AFRL-SR-AR-TR-07-0382

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE Dec 06, 2003	3. REPORT TYPE AND DATES COVERED Final Report: 12/1/99-5/31/03

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
Unusual Nature of NanoDomains in Ultrahigh Temperature Polymer Derived Ceramics	FA9550-04-1-0154

6. AUTHOR(S)

Rishi Raj

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Department of Mechanical Engineering University of Colorado Boulder CO 80309-0427	Attn: Rishi Raj

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSORING / MONITORING AGENCY REPORT NUMBER
Dr. Joan Fuller	Ceramic and Non-Metallic Materials Program Manager, AFOSR 801 N. Randolph Street, Room 732 Arlington, VA 22203-1977	

12a. DISTRIBUTION / AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE
Approved for public release, distribution unlimited	

13. ABSTRACT (Maximum 200 Words)

This grant has the objective of explaining the unusual properties of polymer–derived–ceramics (PDCs), so called because they are made directly from cross–linked polymers by controlled pyrolysis. The PDCs have unusual properties: (i) They remain structurally and chemically stable up to 1500°C, (ii) They are amorphous in Bragg diffraction although small–angle–xray–scattering shows the presence of nanodomains, (iii) PDCs do NOT show steady state creep despite their amorphous structure, and (iv) PDCs exhibit viscoelasticity at high temperatures. The critical advance made in this grant is the development of a nanodomain model for the PDCs, which is validated by the experimental findings. The model consists of a graphene network interconnected in the form of nanodomains, about 1–5 nm in size. The graphene network stabilizes the amorphous structure of the ceramic. The unusual properties of PDCs are successfully explained by the nanodomain model. The PDCs are a new class of metastable ceramics that are likely to lead to revolutionary new technologies for high temperatures. Their amorphous nature is similar to that of polymers and metallic glasses. However, the chemical and structural stability of the PDCs at ultrahigh temperatures is unique.

14. SUBJECT TERMS		15. NUMBER OF PAGES
Silicon Carbonitride, Silicon Oxycarbonitride, NanoDomains, Non-Crystalline, Creep, Polymer-Derived-Ceramics, PDCs, Ultrahigh Temperature, Amorphous Ceramics		12
		16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

20071015199

FINAL PERFORMANCE REPORT

Unusual Nature of NanoDomains in Ultrahigh Temperature Polymer Derived Ceramics

FA9550-04-1-0154

To:

Dr. Joan Fuller
Ceramic and Non-Metallic Materials Program Manager
Air Force Office of Scientific Research
801 N. Randolph Street, Room 732
Arlington, VA 22203-1977

submitted via the following organization:

submitted by

Rishi Raj (Principal Investigator)

Department of Mechanical Engineering
University of Colorado at Boulder
Boulder CO 80309-0427
rishi.raj@colorado.edu

September 25, 2007

Executive Summary

This grant had the objective of explaining the unusual properties of polymer–derived–ceramics (PDCs), so called because they are made directly from cross–linked polymers by controlled pyrolysis. The PDCs have very unusual properties: (i) Although the pyrolysis is completed below 1000°C their nanostructure remains stable up to 1500°C, (ii) They remain amorphous in Bragg diffraction although small–angle–xray–scattering shows the presence of nanodomains, (iii) PDCs do NOT show steady state creep at temperature up to 1500°C despite their amorphous structure, and (iv) PDCs exhibit viscoelasticity at high temperatures. The critical advance made in this grant is the development of a nanodomain model for the PDCs, which is validated by the experimental findings. The model, shown just below in Fig. 1, consists of a graphene network interconnected in the form of nanodomains, about 1–5 nm in size. The graphene network stabilizes the amorphous structure of the ceramic. The unusual properties of PDCs are successfully explained by the nanodomain model. The PDCs are a new class of metastable ceramics that are likely to lead to revolutionary new technologies for high temperatures. They bear similarity to polymers on the one hand and metallic glasses on the other hand. LIke polymers and metallic glasses they spell the dawning of a new era of functional properties that can be functionally tailored; however, the PDCs have the additional advantage of remaining structurally and chemically stable at ultrahigh temperatures. The current PDC systems that have been studied are comprised of silicon, carbon, nitrogen and oxygen.
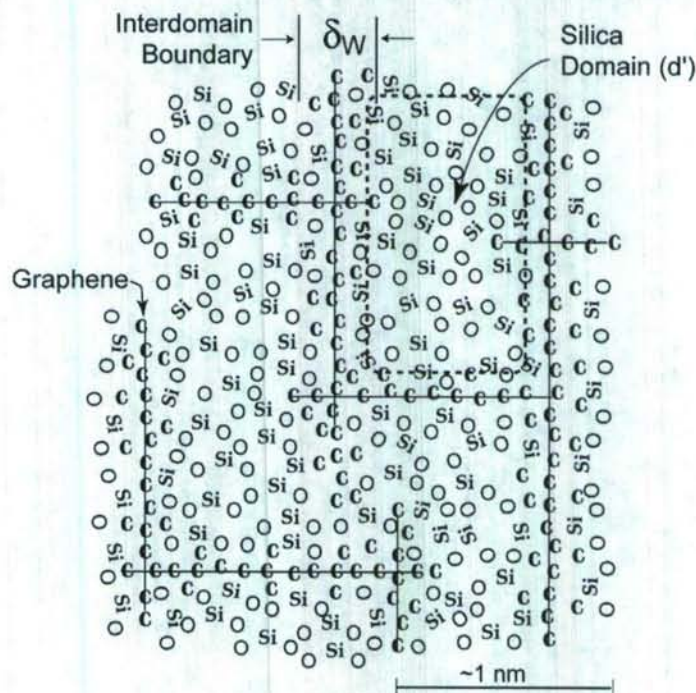

Figure 1: The structure of the PDCs is characterized by a network of graphene which creates nanodomains. The silica molecules sequestered within the domains are unable to crystallize, or to creep because long range diffusion is suppressed. Note the contrast with nanocrystalline materials: the grain boundaries in polycrystals degrade resistance to creep since they serve as paths for fast diffusion. In the PDCs the refractory nature of the graphene "interfaces" suppresses diffusion leading to unusual high temperature properties. There is increasing evidence that the graphene can be functionalized, in the same way as carbon chains are functionalized in organic polymer, to inculcate a wide array of multifunctional properties. Thus the PDCs will have a unique place in the materials world, as the only known "amorphous" materials with remarkable resistance to creep and with tailorable functional properties for high temperature applicaitons.

Publications from the Current Grant (FA9550-04-1-0154):

1. "The Role of Carbon in Unexpected Visco(an)elastic Behavior of Amorphous Silicon Oxycarbide above 1273K", A. Scarmi, G. D. Sorarù and R. Raj, Journal of Non-Crystalline Solids, Vol. 351[27-29], 2238-2243 **(2005)**.

2. "Crystallization Maps for Amorphous SiCO", A. Saha and R. Raj, Journal of American Ceramic Society, 90 [2] 578–583 **(2007)**.

3. "A Model for NanoDomains in Polymer-Derived SiCO", A. Saha, D. L. Williamson, and R. Raj, Journal of American Ceramic Society, Vol. 89[7], 2188-2195 **(2006)**.

4. "Titanium Nitride Interconnects for Polymer-Derived Silicon-Carbonitride Semiconductors for Service at Temperatures up to 1300°C", H.-Y. Ryu and R. Raj, Journal of American Ceramic Society, Vol. 90[1], 295-297 **(2007)**.

5. "Mechanical and Tribological Behavior of Polymer–Derived Ceramics Constituted from $SiC_xO_yN_z$", T. Cross, R. Raj, S. V. Prasad, T. E. Buchheit and D. R. Tallant, Journal of American Ceramic Society, Vol. 89[12], 3706–3714 **(2006)**.

6. "Preparation of Ultrathin–Walled Carbon–Based Nanoporous Structures by Etching Pseudo–Amorphous Silicon Oxycarbide Ceramics", R. Peña–Alonso, G. D. Soraru` and R. Raj, Journal American Ceramic Society, Vol. 89[8]. 2473-2480 **(2006)**.

7. "Novel Composites Constituted from Hafnia and a Polymer–Derived Ceramic as an Interface Phase for Severe Ultrahigh Temperature Applications", B. Sudhir and R. Raj, Journal of American Ceramic Society, Vol. 90[10], 3171-3176 **(2007)**.

8. "Synthesis, Deposition, Microstructure, and Tribological Behavior of Thin Film Silicon Carbonitride Derived from Poly(urea)methyl Vinyl Silazane", T. J. Cross, R. Raj, S. V. Prasad, and D. R. Tallant, Journal of Applied Ceramic Technology, Vol. 3[2], 113-126 **(2006)**.

9. "Passive oxidation of an effluent system: The case of polymer-derived SiCO", S. Modena, G. D. Soraru`, Y. Blum and R. Raj, Journal of American Ceramic Society, Vol 88[2], 339-345 **(2005)**.

10. "Oxidation Behavior of SiCN-ZrO_2 Fiber Prepared from Alkoxide Modified Silazane" A. Saha, S. R. Shah and R. Raj, Journal of American Ceramic Society , Vol. 87[8], 1556-1558 **(2004)**.

11. "Characterization of NanoDomains in Polymer-Derived SiCN Ceramics Employing Multiple Techniques", A. Saha, D. L. Williamson, H.-J. Kleebe and R. Raj, Journal of American Ceramic Society vol. 88 [1], 232-234 **(2005)**.

Publications from the previous AFOSR Grant (F49620-00-1-0109):

1) Nanoscale Densification Creep in Amorphous Silicon Carbonitride", S. Shah and R. Raj, *J.Amer. Ceram. Soc.*,Vol. 84[10], 2208-12 **(2001)**.

2) "Oxidation Kinetics of An Amorphous Silicon Carbonitride Ceramic", Rishi Raj, Linan An, Sandeep Shah, Ralf Riedel, Claudia Fasel, and H-Joachim Kleebe, *J.Amer. Ceram. Soc.*, Vol 84[8], 1803-1810 **(2001)**.

3) R. Raj, R. Riedel and G. D. Soraru, *Special Issue of the J. American Ceramic Society* on "Ultrahigh Temperature Polymer Derived Ceramics", Eds. R. Raj, R. Riedel and G. D. Soraru, *J.Amer. Ceram. Soc.*, Vol 84[10], pp 2158-2264 **(2001)**.

4) "Mechanical Properties of a Fully Dense Polymer Derived Ceramic Made by a Novel Pressure Casting Process", S. R. Shah and R. Raj, *Acta Materiala*,Vol 50[16], 4093-4103 **(2002)**.

5) "Crystallization of Polymer Derived Silicon Carbonitride at 1873K under Nitrogen Overpressure", M. Friess, J. Bill, J. Golczewski, A. Zimmermann, F. Aldinger, R. Riedel, and R. Raj, *J.Amer. Ceram. Soc.*, Vol. 10, 2587-2589 **(2002)**.

6) "Pyrolysis Kinetics for the Conversion of a Polymer into an Amorphous Silicon Oxycarbide Ceramic", G. D. Soraru, L. Pederiva and R. Raj, *J.Amer. Ceram. Soc.*, Vol 85[9], 2181-2187 **(2002)**.

7) "Amorphous Silicon Carbonitride Fibers Drawn from Alkoxide Modified Ceraset[TM]", A. Saha, S. R. Shah and R. Raj, *J.Amer. Ceram. Soc.*, 86 [8]: 1443-1445 **(2003)**.

8) "Influence of the Distributed Particle Size on the Determination of the Parabolic Rate Constant for Oxidation by the Powder Method", S. R. Shah, A. Saha and R. Raj, *J.Amer. Ceram. Soc.*, Vol. 86[2], 351-353 **(2003)**.

Summary of Results and the Future

OVERVIEW

This report is in two sections. The first section provides the scientific underpinning for the nanodomain model shown schematically in the Executive Summary. Here the experiments and spectroscopic observations that led to this model are described. Next, the model is developed quantitatively to predict the thickness of the domain wall (in pm) and size of the nanodomains in nm. It is shown how the mere composition of the amorphous ceramic can be used to calculate these two parameters for the nanodomain structure. The results of this analysis have been displayed in "maps" which can be read quickly to estimate the thickness of the domain wall and the domain size.

The second section of this summary outlines my thoughts about the possible applications of the PDCs in the field of ultrahigh temperature structural ceramics. A paper, just published in the J. Amer. Ceram. Soc.[13] shows how the PDCs can create a refractory phase in high temperature oxides such as hafnia, imparting to them properties that cannot be achieved by the conventional sintering processes. Other work carried out separately under a contract (from ARO led by Honeywell) on environmental barrier coatings shows the great promise of PDCs as a bond coat, and as an additive to the top coat in a multilayer design[10–12].

It is my hope that after a hiatus, support for work on PDC inspired ultrahigh temperature materials for structural and sensor applications can resume at the University of Colorado, under AFOSR's sponsorship.

THE HISTORY AND THE DESCRIPTION OF THE NANODOMAIN MODEL FOR THE PDCS

Two high temperature properties of PDCs, discovered in the 1990s, could not be explained by conventional wisdom. The first was that silicon carbonitrides made from the pyrolysis of heavily crosslinked polysilazanes resisted crystallization up to temperatures as high as 1600°C[1]. The second observation, from the PI's laboratory, was that despite their amorphous structure the PDC exhibited non–detectable steady state creep[2,3]. Normal glasses like silica either crystallize or flow viscously when raised to high temperatures. The absence of crystallization and creep suggested that the molecular structure of PDCs is different than that of inorganic glasses.

Since PDCs are pseudo–amorphous materials their nanostructure is studied by spectroscopic techniques such as IR (infrared absorption), Raman, NMR (nuclear magnetic resonance) and SAXS (small angle x-ray scattering). These studies carried out principally at the Max Planck Institute for Metallforschung in the late nineties until about 2005, gave the following information: (i) Raman suggested the presence of long range graphene structures, (ii) NMR studies showed the presence of sp^2 carbon-carbon structures, consistent with Raman, but also the presence of mixed tetrahedral bonds between Si, carbon and nitrogen, and (iii) SAXS gave strong signals for nandomains in the 1-5nm size range; these signals suggest the presence of density fluctuation but

cannot provide information regarding the chemistry of these molecular clusters. On the other hand NMR gives chemical information about the nearest neighbor bonds but cannot provide details of chemical bonding on the length scale of several bond lengths.

Thus the spectroscopic information is fragmented and cannot by itself elucidate the molecular structure of the PDCs. The approach adopted by the Colorado group was to propose models for the nanostructure that are consistent not only with the spectroscopic information but also with the phenomenological observations of the high temperature properties of the PDCs are described above.

At first two possible nanodomain models, both of which were consistent with the spectroscopic data were proposed:

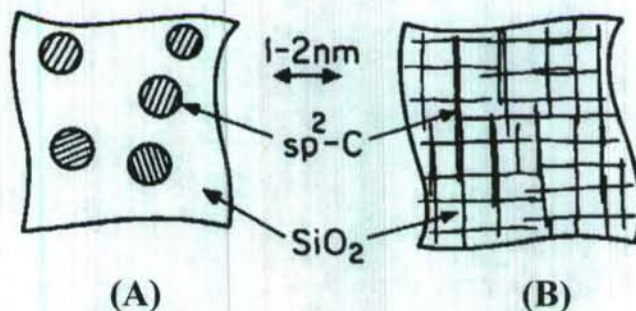(A)   (B)

Figure 2: Two possible models for the nanodomain structure of the PDCs. Both models are consistent with the spectroscopic information obtained from Raman, NMR and SAXS (using silicon oxycarbide as an example).

Both models contain nanodomains, sp^2 carbon, and mixed bonds at the interfaces of graphene and silica. The principal difference between them is that in (A) the domains are formed by carbon, while in case (B) the domains consist of silica tetrahedra. We try to choose between these two models by considering their consistency with the creep experiments. Here we expect to see a difference. In (A) the creep may be somewhat retarded because viscous silica is filled with small particles, but cannot be suppressed. However, in case (B) steady state creep would be suppressed since the applied stress will become supported by the graphene network, which cannot deform by creep.

Thus the model in (B) is consistent with both the creep experiments and the spectroscopic data for the PDCs. However, this model makes a prediction: the material must be viscoelastic since the silica domains can relax by creep, gradually unloading the stress on them on to the graphene structure. When the applied stress is removed the graphene structure will spring back as the silica domains regain their original shape. Experiments were carried out to test this prediction. The results are presented in Fig. 3. They confirm the high temperature viscoelastic behavior of the PDC[4]. The figure compares the creep behavior of pure silica with that of a silicon oxycarbide polymer–derived–ceramic. Note that wheras pure silica shows large–scale creep at

1000°C at 20 MPa, the SiCO shows negligible steady state viscous creep, and instead exhibits viscoelastic behavior as predicted by model (B) in Fig. 2.
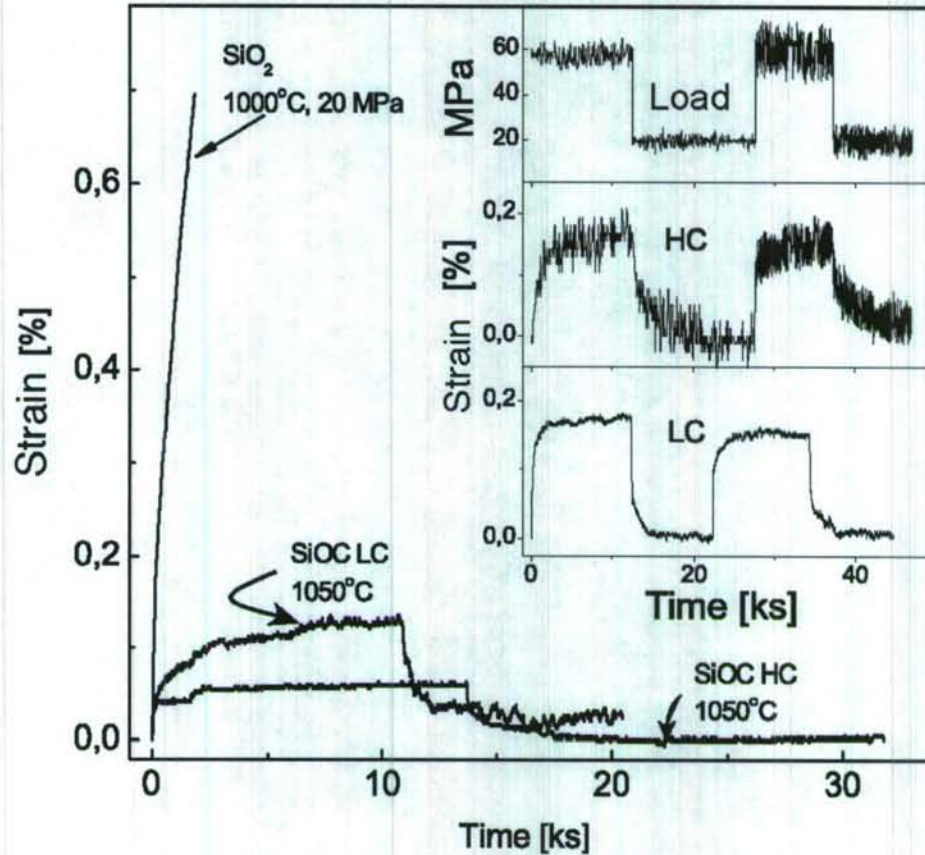

Figure 3: Viscoelastic behavior of polymer–derived silicon oxycarbide as compared to the viscous creep fo silica. The viscoelasticity is consistent with model (B) in Fig. 2.

The next phase in our research was to quantify the nanostructural parameters for the nanodomain model in detail. A detailed picture, also shown in the Executive Summary, was visualized. The two key parameters in the model are the width of the domain wall, δ_w, and the domain size, d'. The composition of the PDC can be generally written as SiC_xO_y. Thus, conceptually, it should be possible to related the two known parameters, x and y in the composition, to δ_w and d'. The main assumption in the analysis[5] is for the relative distribution of the mixed bond as the interface between the graphene interface in the silica domain. This information is provided from NMR data. The results were mapped into the composition diagram for different distributions of the
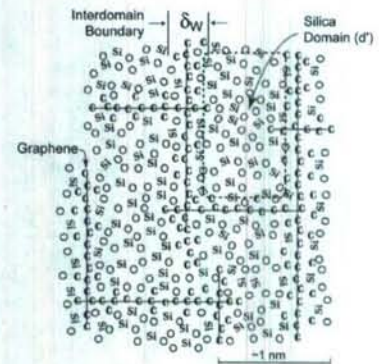

Fig. 4: The width of the domain wall, and the size of the domains are the two key features of the model.

mixed bond geometries. Two of these results are shown in Fig. 5. On the left is the case where the mixed bond populations are randomly distributed (p=0.5), while the other case, p=0.75, assumes the Si-C-O bond distributions to be enriched in carbon.
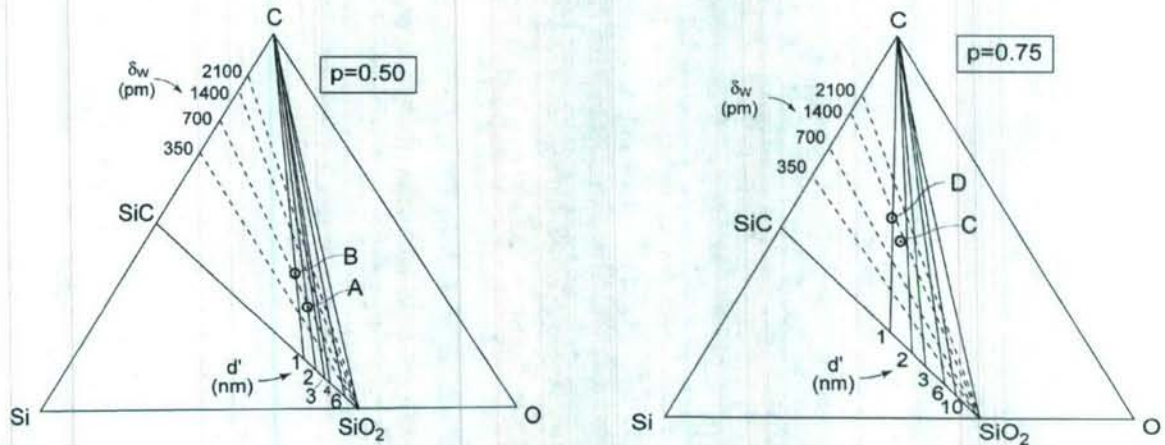

Figure 5: The quantitative model for the domains is developed into maps which can be read quickly to yield values for the width of the domain walls and the domain size. The solid points derive from experiments, which confirm the domain size measurements by SAXS.

Further experimental validation of the nanodomain model is obtained from experiments where the PDC was etched with hydrofluoric acid. This procedure removed the silica molecules within the domains (but not the mixed bonds adhering to the graphene walls) leaving behind an scaffolding of ultrathin graphene[6]. These structures had very high surface area, comparable to that of carbon nanotubes, and a pore size which was in agreement with the domain size measured by SAXS.

In addition to creep resistance at high temperatures, the PDCs also have many multifunctional properties. These properties are attributed to the interfacial functionalization of the graphene domain walls[7].

THE FUTURE AND THE TECHNOLOGICAL POTENTIAL

The PDCs occupy a unique place in the materials–world. They are the first example of amorphous ceramics. In this sense they compare with metallic glasses; however, their metastability extends to much higher temperature than that of metallic glasses. Their graphene nanodomain structure may also be compared to organic polymers: whereas organics contain linear carbon chains, the PDCs contain networks of two–dimensional graphene. Like polymers the carbon networks can be functionalized in different ways to introduce a wide range of functional properties. These scientific innovations are likely to continue for several years. High temperature sensors[8] and catalysis[9] made from PDCs are likely to be the first technological applications.

The vitality of PDCs in the design and construction of ultrahigh temperature environmental barrier coatings [EBCs] has been demonstrated in work in the PI's

laboratory (under ARO–Honeywell support from 2002-2006). Results from this work are presented in Fig. 6. The details are given in Refs [10–12].
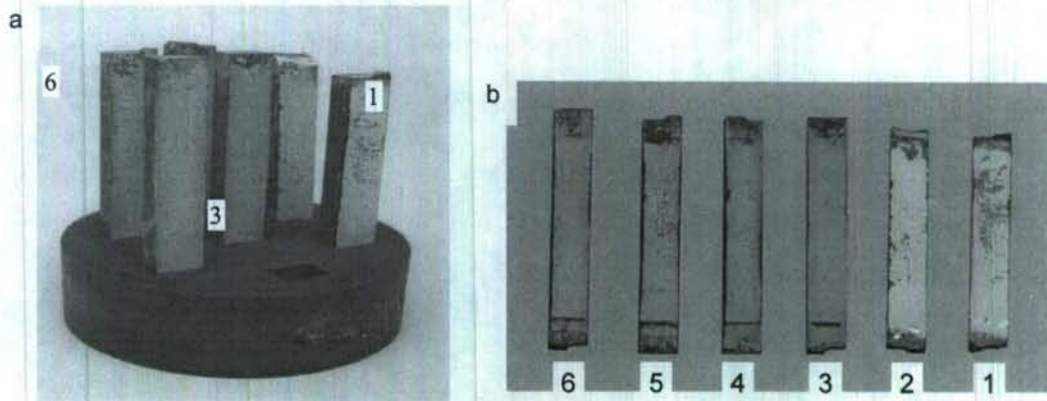

Figure 6: (a) Photograph of the samples in the HPBR sample holder. Samples 1 and 2, which had the Type 2 coating, were exposed to 50 hours of testing. Samples 3, 4, 5 and 6 had the Type 1 coating; these were subjected to 30 hours of testing. Overall, all the samples have performed successfully. Photographs and data provided by Dr. Dongming Zhu, NASA.

The EBC coatings in Fig. 6 were prepared on silicon nitride coupons. PDC was used as the bond coat while the top coat was made from porous hafnia bonded at grain boundaries with PDC interfacial phase[13]. The coatings were tested in High Pressure Burner Rig (HPBR) at NASA. The HPBR tests were conducted at 6 atmospheres total pressure, at temperature in the range 2300-2350°F (1260-1290°C). The temperature was measured with a pyrometer. The pyrometer was focused at the specimen in the middle, noted as #3 in Fig. 4. An 8mm pyrometer was used, with an emissivity of 0.96 which gives reliable temperature measurement. The results in Fig. 6 show that the specimens perform well under HPBR exposure. It can be concluded that coatings demonstrated durability in the high temperature burner rig environments.

Acknowledgement

References

1. "A silicoboron carbonitride ceramic stable to 2000°C", R. Riedel, A. Kienzle, W. Dreßler, L. Ruwisch, J. Bill, and F. Aldinger, *Nature*, Vol. 382, p.796 (1996).

2. "Amorphous Silicoboron Carbonitride Ceramic with very high Viscosity at Temperatures above 1500°C ", R. Riedel, L. M. Ruswisch, L. An and R. Raj, *J. Amer. Ceram. Soc.*, Vol. 81, p.3341 (1998).

3. "Compression Creep Behavior of Precursor Derived Amorphous Si-C-N Ceramics", G. Thürn, J. Canel, J. Bill and F. Aldinger, *J. Eur. Ceram. Soc.*, Vol. 19, p. 2317 (1999).

4. "The Role of Carbon in Unexpected Visco(an)elastic Behavior of Amorphous Silicon Oxycarbide above 1273K", A. Scarmi, G. D. Soraru and R. Raj, Journal of Non-Crystalline Solids, Vol. 351[27-29], 2238-2243 **(2005)**.

5. "A Model for NanoDomains in Polymer-Derived SiCO", A. Saha, D. L. Williamson, and R. Raj, Journal of American Ceramic Society, Vol. 89[7], 2188-2195 **(2006)**.

6. "Preparation of Ultrathin–Walled Carbon–Based Nanoporous Structures by Etching Pseudo–Amorphous Silicon Oxycarbide Ceramics", R. Peña–Alonso, G. D. Soraru` and R. Raj, Journal American Ceramic Society, Vol. 89[8]. 2473-2480 **(2006)**.

7. "Nanodevices that explore the synergies between PDCs and carbon nanotubes", S. R. Shah and R. Raj, Journal of European Ceramic Society, Vol. 25[2-3], 243-249 (2005).

8. "A novel micro glow plug fabricated from polymer-derived ceramics: in situ measurement of high-temperature properties and application to ultrahigh-temperature ignition" Liew LA, Bright VM, Raj R, Sensors & Actuators A-Physical, Vol. 104 (3): 246-262 (2003).

9. "PicoScale Catalyst for Hydrogen Generation from $NaBH_4$", R. Peña–Alonso, A. Sicurelli, E. Callone, G. Carturan and R. Raj, Journal of Power Sources, Vol. 165, 315-323 (2007).

10. "Multilayer Design and Evaluation of a High Temperature Environmental Coating" S. R. Shah and R. Raj, Journal of American Ceramic Society, Vol. 90[2], 516–522 (2007).

11. "Effect of Steam Velocity on Hydrothermal Oxidation/Volatilization of Silicon Nitride", B. Sudhir and R. Raj, Journal of American Ceramic Society, Vol. 89[4], 1380-1387 (2006).

12. "Novel Composites Constituted from Hafnia and a Polymer–Derived Ceramic as an Interface Phase for Severe Ultrahigh Temperature Applications", B. Sudhir and R. Raj, Journal of American Ceramic Society, Vol. 90[10], 3171-3176 (2007).

13. "Novel Composites Constituted from Hafnia and a Polymer–Derived Ceramic as an Interface Phase for Severe Ultrahigh Temperature Applications", B. Sudhir and R. Raj, Journal of American Ceramic Society, Vol. 90[10], 3171-3176 **(2007)**.

Personnel Supported

Atanu Saha: Post-Doc, University of Colorado, Boulder, CO.
Raquel Peña–Alonso, Post-Doc, University of Colorado, Boulder, CO
Dongjoon Ahn: Ph.D. Student, University of Colorado, Boulder, CO
Alberto Scarmi: MS Student, University of Colorado, Boulder, CO
T. Cross: Ph.D. Student, University of Colorado, Boulder, CO
B. Sudhir: Post Doc, University of Colorado, Boulder, CO