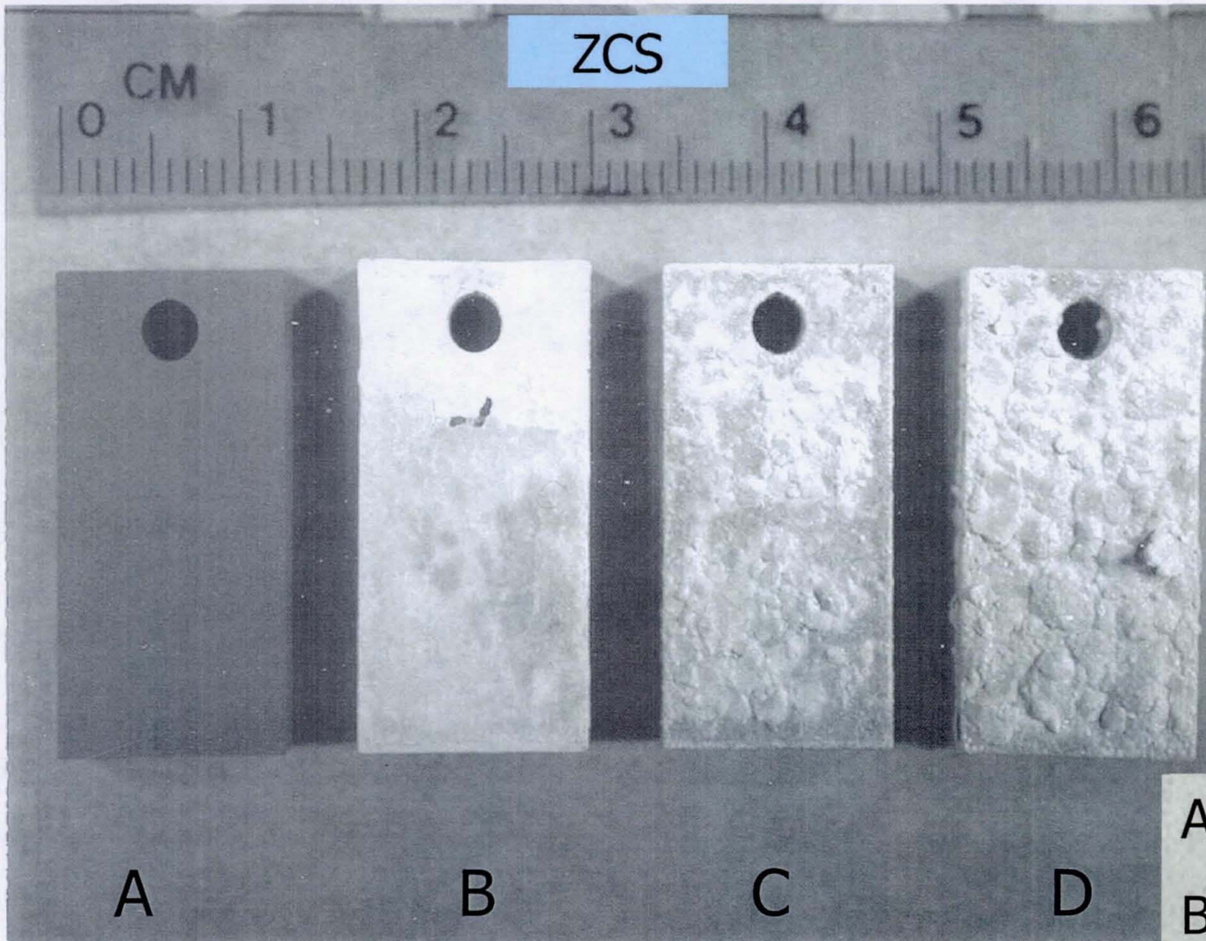
ZS Cross-Section at 1300°C in 90% Water Vapor

GLENN RESEARCH CENTER



ZCS Macrographs in 90% Water Vapor

GLENN RESEARCH CENTER



A: As Received

B: 1200°C, 10 hr

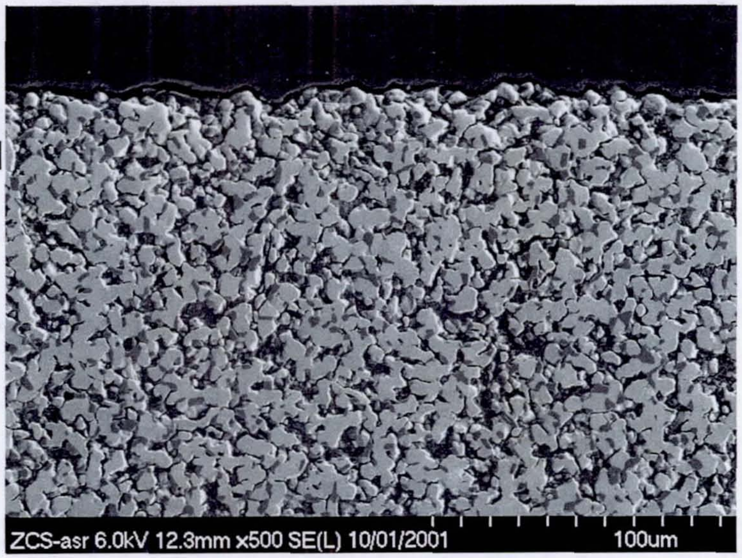
C: 1300°C, 10 hr

D: 1400°C, 10 hr

Cross-Section SEM ZCS in 90% Water Vapor after 10 hrs

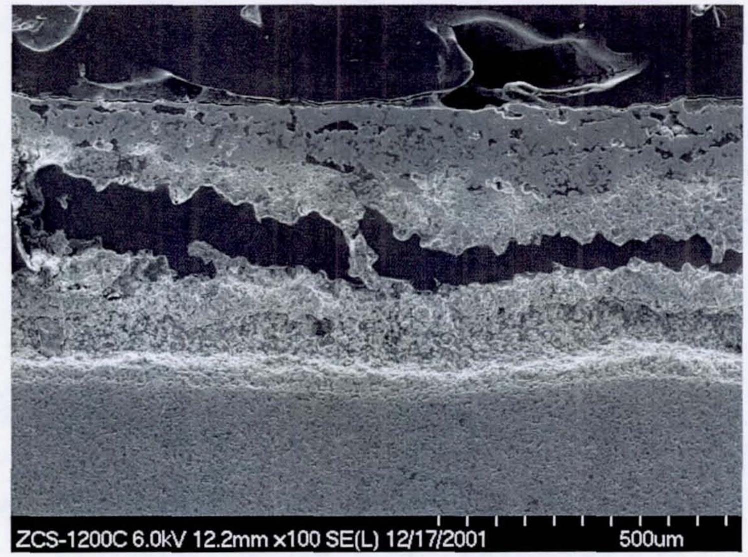
GLENN RESEARCH CENTER

As Received



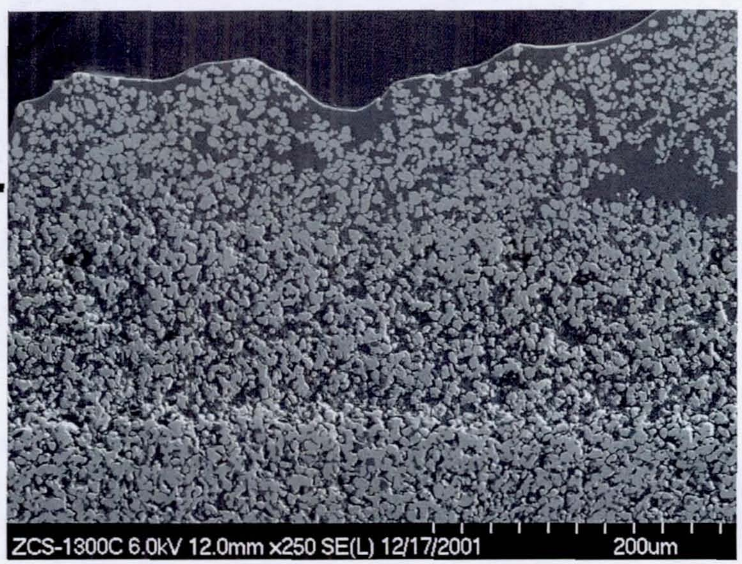
1200°C

100 μm



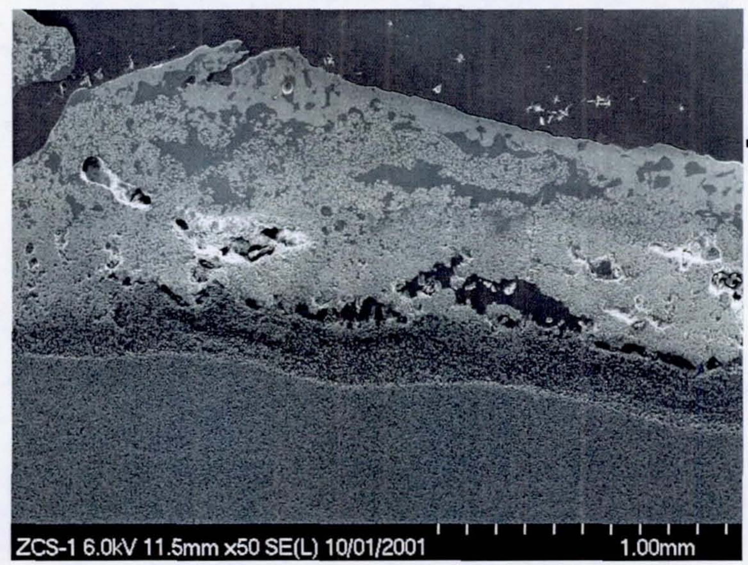
1300°C

40 μm



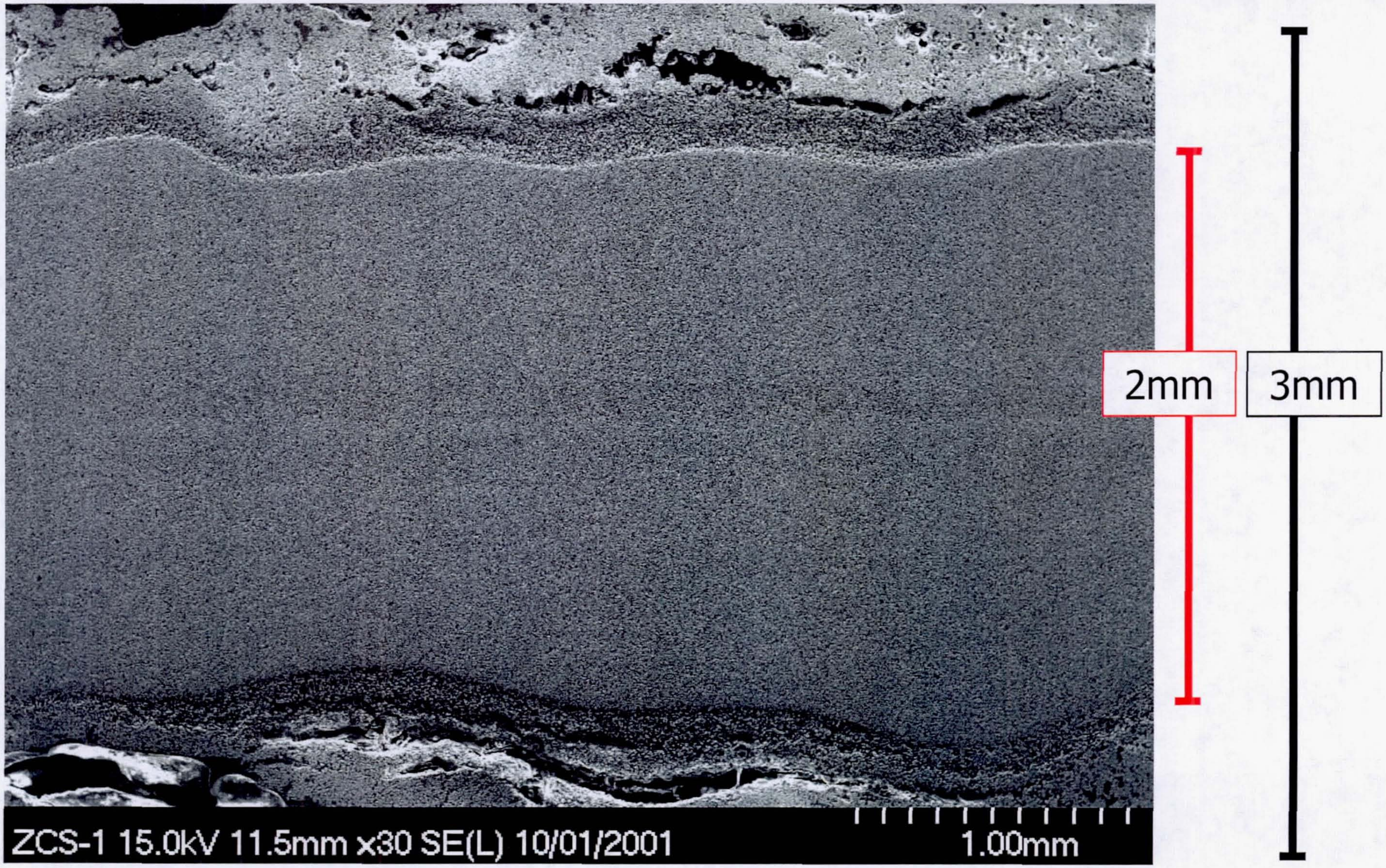
1400°C

200 μm



ZCS Cross-Section at 1400°C in 90% Water Vapor

GLENN RESEARCH CENTER



Recession and Weight Change Table for 90% Water Vapor

GLENN RESEARCH CENTER

	Total Recession 90% H_2O Vapor	Specific Weight Change 90% H_2O Vapor
	1400°C 10h (µm per side)	1400°C 10h (mg/cm^2)
HS	35.0 ± 0.01 (26 hrs)	3.0
ZS	86.5 ± 0.03	11.0
ZCS	535.0 ± 0.10	22.8

Oxidation Rate Comparison for 90% Water Vapor vs. Air

GLENN RESEARCH CENTER

	1300°C in 90% H_2O (mg^2cm^4/h)	1327°C in Air (mg^2cm^4/h)
HS	0.35	0.48 *
HS	0.29	----
ZS	16.56	4.94[3]
ZS	10.19	6.29[3]
ZCS	15.40	17.2[3]
ZCS	11.03	----

No Significant Difference between Oxidation Rates in Low Velocity Water Vapor and Stagnant Air

*Opila – unpublished
Levine et al. (2002)

GLENN RESEARCH CENTER

High Pressure Burner Rig (HPBR) Macrographs

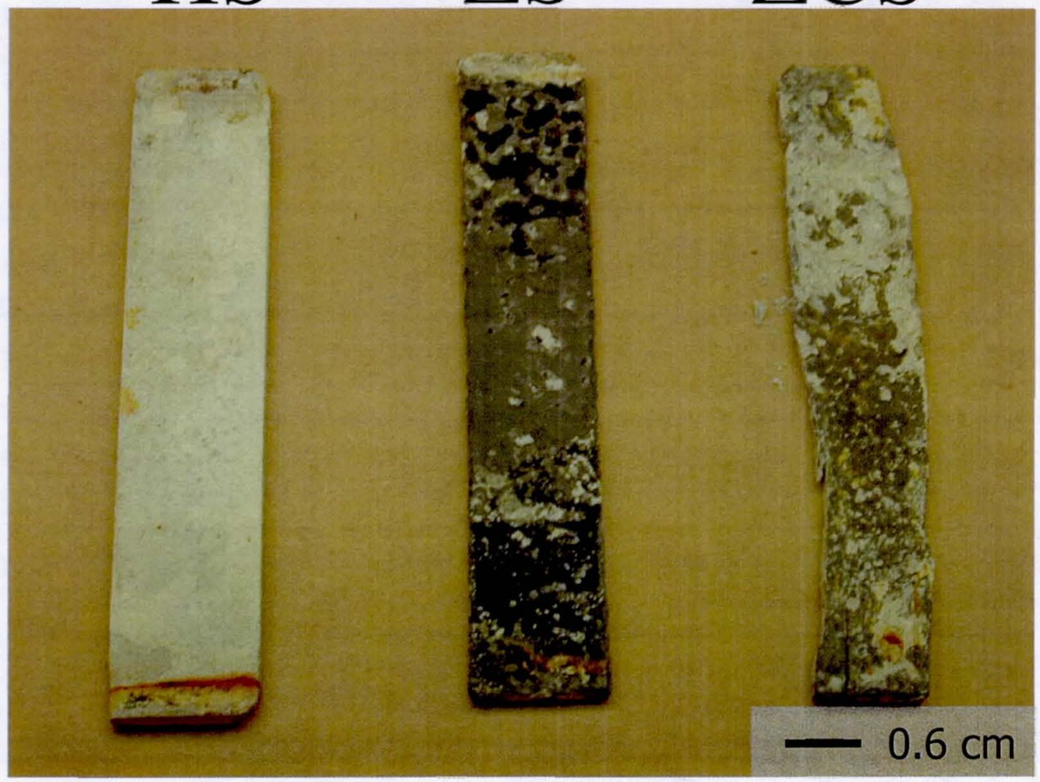
50 hour exposure at 1300°C

HPBR Test Conditions:

- 6 atm
- 18 meters/sec
- f/a = 0.060

Sample Size:
1.3 x 7.6 x 0.3 cm

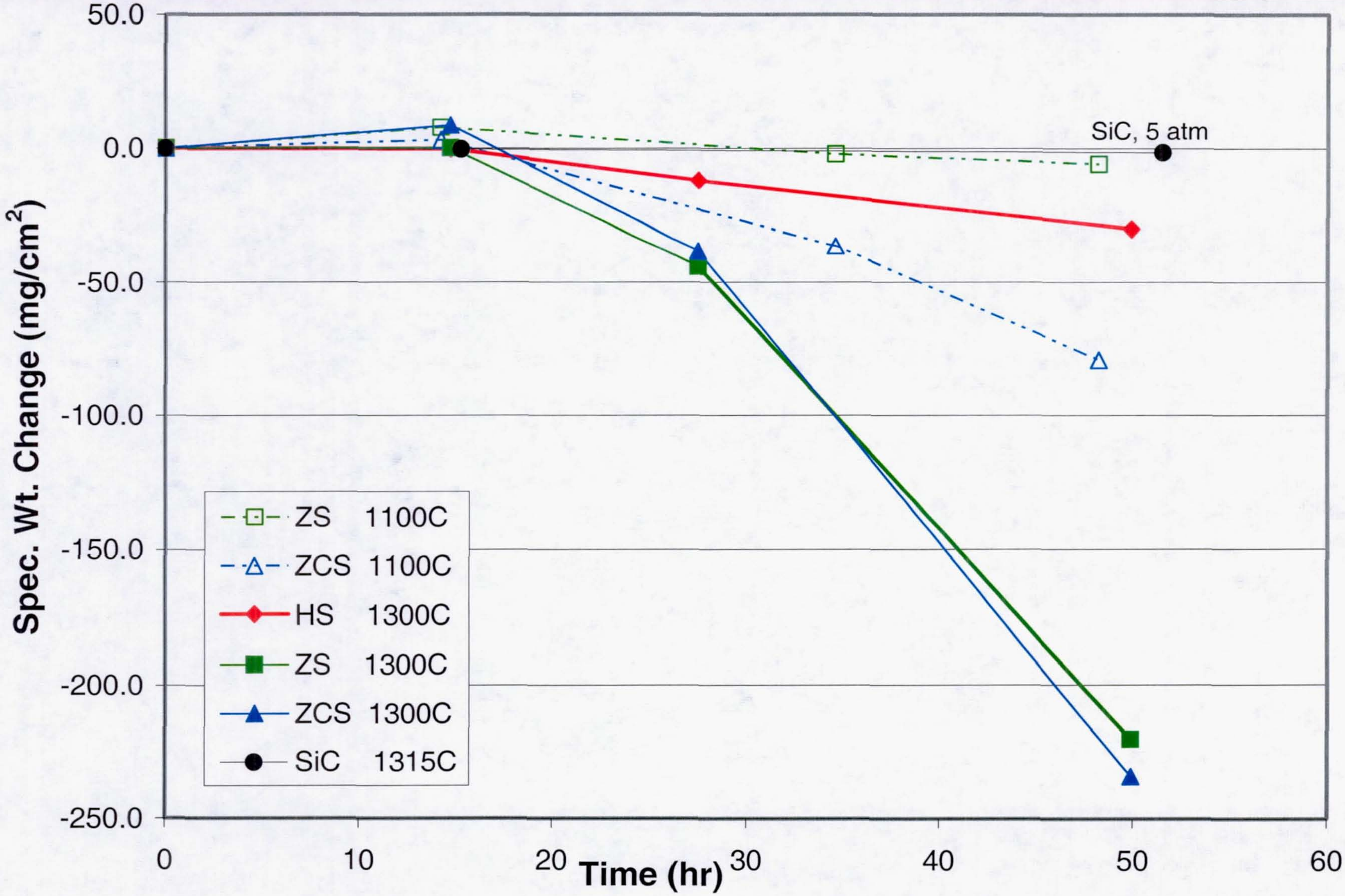
HS ZS ZCS



•Wt loss = HS (3%) ZS (36%) ZCS (48%)

Specific Weight Change in HPBR

GLENN RESEARCH CENTER



HPBR Weight Change and Recession Measurements

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

Paralinear Weight Loss and High Recession Rates due to Volatility and Spallation Effect

Summary

- 3 Compositions (**HS, ZS, ZCS**) of UHTCs were Evaluated in a 90% Water Vapor Cyclic Furnace for Ten Hours
- High Oxide Growth were Observed for all UHTCs Compared to that of SiC Control. The Most Oxidation Resistant UHTC in this Study is HS
- Results were Compared to that of Stagnant Air and HPBR (6atm)

  Factors to Take into Account:

  vs. **Stagnant Air:** → Similar Oxidation Rates

  vs. **HPBR:** → High Velocity causes Volatility and Scale Spallation
  → Accelerated Recession

Conclusions

- 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
- UHTC Materials are Inappropriate for Long Term Aeropropulsion Applications

References

GLENN RESEARCH CENTER

[1] Bull, J.D. and D.J. Rasky, in **"Stability Characterization of Diboride Composites Under High Velocity Atmospheric Flight Conditions"**/1992, p. T1092, the 24th International SAMPE Technical Conference. (October 20-22, 1992)

[2] Rasky, D.J., Bull, J.D. and H.K. Tran, in **"Ablation Response of Advance Refractory Composites,"**/1991, J.D. Buckley, Editor NASA Conference Publication 3133 Part 1, p. 153, The 15th Conference on Metal Matrix, Carbon, and Ceramic Matrix Composites, (1991).

[3] Levine, S.R., Opila, E.J., Halbig, M.C., Kiser, J.D., Singh, M., and J.A. Salem, **"Evaluation of Ultra-high Temperature Ceramics for Aeropropulsion Use,"** J. of the European Ceramic Society **22** p. 2757-2767 (2002)