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14. ABSTRACT

The objective of this MEANS program was to develop new methodologies for quantifying the variability in the performance of high temperature systems by coupling basic concepts from materials science with system design and engineering. The methodologies were validated by the fabrication and evaluation of new high temperature MEMS devices made from a novel polymer-derived ceramic material. The new results demonstrate two unique features: 1) how to hybridize computational approach with closed form models from materials science, and 2) how to account for the highly non-linear nature of temperature dependent material behavior in predicting variability. A Human-Machine-Interface that successfully predicts the remaining life of a microignitor working above 1300°C, which is built upon these concepts has been demonstrated. Closed form results that link variability in temperature to variability in life-time via the activation energy of fundamental diffusion coefficients have been obtained, and validated by experiments. These results also show that a Gaussian distribution in temperature can lead to a log-normal distribution in lifetimes. More than fifteen publications, and two doctoral dissertations have resulted from this MEANS program.

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FINAL TECHNICAL REPORT

NOVEL SICN CERAMICS FOR HEALTH MONITORING OF HIGH TEMPERATURE SYSTEMS

F49620-01-1-0527

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Abstract: The objective of this MEANS program was to develop new methodologies for quantifying the variability in the performance of high temperature systems by coupling basic concepts from materials science with system design and engineering. The methodologies were validated by the fabrication and evaluation of new high temperature MEMS devices made from a novel polymer-derived ceramic material. The new results demonstrate two unique features: 1) how to hybridize computational approach with closed form models from materials science, and 2) how to account for the highly non-linear nature of temperature dependent material behavior in predicting variability. A Human-Machine-Interface that successfully predicts the remaining life of a microignitor working above 1300^{0}C, which is built upon these concepts has been demonstrated. Closed form results that link variability in temperature to variability in life-time via the activation energy of fundamental diffusion coefficients have been obtained, and validated by experiments. These results also show that a Gaussian distribution in temperature can lead to a log-normal distribution in lifetimes. More than fifteen publications, and two doctoral dissertations have resulted from this MEANS program.

Overall Objective of This MEANS Program

An interdisciplinary team at the University of Colorado is working under the Materials Engineering for Affordable Novel Systems (MEANS) program to develop a fundamental new methodology for predicting the variability in the performance of high temperature systems. This new approach, illustrated by the graphic in Fig. 1, seeks a quantitative assessment of uncertainty in life prediction by linking fundamental concepts and models from the field of materials science to system engineering.

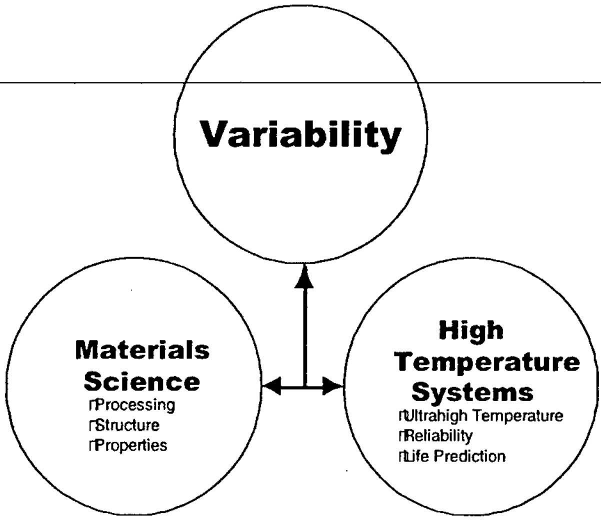


Figure 1: The goal of this MEANS program is to develop new methodologies, that combine elements of fundamental materials science and system engineering, for predicting the variability in the lifetime of high temperature systems.

Small scale high temperature systems, e.g. MEMS sensors and actuators, are serving as the model systems for experimental validation of the results. These MEMS structures are fabricated in-house from a novel polymer derived silicon carbonitride (SiCN) material, which resists creep and oxidation at ultrahigh temperatures, and which, at the same time has multifunctional properties, e.g. semiconductivity up to 1400°C.

Executive Summary

The life prediction and on-going life assessment of high temperature systems encounters several uncertainties. The uncertainty arises from several sources. These sources can be separated into four categories:

1) *Variability due to imperfect state of the microstructure.* The microstructure can vary not only due to uncertainty in the control of the processing protocol, but, in high temperature service, the microstructure is dynamic: it changes with time.

2) *Uncertainty in the operating environment.* The operating environment, especially the temperature, can affect the remaining life exponentially because the diffusion coefficient, which often controls failure mechanisms such as oxidation, deformation and fracture at high temperatures, is Arrehenius. Therefore, even a small variability in the temperature, can have a very large influence on the variability in system lifetime.

3) *Uncertainty in the basic models.* Models developed within the field of Materials Science are nearly always based upon monolithic descriptions of the microstructure. However, the microstructure is nearly always "stochastic". Credible descriptions of lifetime prediction require stochastic models of material behavior at high temperatures.

4) *Variability in shape and defects arising from imperfect manufacturing.* This aspect of variability is self-evident and, therefore, is most often considered in engineering analysis. However, in the case of high temperature systems, it is of relatively lower significance than the three issues described above.

The key achievement of this MEANS project has been to create a body of publications in major international journals that address the above issues in a fundamental way. More than fifteen papers have been published or submitted for publication. In addition two doctoral thesis, one from the Department from Aerospace Engineering and the other from Mechanical Engineering at the University of Colorado have been awarded. The following paragraphs summarize the key achievements in these publications (which are listed in the next section). The important results are shown in the graphic in Fig, 2, on the next page. The five significant results from this MEANS program are numbered as A, B, C, D and E. In each instance the theoretical analysis was accompanied by experimental validation. The Ph.D. students and post-docs (the participation of the three faculty members, Raj, Maute and Frangopol is implied) working in each of these three areas are listed, as are the publications in the literature. The publication number refers to the list given in the following section. The left column describes the topic and the middle column summarizes the key result. In the following paragraphs these results, for each topic are discussed briefly, highlighting how the present work distinguishes itself from prior work in the literature.

New Methodologies Developed

	Topics	Key Results	People & Publications
A.	MEMS Electrostatic Actuator Made from Novel High Temperature Polymer Derived Ceramic	Uncertainty in the Air-Gap, not the Distortion in the Shape of the Actuator is the Principal Source of Uncertainty	Raulli (Ph.D.) Saravanan (PostDoc) Kong (PostDoc) *Publications:* 10, 9, 5, & 2
B.	MEMS $1300^{\circ}C$ Microignitor Made from Polymer Derived Ceramic	Developed Human-Machine Interface for the Prediction of Remaining Life in Real Time	Ryu (Ph.D.) Saravanan (PostDoc) Kong (PostDoc) *Publications:* 19, 18, 16, 7, 6, 4
C.	Relating Temperature Uncertainty to Lifetime Variability via the Activation Energy for Diffusion	This "First Time" Work Shows Explicitly How Activation Energy Relates Lifetime and Temperature Variability	Jie Bai (PostDoc) Kong (PostDoc) *Publication:* 11
D.	Linking Grain Size Variability to Uncertainty in the Creep Behavior of Polycrystals	This Important New Work Develops a Stochastic Model for Predicting Transitions between Mechanisms.	Jie Bai (PostDoc) *Publications:* 15, 14
E.	Microstructure and Architectural Design of Environmental Barrier Coatings for Silicon Nitride	A New Quantitative Model for EBC Delineates the Regimes for SAFE/FAIL Design	Jie Bai (PostDoc) *Publication:* 17

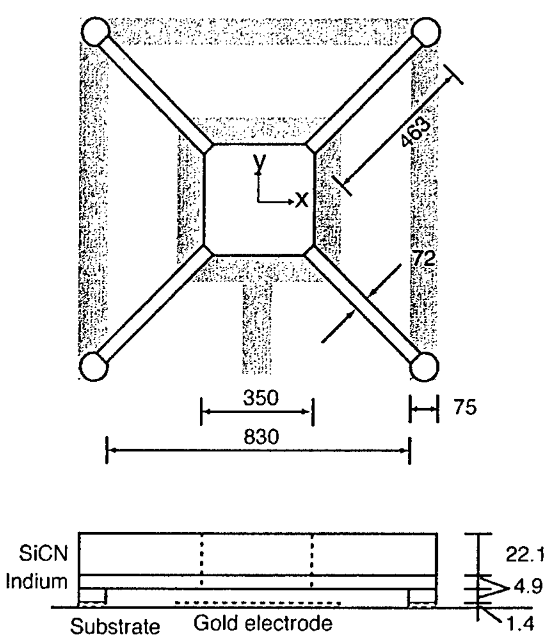
Figure 2: The five key achievements in the MEANS Program, and the people who carried them out. The publications refer to the list given in the following section.

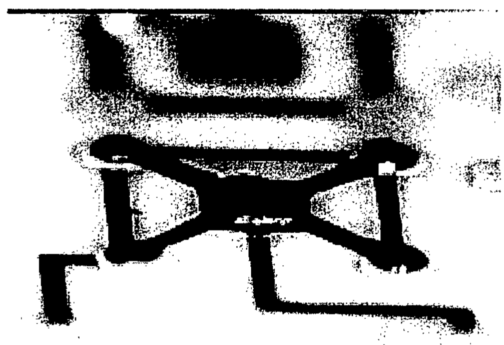
A. Electrostatic MEMS Actuator Made from a Novel High Temperature Polymer Derived Ceramic (PDC).

The PDCs are new high temperature ceramics with high potential for MEMS applications in harsh environments [Raj, et al., Am. Ceram. Soc.Bulletin, Vol 80[5], 25-30, 2001]. The PDC-MEMS are fabricated by a new process. First the MEMS device is constructed in the polymer state, and it is then pyrolyzed into the ceramic state [Pederiva et al., J. Amer. Ceram. Soc., Vol 85[9], 2181-2187, 2002]. During pyrolysis the density of the material increases two fold leading to significant shrinkage in the physical dimensions of the device. Most importantly the shrinkage can result in distortion. Therefore, we were concerned with which geometrical parameter was most critical in affecting the variability in the performance. A further concern was the variability in the processing conditions can affect the elastic modulus of the PDC.

The methodology developed to address the above issue consisted of a hybrid of numerical and closed form results. By comparing theory and experiment closed form equations were developed to estimate the deflection in the actuator as a function of its key geometrical parameters. The approximations in the analysis were shown to be reasonably valid by numerical analysis. This approach significantly simplified the computational analysis of variability against other parameters (e.g. air-gap and applied voltage). It was shown that the variability in displacement increased non-linearly with the applied voltage, that is with the displacement in the actuator. The second important result is shown in Fig. 3 below.

All dimensions in μm





The SiCN-PDC Actuator Fabricated in Raj's Ultrahigh Temperature Laboratory at the University of Colorado.

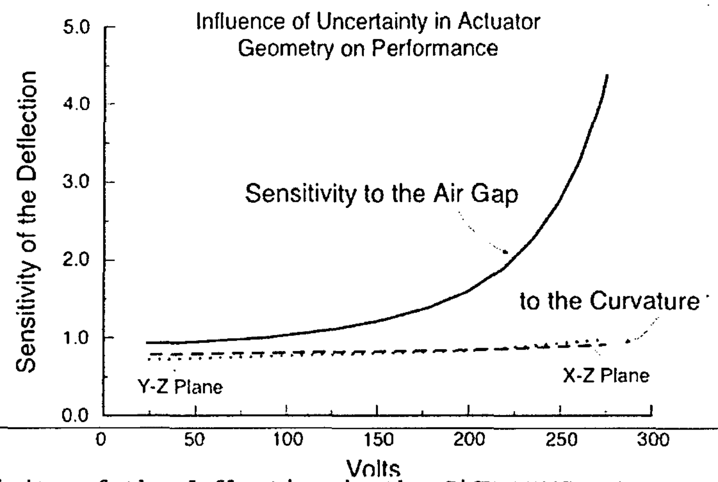
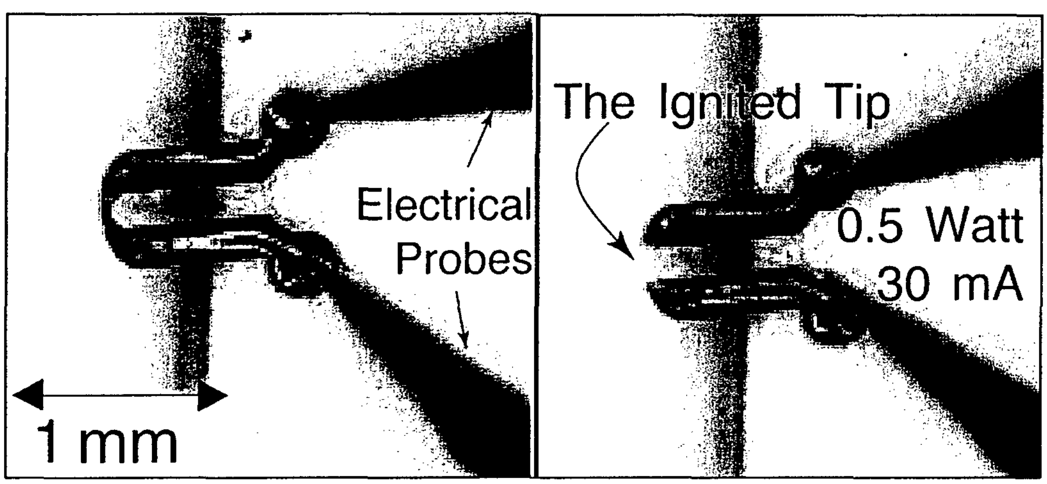


Figure 3: The sensitivity of the deflection in the SiCN MEMS-actuator to distortion in the SiCN head (characterized by curvature) and to uncertainty in the air gap. These results suggest that the manufacturing process should pay more attention to controlling the air gap.

B. Ultrahigh Temperature MEMS Microignitor Made from a Novel High Temperature Polymer Derived Ceramic (PDC).

Polymer-Derived Ceramics are multifunctional materials. These multifunctional properties, e.g. electronic semi-conductivity persist to ultrahigh temperatures. This project was undertaken to explore how well the remaining lifetime of a microignitor fabricated from SiCN-PDC could be predicted. The prediction process is dynamic since gradual oxidation at the surface of the microignitor changes its effective resistance, and therefore its temperature. The oxidation kinetics (a materials science phenomenon) was coupled to the electrical characteristics and the temperature of the microignitor (a system engineering problem) to predict the remaining life of the igniter in real time. A live human-machine-interface was developed and was shown to successfully predict the remaining life when experimentally coupled to "live' igniter operating at temperature > 1300^0C. These results are shown in Fig. 4 below.



SiCN-MEMS Temperature Sensor and Igniter

QuickTime™ and a
Video decompressor
are needed to see this picture.

Figure 4a: The architecture of the HMI. The temperature of the sensor, and the remaining life are calculated from analytical materials science based models. The HMI can also be used to control the operating parameters of the igniter/sensor such as current, temperature and the estimate of the remaining life.

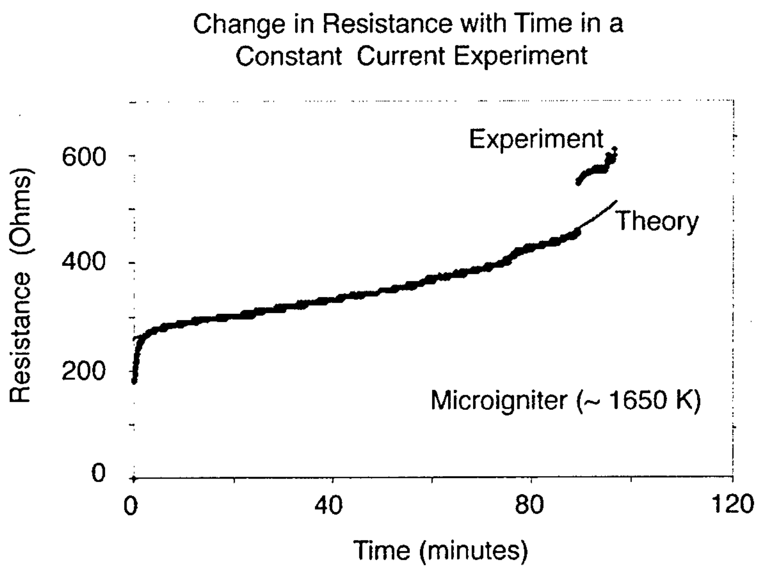


Figure 4b: The agreement between theory and experiment for the change in the resistance of the microigniter/sensor due to oxidation. The theory is based upon simple models of thermally activated oxidation, Mott's model for the temperature dependent resistance of polymer derived SiCN, and black body radiation.

C. Relating Temperature Variability to Uncertainty in the Lifetime for High Temperature System by a Closed Form Relationship.

The most significant source of uncertainty in the life prediction of high temperature system is temperature. Since the rate of the diffusion processes, which nearly always control the failure process, depend exponentially upon the temperature, the uncertainty in temperature often outweighs uncertainties arising from variability in the applied load, the geometry, and even the microstructure. This concept is highlighted in the following equation.

$$t_f = (\text{Stress Loading})(\text{System Geometry})(\text{Microstructure and Material Constants})\, e^{\frac{Q}{RT}}$$

Here Q is the activation energy, t_f is the time to failure, and T is the temperature. The key result from the MEANS work was to develop an explicit relationship between the statistical variation in temperature to the statistical variation in the time to failure. Two important results were obtained: a) that a normal or Gaussian distribution in the temperature leads to a log-normal distribution in the time to failure, and b) that the standard deviation in the Gaussian distribution for temperature is related to the standard deviation in the lifetime explicitly through the activation energy as given by the following equation

$$Q = \frac{S_t . RT_p}{\left(S_T . / T_p\right)} kJmole^{-1}$$

Here S_t is the standard deviation for the log-normal distribution of the time to failure, S_T is the standard deviation for the Gaussian distribution for temperature, and T_p is the peak or the mean temperature in the Gaussian distribution.

The relationship in the above equation was experimentally investigated by measuring the lifetime of tungsten bulbs. These data, that link the distribution of the wattage of the bulbs to their lifetimes is shown in Fig. 5 below:

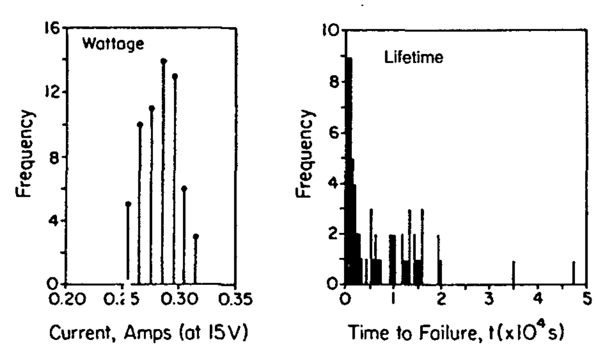


Figure 5: The distribution of temperature of tungsten filament lamps (which is directly proportional to its wattage), and the results distribution of the lifetime. Note that the first is close to a Gaussian distribution while the lifetime reflects a log-normal distribution.

When above data were analyzed by the equation given on the preceding page the following estimate of the activation energy for self diffusion in tungsten was obtained:

$$Q_{tungsten} = 664 \pm 218 kJmole^{-1}$$

This value for the activation energy encompasses the handbook value for lattice self diffusion in tungsten. This is the first time that system level distribution of lifetime data has been used to estimate a fundamental materials science parameter, the activation energy for self diffusion.

D. Integration of Power-Law and Diffusional Creep Mechanisms in Polycrystals with a Distributed Grain Size.

The purpose of micromechanical models in materials science is to relate mechanical behavior to the microstructure. The most important microstructural parameter that controls the high temperature creep behavior of polycrystals is the grain size. However, nearly all models in the literature assume the grain size to be single valued. In actuality the grain size can have a wide distribution. In the present work it is shown that the transition from diffusional creep, which is grain size dependent, to power-law creep which is grain size independent can span several orders of magnitude in strain rate. The two mechanisms can be distinguished by the stress exponent for the strain rate in the creep equation. The stress exponent, n, is unity for diffusional creep but is a high number, about 5, for power law creep. The experimental work published in the literature shows intermediate values for n, for which various explanations have been offered. The present work demonstrates that the wide range of transitional values for n can be simply explained in terms of the distribution in the grain size. One key result from the published work that shows the broadening of the transition in terms of the standard deviation for the grain size is given in Fig. 6 below.

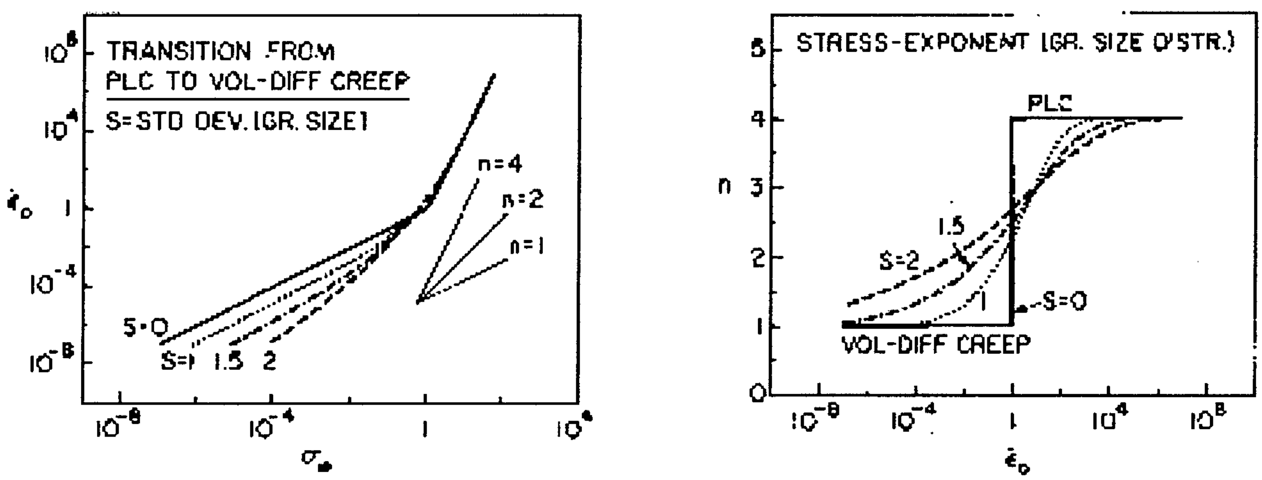


Figure 6: (left) The logarithmic stress-strain rate plots for different values of the standard deviation for the grain size distribution. Diffusional creep is assumed to be volume diffusion controlled. (right) The change in the "n" value in the transition regime, as a function of the strain rate. Note for example, that the 2<n<3 over nearly six orders of magnitude in the strain rate when S=1.5.

E. The Design of an Environmental Barrier Coating (EBC) for High Temperature Performance of Silicon Nitride.

This work shows how fundamental research that combines theory and experiment can be employed to design new materials systems for high temperature applications. In this instance a design methodology for EBCs is developed. The purpose of the EBCs is to protect the silicon nitride surface from streaming water vapor environment at very high temperatures. Without this protection the silicon nitride surface suffers weight loss from oxidation into $Si(OH)_4$ followed by volatilization of the hydroxide. The paradox is that materials that can withstand the environment streaming and humid environment of the gas turbine are transition metal oxides such as zirconia and hafnia, but these oxides have a thermal expansion coefficient that is three times greater than that of silicon nitride, which leads to spalling. The design concept developed in this work is to use a compliant columnar structure as a bond coat, as illustrated in Fig. 7 to accommodate the thermal expansion misfit without causing the coating to spall. The mechanical analysis leads to the design map shown on the right in Fig. 7, which highlights the SAFE design regime. Experiments conducted in our laboratory are consistent with these design predictions.

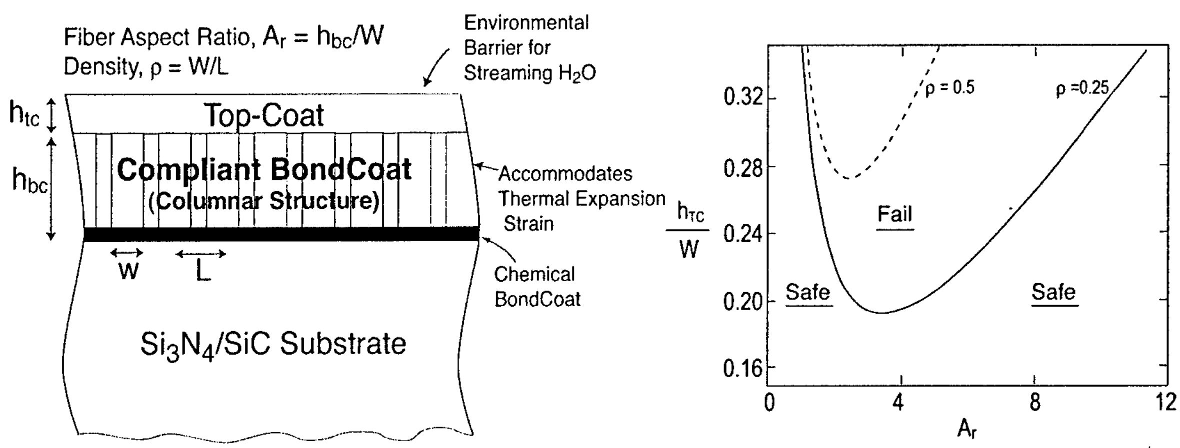


Figure 7: The design of EBC consists of an oxide as a topcoat, which resists the enviroment and a compliant bond coat which accommodated the thermal expansion mismatch. The figure on the right shows the design map for the coating, pointing out the regimes where the aspect ratio of the columns, their width and the thickness of the topcoat are safe against fracture and delamination.

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Publications and Ph.D. Dissertations

Ph.D. Theses

Hee-Yeon Ryu, "Semiconductive Behavior of and the Fabrication of a p-n Junction Diode from Amorphous Polymer-Derived Ceramics", Ph.D. Thesis, December 2005, Department of Mechanical Engineering, University of Colorado at Boulder.

Michael Raulli, "Optimal Design for Electrostatically Actuated Microsystems", Ph.D. Thesis, Department of Aerospace and Engineering Science, University of Colorado at Boulder, May, 2004.

Publications

2006

19. "A p-n Junction Diode Constructed from B and N Doped Polymer Derived Silicon and Carbon Based Amorphous Ceramic", H.-Y. Ryu and R. Raj, in preparation.

18. "Semiconductive Behavior of Polymer-Derived Silicon Oxycarbonitide (SiCNO) at Ultrahigh Temperature", H.-Y. Ryu and R. Raj, in preparation.

17. "Mechanical Design for Accommodating Thermal Expansion Mismatch in Multilayer Coatings for Environmental Protection at Ultrahigh Temperatures", J. Bai, K. Maute, S. R. Shah and R. Raj, *Journal of American Ceramic Society*. in review (2006).

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Transitions and Awards

None.