Aerospace Materials for Extreme Environments

Presented at the AFOSR Spring Review 2013, 4-8 March, Arlington, VA.
NAME: AEROSPACE MATERIALS FOR EXTREME ENVIRONMENTS

BRIEF DESCRIPTION OF PORTFOLIO:
To provide the fundamental knowledge required to enable revolutionary advances in future Air Force technologies through the discovery and characterization of materials that can withstand extreme environments.

LIST SUB-AREAS IN PORTFOLIO:

• Theoretical and computational tools that aid in the discovery of new materials.
  • Ceramics
  • Metals
  • Hybrids (including composites)
• Mathematics to quantify the microstructure to Predictive materials Science
• Physics and chemistry of materials in highly stressed environments
• Experimental and computational tools to address the complexity of combined external fields at extreme environments.
OUTLINE

I. Predictive Materials Science
   Bulk Metallic Glasses
   Carbides (SiC, TaC, Ta$_4$C)
   Textile Based Hybrid Composite

II. Materials Far from Equilibrium
    Micro-Architectured Surfaces
    Surface Catalysis at Extreme Environment

III. Challenges, Motivations and New initiatives.
“The Dream:”
Computational Material Design
W. Windl (OSU), K. Flores (WASHINGTON U.), D. Hoffmann (CALTECH), E. Marquis (U. MICHIGAN)

Pick a set of structures & compositions
Calculate their properties

“Optimal?”
Yes
No

Improve structure/composition

Experimental fabrication & testing
Ab-Initio Calculations

**Input:**

\[ H\psi = E\psi \]

**Output:**

Structure, Energy

Band structure

EELS spectra

Kinetic parameters

Thermal properties

Mechanical prop’s

W. Windl (OSU), K. Flores (WASHINGTON U.), D. Hoffmann (CALTECH), E. Marquis (U. MICHIGAN)
Calculating Glass-Forming Ability

W. Windl (OSU), K. Flores (WASHINGTON U.), D. Hoffmann (CALTECH), E. Marquis (U. MICHIGAN)

Crystallization inhibitors:
1. Driving Force: Icosahedra
2. Kinetics: Viscosity (fragility)

Direct Measurement:
Critical Cooling Rate
- Not computationally feasible
- Real time: 1 ms
- 20 CPUs: 200 Years

Good packing density
No crystalline symmetry (5-fold)

Stabilize liquid; don't lead to crystal nuclei

Interatomic Potentials

W. Windl (OSU), K. Flores (WASHINGTON U.), D. Hoffmann (CALTECH), E. Marquis (U. MICHIGAN)

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**Chosen Method:** Green-Kubo

\[
\eta = \lim_{t \to \infty} \frac{V}{k_B T} \int_0^t \langle P_{\alpha\beta}(t_0 + s) P_{\alpha\beta}(t_0) \rangle ds
\]

\[
\eta = \eta_0 \exp \left( \frac{T_0}{T - T_0} \right)
\]

- Vogel-Fulcher-Tammann relation used to model viscosity.
- Known to describe BMGs

**Glass Formable regions**

Ward, Agrawal, Flores, Windl (to be published)

- Al_{66.4}Ni_{25}Zr_{8.6}
- Glassy & Ductile!
Metallic glass electrode - A closer look

A. Taylor (YALE)
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III. Challenges, Motivations and New initiatives.
Direct MD prediction compared to fracture and dislocation nucleation models for SiC

D. Warner (CORNELL U.)

- Activation energy predicted by the continuum model
- Elastic constants(T) + surface energies(T) + unstable stacking fault energies(T) +

\[
\frac{Q_{3D}}{k_B T} = \ln\left(\frac{k_B T N \alpha_0}{-\dot{K}_I \frac{dQ_{3D}}{dK_I}}\right)
\]
Orientation Relationship of TaC and Ta₄C₃ phase

G. Thompson (U. ALABAMA)

TaC FCC-like structure yields **FOUR {111} variants** – leads to equivalent precipitation habit planes for Ta₄C₃ -criss-cross pattern morphology of laths

Fracture Toughness with Vol Ta₄C₃ Correlation

Volume % Ta₄C₃

Loss of C on {111} plane to yield Ta₄C₃
• Deviation from linearity
• Pop-in or displacement bursts, buckling, cracking
• Max CRSS on \{111\} planes
• Plastic flow due to formation of slip bands
• Shearing and cracking rather than catastrophic fracture specially in 6\(\mu\)m pillars
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III. Challenges, Motivations and New initiatives.
Highly integrated research program: graduate students & post docs

35 journal publications; 23 plenary/keynote presentations at international conferences (including Mueller award lecture at ICACC'12, 4 lectures at 2012 Ceramics Gordon Conference); 12 conference proceedings; 25 other conference papers

Active collaborations with 10 universities.

Sharing of data & modeling with AFRL, Army, NASA, Rolls Royce


www.nhsc-ms.org
Statistical description of geometry

- Tow paths
- Cross-sectional areas
- Orientation of cross section
- Deviations from mean
- Correlation lengths

analogue of Markov chain method for tow axis coordinates ⇒ stochastic irregular elliptical cylinder for each tow

problem: interpenetration
solution: enforce known topology of textile

create replicas of textile reinforcement with same statistics as those measured

3-D image of C-SiC composite

computational mesh from geometric model
In-Situ 3D Tomography at 1750°C

R. Ritchie (UC BERKELEY)

In-situ testing SiC<f>/SiC<sub>m</sub> at 25°C

In-situ testing SiC<f>/SiC<sub>m</sub> at 1750°C

Nature of Materials 2013
Comparison of Simulation and in-situ Tomography

D. Marshall, B. Cox (TELEDYNE), F. Zok (UCSB), Q. Yang (U. MIAMI), R. Ritchie (UC BERKELEY)
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Materials Far from Equilibrium: Micro-Architectured Surfaces

N. Ghoniem / UCLA

Plasma Erosion & Modeling (Wirz - UCLA).
Plasma Source Development (Goebel – JPL/UCLA)
Materials Characterization (Thompson - UA).
High Heat Flux Testing (Ghoniem - UCLA).
Manufacturing of Micro-architectured Materials (Williams - ULTRAMET).
Multiscale Modeling of Material Damage (Ghoniem - UCLA).

Hole formation
[1994(MJ/m²), 0.2 (MW/m²)]
Damage for Heat flux < 1 MW/m$^2$

N. Ghoniem (UCLA), Y. Raitses and I. Kaganovich (PRINCETON), G. Thompson (U. ALABAMA), B. Williams (ULTRAMET)

- No damage: [128(MJ/m$^2$), 0.02 (MW/m$^2$)]
- Fine hole formation: [641(MJ/m$^2$), 0.2 (MW/m$^2$)]
- Limited damage: [721(MJ/m$^2$), 0.4 (MW/m$^2$)]
- Hole formation: [360 (MJ/m$^2$), 0.2 (MW/m$^2$)]
- Hole formation: [1441(MJ/m$^2$), 0.2 (MW/m$^2$)]
- Hole formation: [1994(MJ/m$^2$), 0.2 (MW/m$^2$)]
Hopping of the adatom is the dominant mechanism on (110) surface. The formation and the movement of surface crowdions contributes mostly on (001) surface. Exchange mechanism is also important on (001) surface, biaxial strain can manipulate the relative contribution of Path-Ex and Path-Crow.

MD simulation indicates that the bombardment of a Xe atom induces ballistic diffusion of W atoms (W1 in the graph) and causes the formation and evolution of crowdions near the surface.

$\rho(r)$ of surface crowdion indicates the high mobility and strong anistropy of its movement.

Snapshots of the bombardment of a Xe atom (KE = 100 eV) on W(001) surface at $T = 200$ K.
Vacancy Production in Surface Layers Leads to Surface Instabilities

N. Ghoniem (UCLA)

\[ \nabla \cdot U = -zm \Delta \xi, \]

\[ \frac{c^2 h^2}{12} \Delta^2 \xi - \frac{c^2}{2} \sigma_{ij} \partial_{ij} \xi + \frac{\theta_v}{\rho h} (C_+ - C_-) = 0, \]

\[ \frac{\partial_t C}{C} = D_\perp \partial_{zz}^2 C + D_\parallel \Delta C - \frac{C}{\tau} + \nabla \frac{\theta_v D_\parallel C}{kT} \nabla (\nabla \cdot U) \]

Fig. 14.20. Groove patterns seen under a biaxial stress state in which one side is under tension and the other is under compression [713].


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Surface Catalysis Testing in a 30kW ICP Torch Facility
D. Fletcher (U. VERMONT), J. Marshall (SRI), M. Akinc (ISU), J. Prepezko (U. Wisconsin)

**Approach:** Compare surface-catalyzed reaction efficiencies for flexible and rigid materials with same elemental composition by measuring relative atom density and temperature gradients above material samples in the 30 kW ICP Torch Facility using laser induced fluorescence.

\[ N + N + [s] \rightarrow [s] + N_2 \]

Spatially resolved measurement location

Flight environment to ground facility testing comparison
Relative N atom concentration measurements for quartz and monolithic $\alpha$-SiC

Increasing concentration toward wall indicates low surface catalyzed reaction efficiency

From the $n_N$ plot, it can be seen that $\alpha$-SiC ($T_w = 1300$ K) is of comparable catalycity to quartz ($T_w < 1000$ K)
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Demkov 2010

Inoue 2009

Heidger 2012

Electron Energy Loss Spectroscopy

Demkov: Diffuse Interface

Inoue: Stoichiometry of Hf$_{1-x}$O$_{2-x}$

Heidger: Termination

Interfacial dielectric response

A. Demkov, unpublished work
SUMMARY

I. Predictive Materials Science

Bulk Metallic Glasses
Carbides (SiC, TaC, Ta₄C)
Textile Based Hybrid Composite (NHSC)
2012 MURI: Mosaic of Structure (CMU): Descriptor Challenge (wt. Dr. Fahroo)
2012 MURI: Atomic Scale Interface (LEHIGH) / (Dr. Shifler / ONR)
2013 MURI: Peridynamics (wt. Drs. Stargel & Fahroo)

II. Materials Far from Equilibrium

Micro-Architectured Surfaces
Surface Catalysis at Extreme Environments
2013 BRI: Layered Structured Materials (2D E-Gas)

III. Challenges, Motivations and New initiatives

2012 MURI: Template-Directed Directionally Solidified Eutectic Metamaterials
2013 MURI: Magneto-Electric Energy Conversion Materials and Terahertz Emission in Unbiased Dielectrics (wt. Dr. Luginsland)
2013 BRI: Metal Dielectric Interface: Charge Transfer in Heterogeneous Media under Extreme Environments (wt. Dr. Luginsland)