OXIDATION STUDY OF AN ULTRA HIGH TEMPERATURE CERAMIC COATINGS BASED ON HfSICN

Dagny Sacksteder *, Deborah L. Waters and Dongming Zhu

Environmental Effects and Coatings Branch, NASA Glenn Research Center, Cleveland, Ohio, USA

42nd International Conference on Advanced Ceramics and Composites (ICACC2018)
Daytona Beach, Florida
January 21-27, 2018

* NASA Intern Student

Introduction

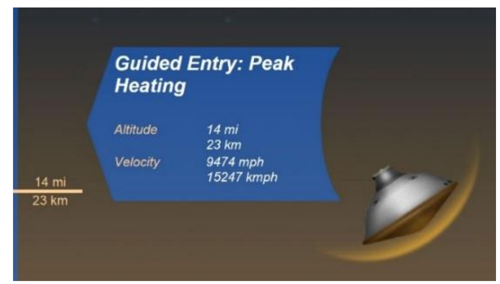
- High temperature fiber-reinforced SiC_f/SiC and C_f/SiC ceramic matrix composites (CMCs) are important for aerospace applications, because the use of the CMCs allows the design of lighter-weight, more fuel efficient aircraft engines and more advanced spacecraft airframe thermal protection systems

- The CMCs have to be protected with advanced environmental barrier coatings (EBCs) when they are incorporated into components for the harsh environments

Fixed Wing Subsonic and Supersonics Aircraft

Hybrid Electric Propulsion Aircraft Advanced Propulsion Materials and Multifunctional Materials

NASA Aeronautics Mission Directorate (STMD) Program: High Efficiency Low Emission Propulsion Engines



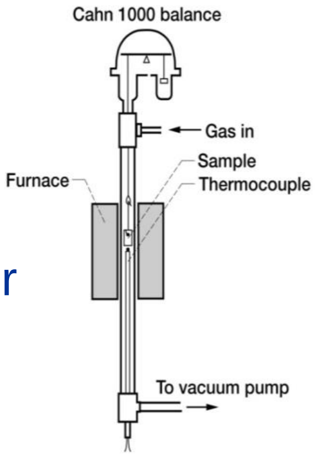
NASA Space Technology Mission Directorate (STMD) Program: Entry, Descending and Landing: Ultra High Ceramics and Coatings (UHTCC)

Outline

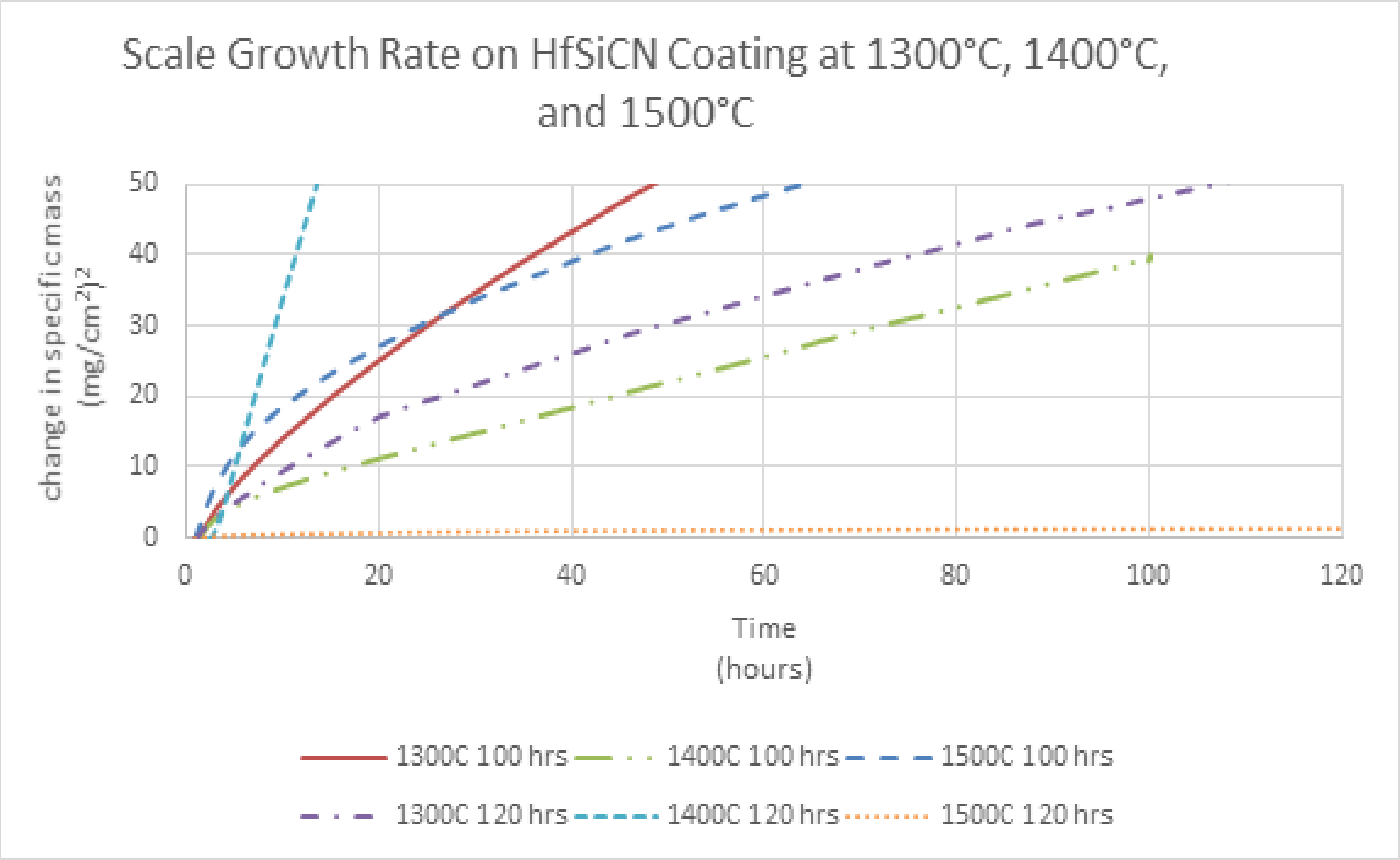
- High temperature oxidation kinetics of an advanced HfSiCN coatings on C_f/SiC CMC substrates investigated at 1300°C, 1400°C, and 1500°C by using thermogravimetric analysis (TGA)
- The coating oxidation reaction mechanisms, and effects of temperature on the oxidation rates
- This oxidation reaction study also focuses on the nature of oxide scales formation and their stabilities
- A per-oxidation test procedure at 1400°C for 20 h on HfSiCN coating oxidation kinetics at various temperatures (1300, 1400, and 1500°C)
- SEM and X-ray characterizations

Experimental

- Study oxidation kinetics of Ultra High Temperature Ceramics (UHTCs)
  - Material
    - HfSiCN coating on Ceramic Matrix Composite (CMC) substrate, processed using magnetron enhanced physical vapor deposition
    - Multi-targets and alloyed targets used for the composite coating processing in both Cathodic Arc and PEMS approaches
    - Specimen dimensions 25.4”x12.7”x2 mm
  - Methods
    - TGA (Thermogravimetric Analysis)
    - SEM (Scanning Electron Microscope)
    - EDS (Electron Dispersive Spectroscopy)

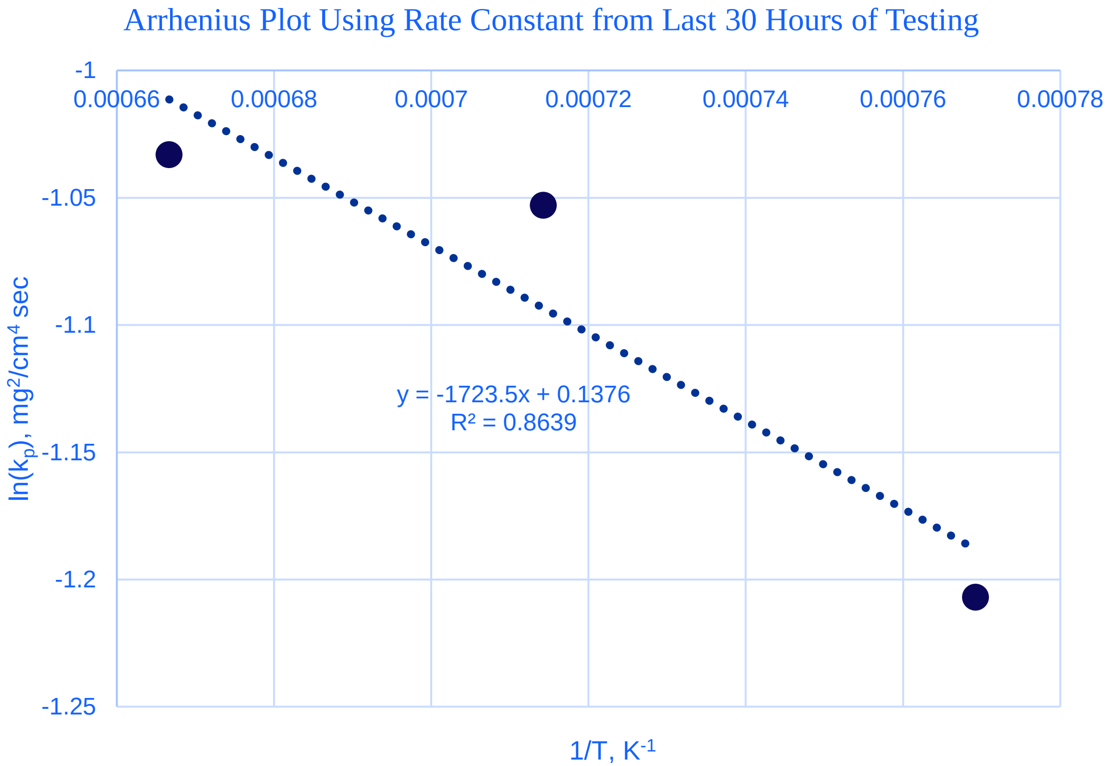


Oxidation Kinetics of HfSiCN Coating Systems



The HfSiCN coating oxidation weight gain squared vs. time. The standard form of a parabolic rate law is $\Delta w^2 = k_p \times t + C$, where Δw is specific weight gain, k_p is parabolic rate constant, C is a constant. As can be seen from the parabolic rate law relation, when the change in specific mass is squared, the graph is linear, and therefore the slope can be treated as an approximation of k_p for the coating system.

Oxidation Kinetics of HfSiCN Coating Systems - Continued



$$k_p = A \cdot exp(-\frac{Q}{RT}) \quad (1a)$$

where A is the pre-exponential factor, Q is the activation energy, R is gas constant. Take the natural logarithm of both sides of Equation (1a),

$$\ln kp = \ln(A) - \frac{Q}{R} \cdot T \quad (1b)$$

where the slope is $-\frac{Q}{R} = -1723.5$, thus the activation energy is

$$Q = -1723.5 \times -1 \times 8.314 \frac{J}{mol\ K} = 14{,}300\ J/mol = 14.3\ kJ/mol \quad (2)$$

Arrhenius plot of ln(k_p) versus inverse temperature (1/T) for HfSiCN oxidation. The fitted line has a slope -1723,5 mg^2/cm^4sec-K

Oxidation Kinetics of HfSiCN Coating Systems – Sample Morphologies

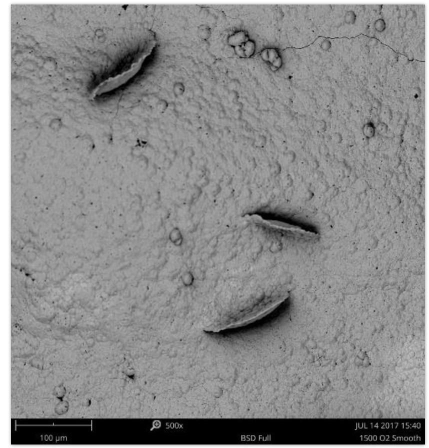
(a)

(b)

(c)

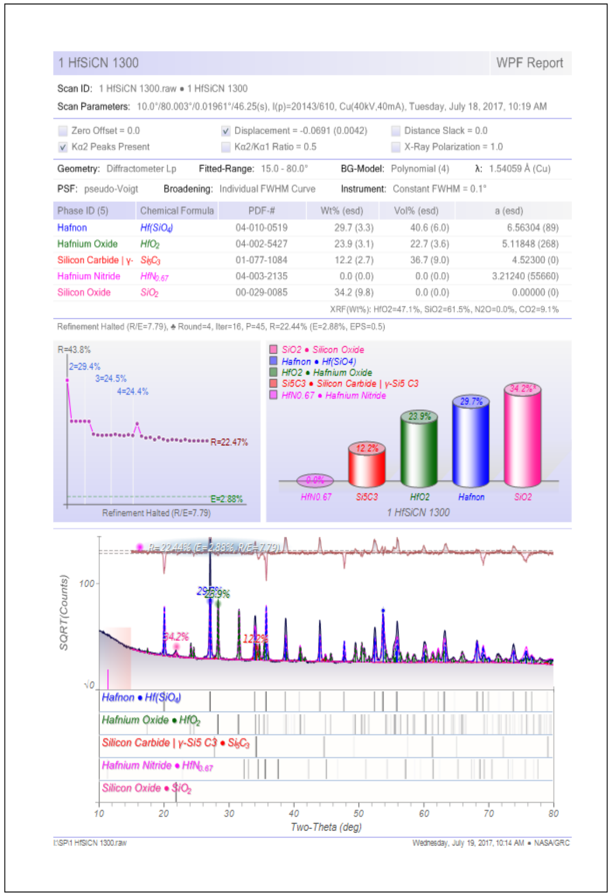
(d)

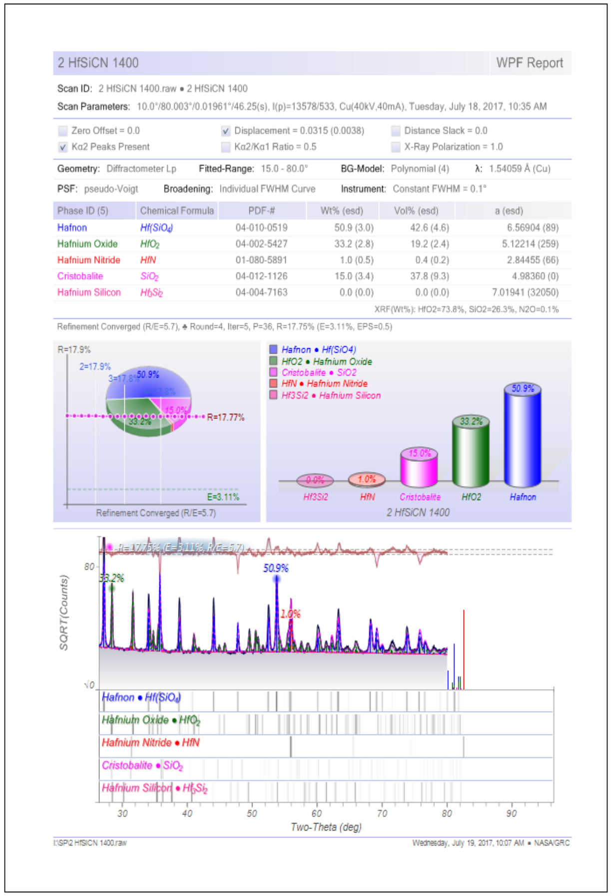
Photo images of oxidized specimens. (a) A pristine sample. (b) Sample tested for 100 hours at 1300°C. (Note that coating loss on the sides of the sample is due to handling after the test). (c) Sample tested at 1400°C for 100 hours. (d): Sample tested at 1500°C for 100 hours. The images illustrate the different amounts of spalling that occurred on the surface of samples. The sample tested at 1500°C had relatively little spalling.

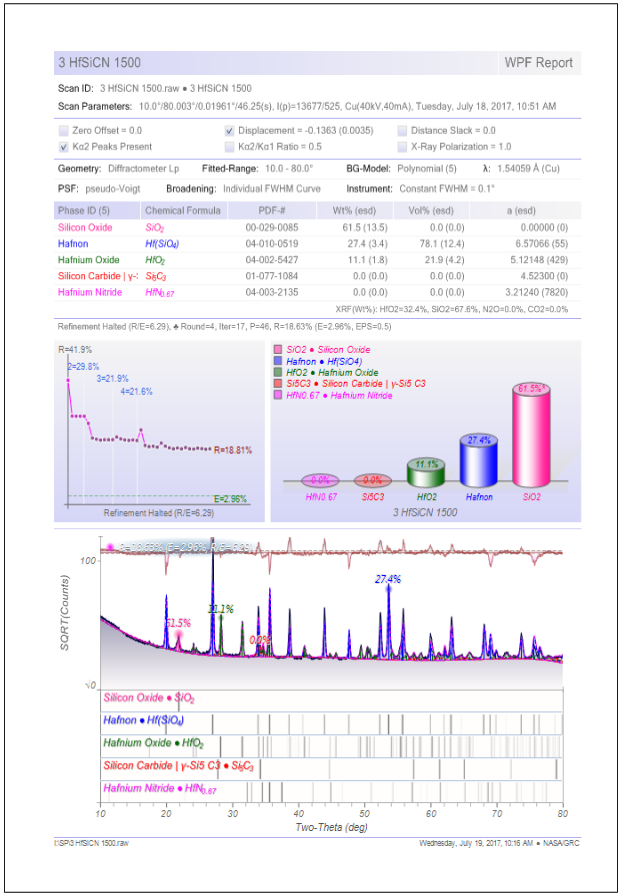


Scanning Electron Microscope (SEM) images of a 1500°C oxidation tested specimen. Image (a) shows the ‘smooth’ side of the sample tested at 1500°C for 100 hours, while image (b) shows the ‘rough’ side of the same sample. One can note the difference in grain texture, as well as the beginnings of spallation on the ‘smooth’ side.

X-Ray Diffraction (XRD) and Phase Analysis of Oxidized HfSiCN







X-ray diffraction spectra and analysis for phase fractions on oxide scales for HfSiCN coating oxidation at various temperatures. (a) 1300° C; (b) 1400° C; (c) 1500° C.

X-Ray Diffraction (XRD) and Phase Analysis of Oxidized HfSiCN – Phase Summaries

Table 1. XRD Phase Analysis of Samples Tested at 1300°C, 1400°C, and 1500°C for 100 hours, in flowing Oxygen

1300°C		1400°C		1500°C	
Phase Chemical Formula	Weight Percent	Phase Chemical Formula	Weight Percent	Phase Chemical Formula	Weight Percent
$Hf(SiO_4)$	29.7	$Hf(SiO_4)$	50.9	$Hf(SiO_4)$	27.4
SiO_2	34.2	SiO_2	15.0	SiO_2	61.5
HfO_2	23.9	HfO_2	33.2	HfO_2	11.1
Si_5C_3	12.2	HfN	1.0		

Summary and Conclusions

- Oxidation kinetics determined for the HfSiCN based Ultra-High Temperature Ceramic coating systems on C_f/SiC CMCs
- Pseudo-parabolic rate law observed for the HfSiCN oxidation, where the reaction rate is initially more rapid during the transient stage, and then slows down at the steady-state. At this steady state oxidation, more protective oxide scales formed and reduced further diffusion fluxes of oxygen and metal hafnium and silicon through the coating scales.
- Samples tested at lower temperatures showed greater recession and spalling because of longer transient state period. Test Results showed that the activation energy of the oxidation reaction was approximately 14.3 kJ/mol).
- XRD analysis showed that the samples tested at 1400°C had the most favorable ratio of hafnia to silica scales, which, along with the steadier reaction rate of samples tested at this condition, suggests that the material is able to maintain stability at this temperature.

Acknowledgements

The authors are grateful to John Setlock, who made all of the TGA testing possible, and Bernadette J. (Sue) Puleo, who assisted the XRD analysis. We would also like to thank all the members of the NASA Glenn Environmental Effects and Coatings Branch, and Mr. Craig Robinson, Chief of the Environmental Effects and Coatings Branch, for their kind willingness to answer questions and offer additional insight, as well as the NASA Glenn Education Office for making this internship possible.

References

[1] Zhu, D., Harder, B., Hurst, J. B., Good, B., Costa, G., Bhatt, R., and Fox, D., "Development of Advanced Environmental Barrier Coatings for SiC/SiC Ceramic Matrix Composites: Path Towards 2700^{o}F Temperature Capability and Beyond," presented at the Conference on Composites, Materials, and Structures, Cocoa Beach, FL, 2017.

[2] Zhu, D., Hurst, J. B., NASA GRC. U.S. Patent Application, "Advanced High Temperature and Fatigue resistant Environmental Barrier Coating Bond Coat Systems for SiC/SiC Ceramic Matrix Composites" Publication No. US 2013/0344319, June 21. 2013.

[3] Luthra, K. L., "Some New Perspectives on Oxidation of Silicon carbide and Silicon Nitride," Journal of the American Ceramics Society, Vol. 74, No. 5, 1991, pp. 1095-1103.

[4] Ahlborg, N., and Zhu, D, "Silicon Carbide Nanotube Oxidation at High temperatures" Ceramic Engineering and Science Proceedings, Vol. 33, No. 3, 2012, pp. 89-97.

[5] Douglass, D. L., Wagner, C., "The Oxidation of Oxygen Deficient Zirconia and Its Relationship to the Oxidation of Zirconium", Journal of the Electrochemical Society, Vol. 113, No. 7, pp. 671-676. July 1966.

[6] Pultz, W. W., "Oxidation of Submicroscopic Fibrous Silicon Carbide," Journal of the American Ceramics Society, Vol. 50, No. 8, 1967, pp. 419-420.

[7] Ionescu, E., Papendorf, B., Hans-Joachim, K., Riedel, R., "Polymer-Derived Silicon Oxycarbide/Hafnia Ceramic Nanocomposites. Part II: Stability Toward Decomposition and Microstructure evolution at T>>1000^{o}C," Journal of the American Ceramics Society, Vol. 93, No. 6, 2010, pp. 1783-1789.