Design and Evaluation of Environmental Barrier Coatings for Protection of Ceramic Matrix Composites in Hydrogen-Based Turbines

NATIONAL ENERGY TECHNOLOGY LABORATORY

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U.S. DEPARTMENT OF ENERGY

Disclaimer

Acknowledgements

Co-Authors

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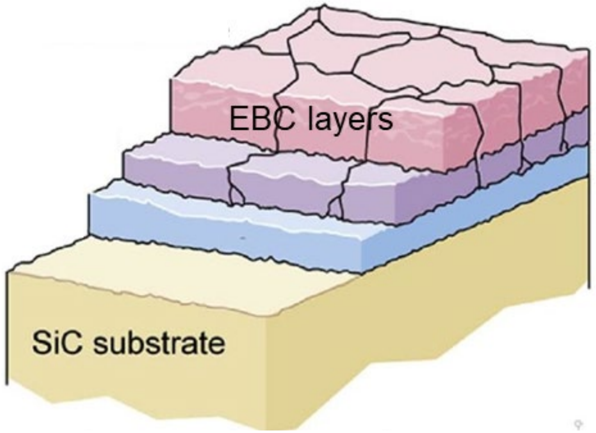
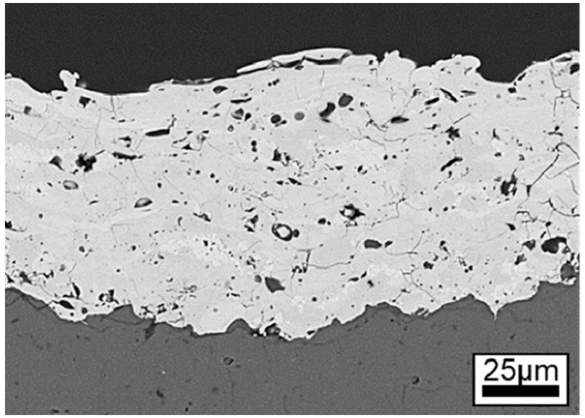
Background and Motivation

High efficiency hydrogen gas turbines

- Switching from natural gas to **hydrogen as a fuel** in industrial gas turbines requires materials with **increased temperature capability**.
- SiC-based ceramic matrix composites (**CMCs**) are among the most promising materials available **for replacing superalloys** in the hottest portions of hydrogen turbines.





- CMCs **require environmental barrier coatings (EBCs)** to protect the SiC material from reaction with the harsh combustion environment.
- Hotter temperatures and higher water vapor contents in hydrogen turbines places **increased reliance on EBCs** for long term durability.

Project Overview

Three main aspects:

1. **Computational design** of new and improved environmental barrier coating (EBC) materials to protect ceramic matrix composites (CMCs) in future hydrogen gas turbines.

2. Capability development and **performance evaluation** of current EBCs and NETL-designed EBCs in hydrogen turbine environments.

3. **Damage modeling** to predict lifetime and guide design of new and improved EBCs. **(see poster!)**

Overarching Goal: Enable use of CMCs in high efficiency hydrogen gas turbines.

Background on EBCs

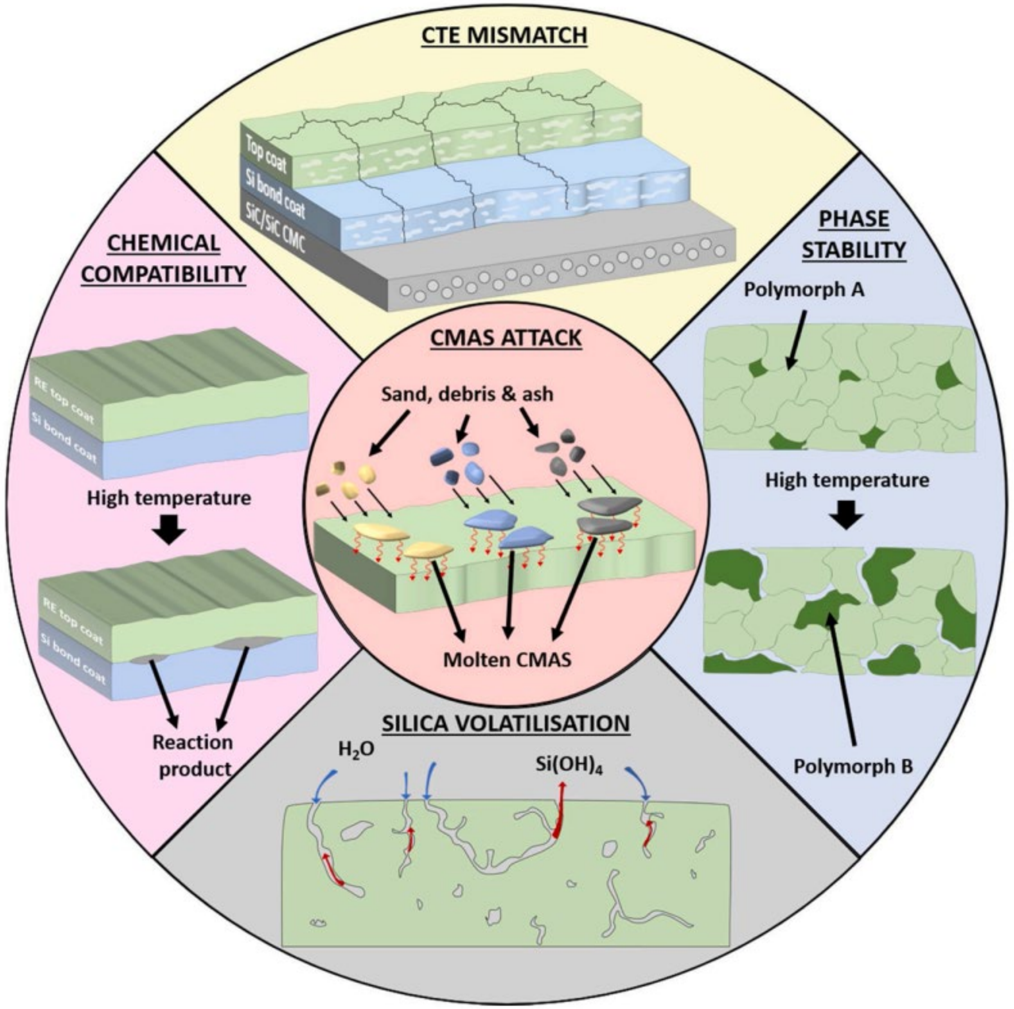
Complex Materials with Many Design Requirements

An ideal EBC should…

- Resist corrosion by **steam**
- Resist corrosion by **molten deposits**
- **Limit oxidation** of underlying material (CMC or bond coat)
- Reduce thermal flux to underlying CMC (act as a **thermal barrier**)

While…

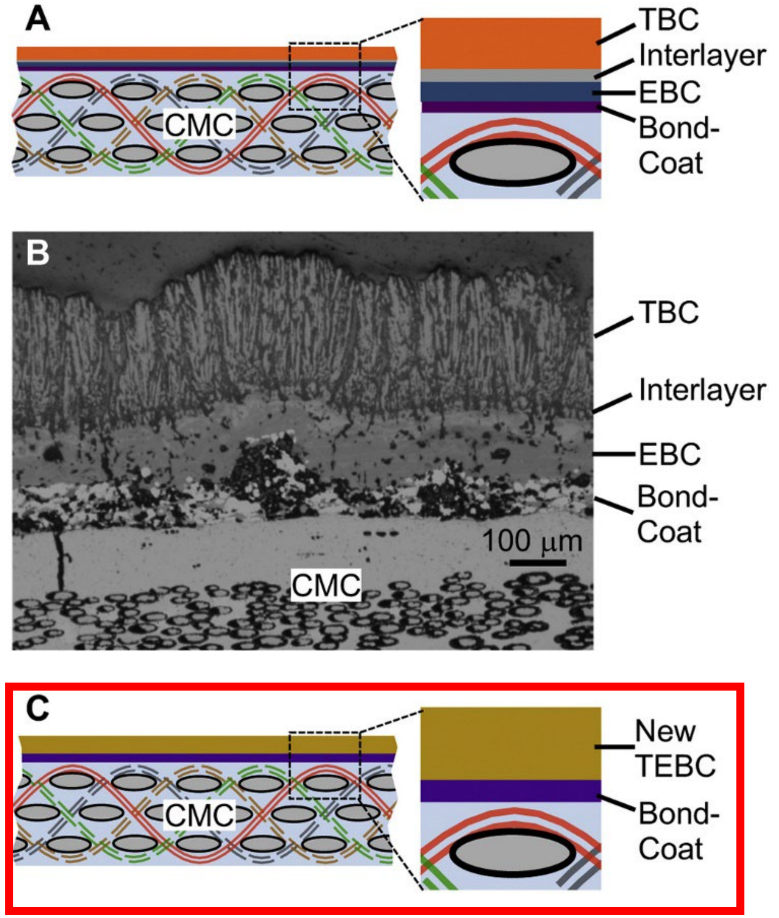
- Minimizing **stresses** induced during high temperature operation:
    - Coefficient of thermal expansion (**CTE**) mismatch
    - **Phase stability**
    - **Interfacial reactions**
- Possessing some **toughness** to handle these stresses without inducing coating failure



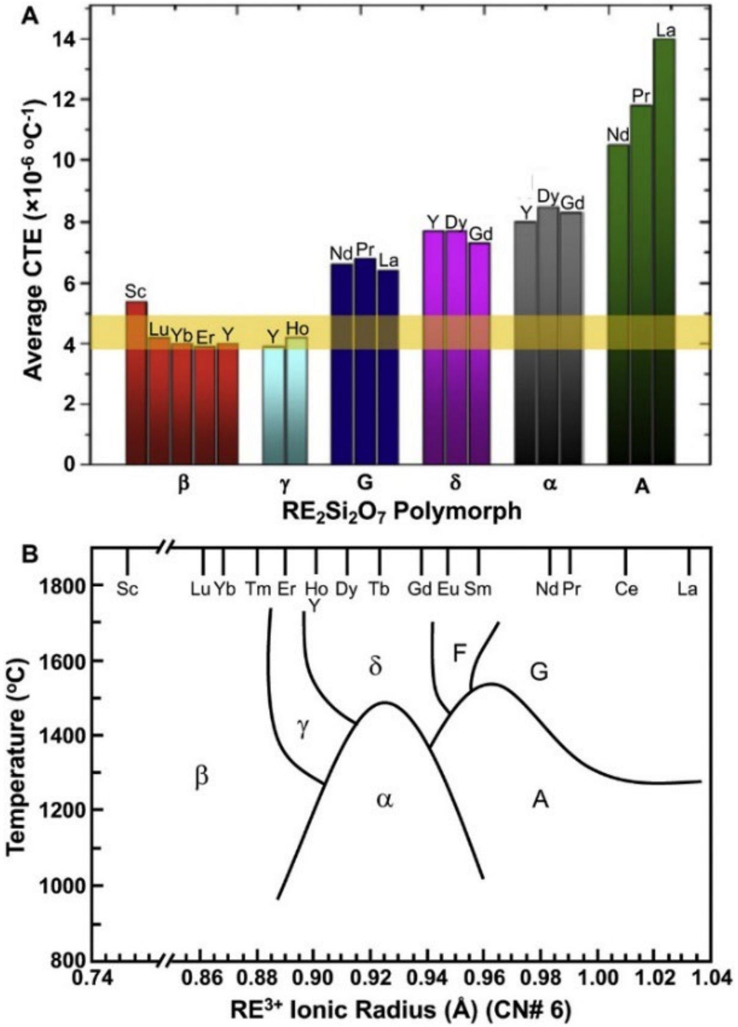
D. Tejero-Martin, C. Bennett, T. Hussain J. Eur Cer. Soc. 41, (2021) 1747-1768

Coating Design Strategy

Initial focus: multicomponent rare earth disilicate ($RE_2Si_2O_7$) material system



L.R. Turcer, N.P. Padture, Scripta Mater. 154 (2018) 111-117



Benefits

- CTE match with CMC
- Phase stability at high temperatures
- Fracture toughness
- Corrosion resistance against water vapor and CMAS
- Potential for low thermal conductivity (< 1 $Wm^{-1}K^{-1}$)

Approach

Use first principles density functional theory calculations to predict:

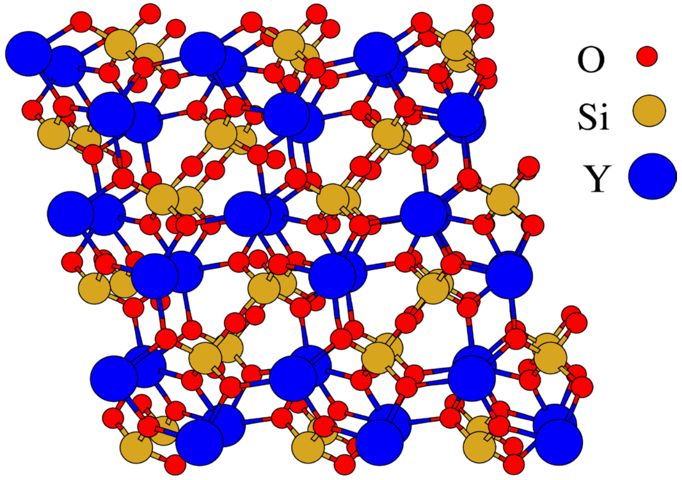
- Structure
- Lattice thermal conductivity
- Coefficient of thermal expansion
- Temperature-dependent elastic properties

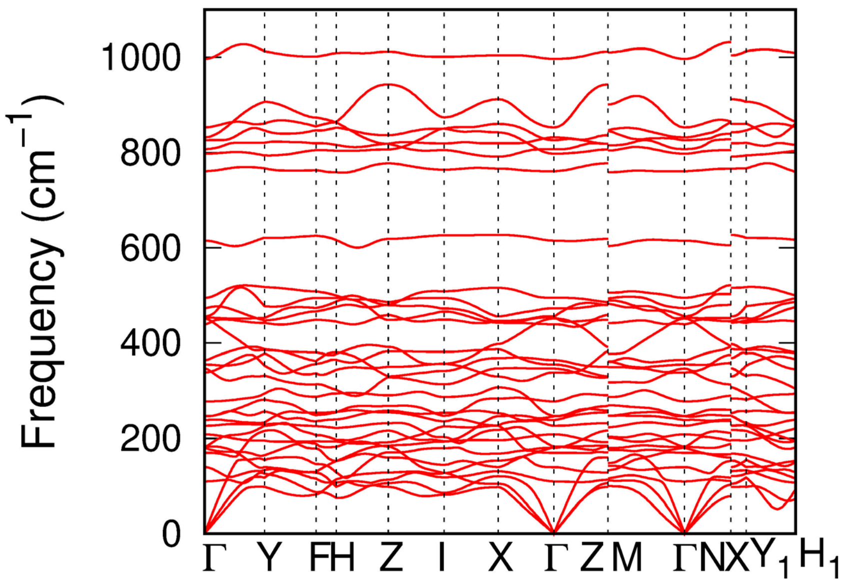
Phonon Dispersion and partial DOS

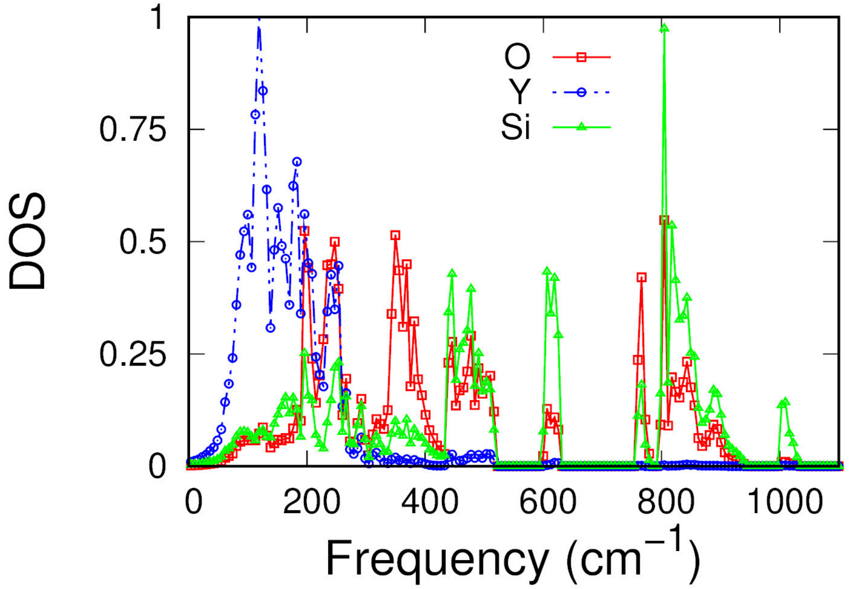
Showing $Y_2Si_2O_7$ as an example

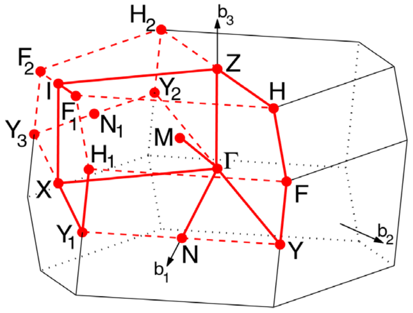
[14] L. Chaput, A. Togo, I. Tanaka, and G. Hug, Phonon-phonon interactions in transition metals, Phys. Rev. B 84 (2011) 094302.

$$D_{ij}^{\alpha\beta}(\vec{q}) = \frac{1}{\sqrt{m_i m_j}} \sum_{l'} \Phi_{l_i l'_j}^{\alpha\beta} e^{i\vec{q}R_{l'}}$$









MCLC$_3$ path: Γ-Y-F-H-Z-I-X-Γ-Z|M-Γ-N|X-Y$_1$-H$_1$|I-F$_1$

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

- Calculating phonon dispersion allows deriving **CTE** and **thermal conductivity.**
- Similar approaches can be used for other $RE_2Si_2O_7$ compounds **and their mixtures.**

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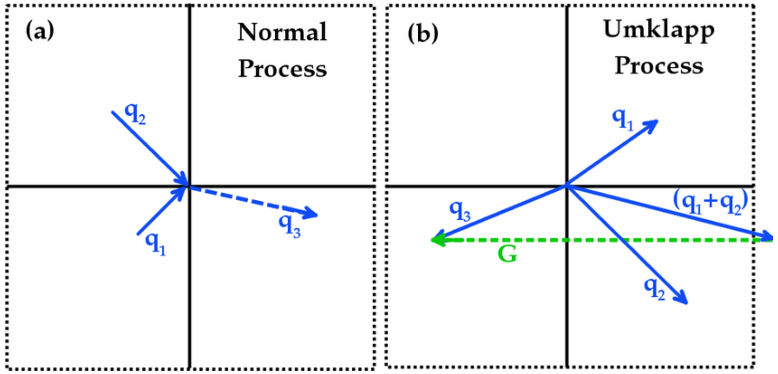
Thermal Conductivity Calculations

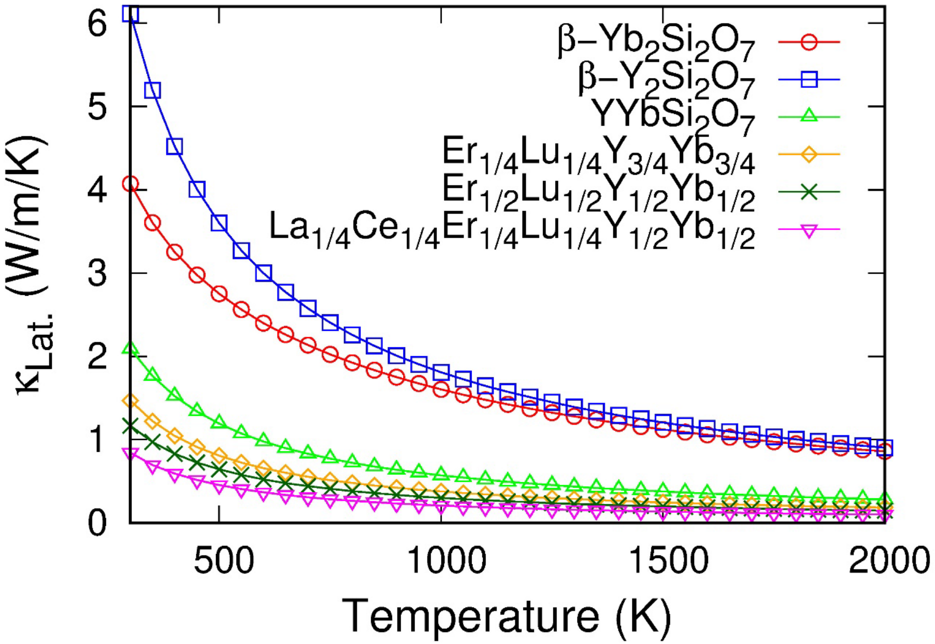
Ultralow thermal conductivities predicted for various multicomponent $RE_2Si_2O_7$

Methods

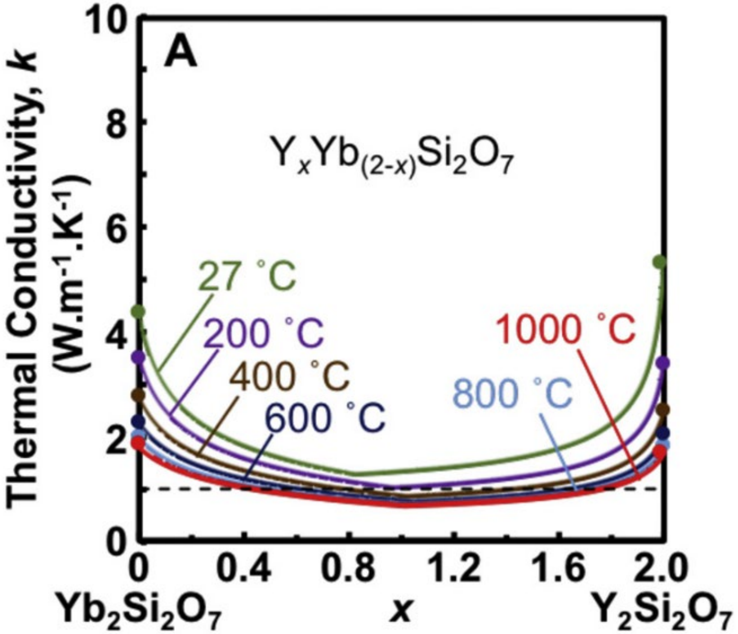


- Debye-Callaway model
- Normal phonon scattering
- Umklapp phonon–phonon scattering
- Not considered: impurity, boundary scatterings.

Results



Literature



- The lattice thermal conductivity of $Yb_2Si_2O_7$, $Y_2Si_2O_7$, and $YYbSi_2O_7$ agree well with literature.
- **$Er_{1/4}Lu_{1/4}Y_{3/4}Yb_{3/4}$ and $La_{1/4}Ce_{1/4}Er_{1/4}Lu_{1/4}Y_{1/2}Yb_{1/2}$ show even lower lattice thermal conductivity.**

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Thermal Expansion Calculations

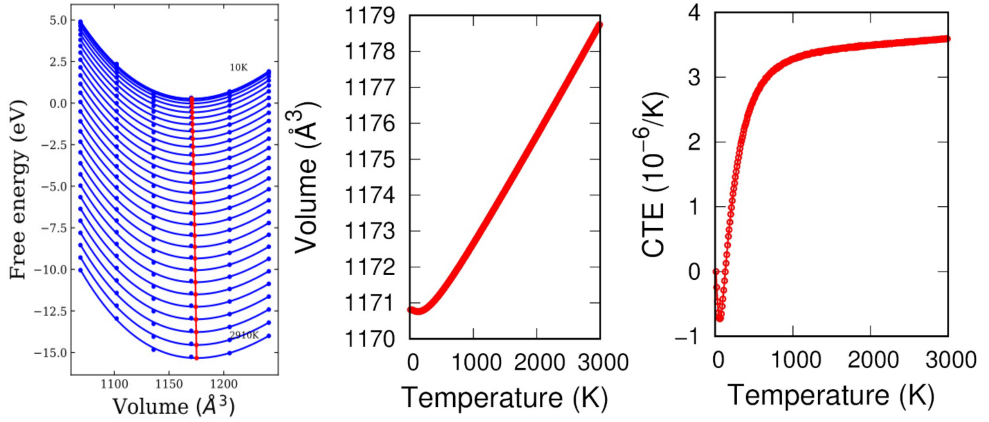
Coefficient of thermal expansion (CTE) can be finely tuned to match SiC CMCs

Methods

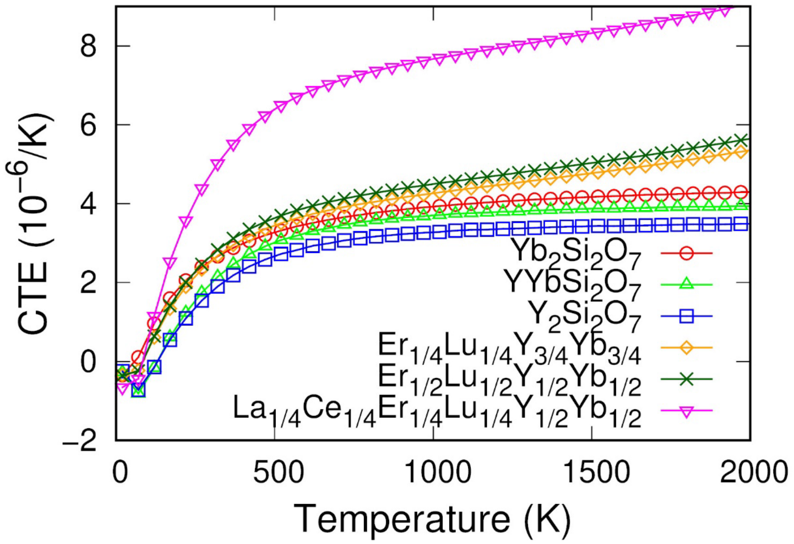
Quasi-harmonic Approximation

$F_{total}(T,V) = E_{DFT}(V) + F_{vib}(T,V).$

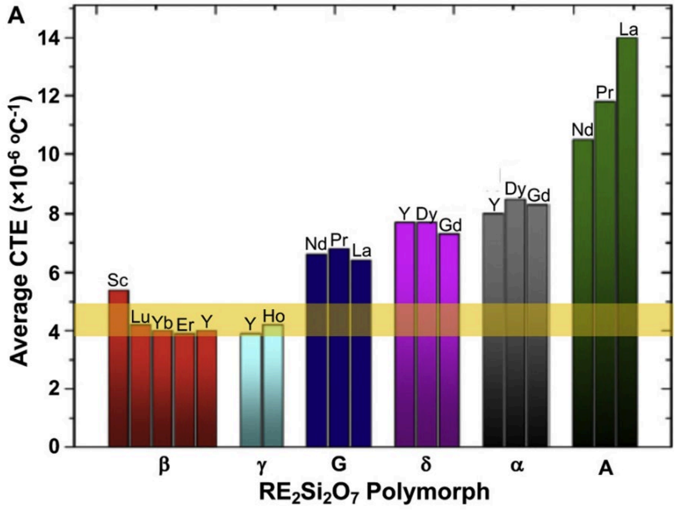
$$F_{\text{vib}} = k_B T \int d\nu\, g(\nu) \ln\left[2\sinh\frac{h\nu}{2k_B T}\right], \quad \beta = \frac{1}{V}\frac{\partial V}{\partial T}$$



Results



Literature



- Calculated CTEs of single component compounds ($Yb_2Si_2O_7$ and $Y_2Si_2O_7$) show **excellent agreement with literature.**
- $Er_{1/4}Lu_{1/4}Y_{3/4}Yb_{3/4}$ exhibits very **close match with SiC** while $La_{1/4}Ce_{1/4}Er_{1/4}Lu_{1/4}Y_{1/2}Yb_{1/2}$ is much higher.

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Mechanical Property Calculations

Calculate elastic constants

Taylor series of potential energy:

$$E(\mathrm{V},\delta) = E(V_0,0) + V_0\left(\sum_i \tau_i \xi_i \delta_i + \frac{1}{2}\sum C_{ij}\,\delta_i \xi_j \delta_j \xi_j\right) + O(\delta^3)$$

$$c_{ij} = \frac{1}{V_0}\frac{\partial^2 E}{\partial \delta_i \partial \delta_j}$$

Elastic stability criteria:

$C_{ii} > 0$ (i=1,2,3,4,5,6)
$C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0$
$C_{33}C_{55} - C_{35}^2 > 0;\ C_{44}C_{66} - C_{46}^2 > 0;\ C_{33} + C_{33} - 2C_{23} > 0$
$C_{22}\left(C_{33}C_{55} - C_{35}^2\right) + 2C_{23}C_{25}C_{35} - C_{23}^2C_{55} - C_{25}^2C_{33} > 0$

$2[C_{15}C_{25}(C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} -$
$C_{12}C_{23}) + C_{25}C_{35}(C_{11}C_{23} - C_{12} * C_{13})]$- $[C_{15}C_{15}(C_{22}C_{33} - C_{23}^2) +$
$C_{25}C_{25}(C_{11}C_{33} - C_{13}^2) + C_{35}C_{35}(C_{11}C_{22} - C_{12}^2)]+ gC_{55} > 0$
$g = C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 + C_{12}C_{13}C_{23}$

Derive mechanical properties

Compliance:

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\ C_{12} & C_{22} & C_{23} & 0 & C_{25} & 0 \\ C_{13} & C_{23} & C_{33} & 0 & C_{35} & 0 \\ 0 & 0 & 0 & C_{44} & 0 & C_{46} \\ C_{15} & C_{25} & C_{35} & 0 & C_{55} & 0 \\ 0 & 0 & 0 & C_{46} & 0 & C_{66} \end{pmatrix} \qquad S_{ij} = C_{ij}^{-1}$$

Voigt:

$$B_V = \frac{1}{9}[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})]$$

$$G_V = \frac{1}{15}[C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})]$$

Reuss:

$$B_R = [S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23})]^{-1}$$

$$G_R = [4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})]^{-1}$$

Young's Modulus:

$$E = \frac{9GB}{3B + G}$$

Poisson's ratio:

$$\nu = \frac{3B - 2G}{2(3B + G)}$$

Vickers Hardness:

$$H_V = 1.887\left(\frac{G}{B^2}\right)^{0.585}$$

Intermetallics 19, (2011) 1275.

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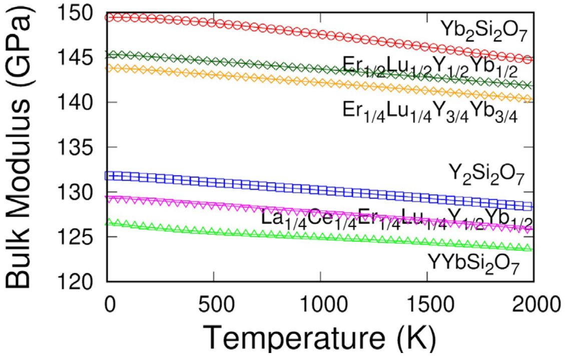
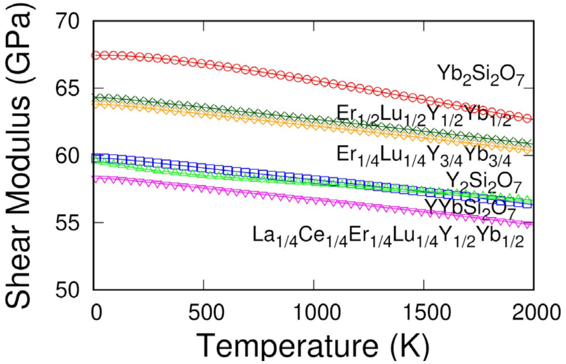
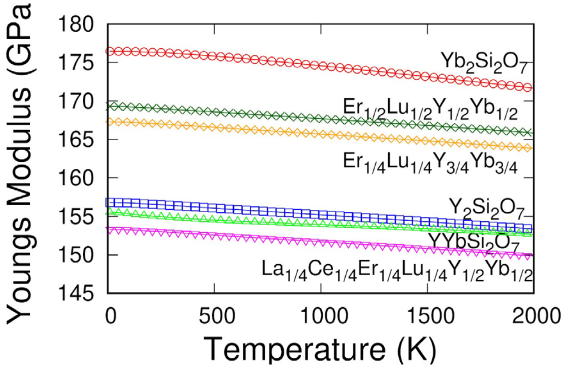
Mechanical Property Calculations

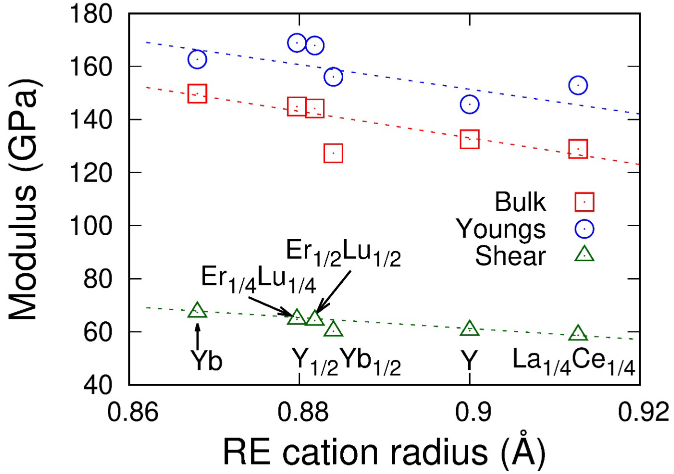
Temperature dependent moduli





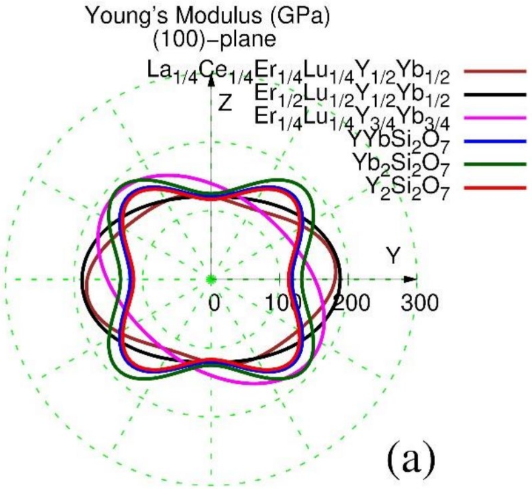


Effect of RE mixture



Negative correlation of moduli with radius of RE element.

Elastic anisotropy



Elastic anisotropy plays an important role in understanding the formation of microcracks within coatings:
A low modulus corresponds to a direction with low fracture energy.

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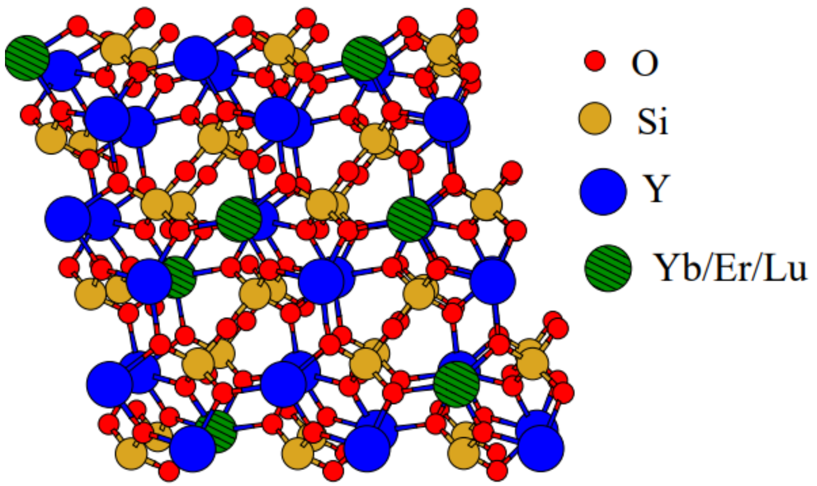
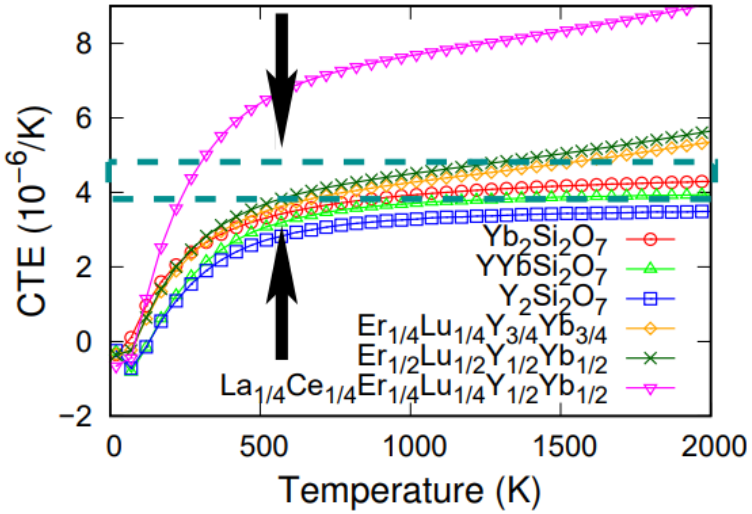
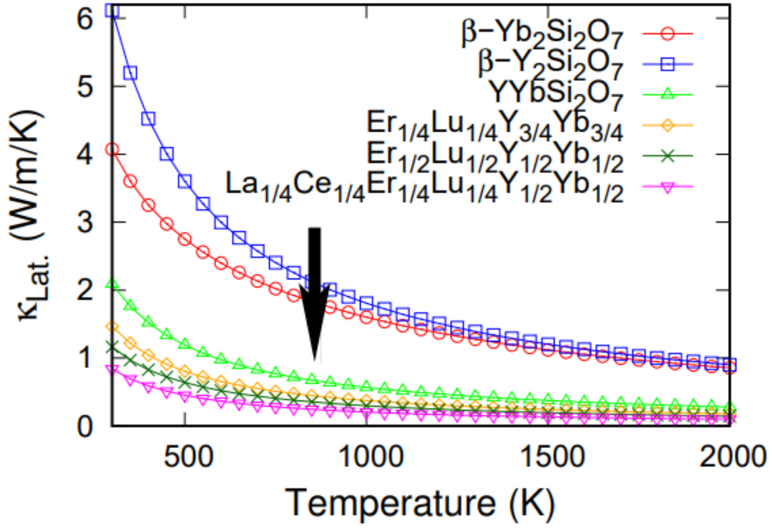
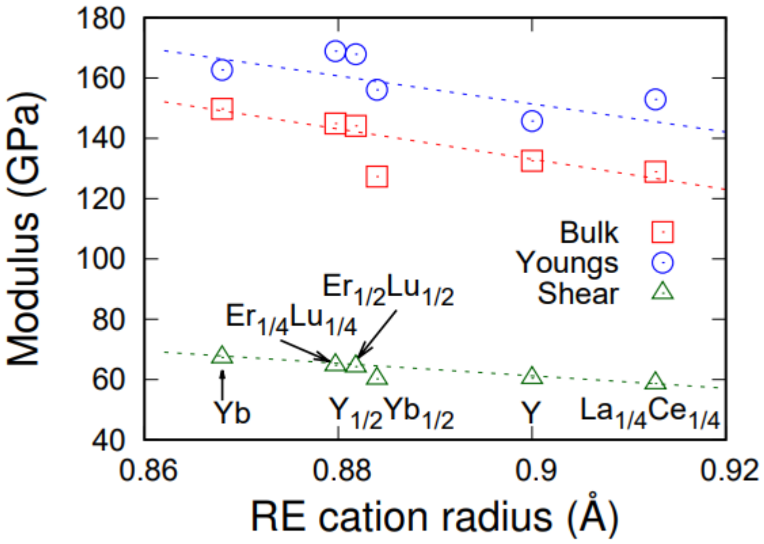
Coating Design Summary









- Combinatory chemistry and first-principles DFT based methods used to design new $RE_2Si_2O_7$ materials with:
  - **CTE match with SiC**
  - **Low thermal conductivity**
  - **Good mechanical properties** (comparable to $Yb_2Si_2O_7$)
- Ongoing work involves optimizing additional important coating properties, such as oxygen diffusion.

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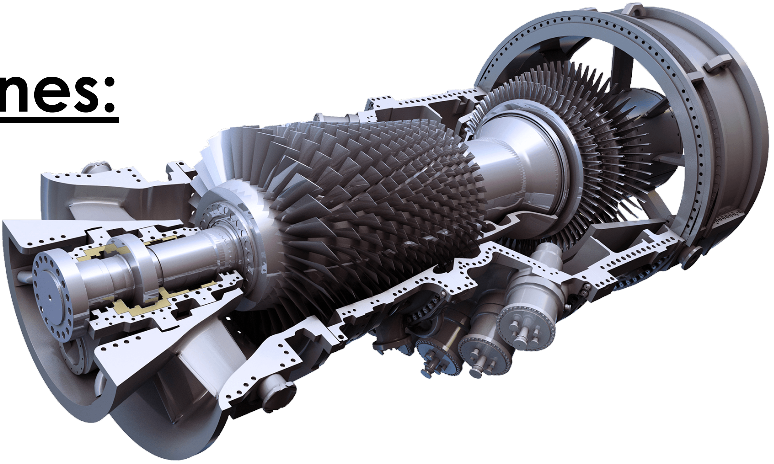
Background: T/EBC Performance Testing

Available techniques for evaluating T/EBC materials

Industrial gas turbines:

- ✓ Ultrahigh temperature
- ✓ Complex gas mixture
- ✓ High velocity
- ✓ High pressure
- ✓ Thermal gradient
- ✓ Long durations

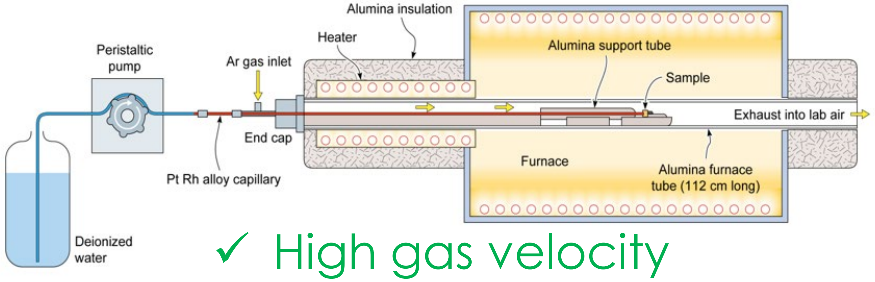


Closely simulating gas turbine combustion conditions is **extremely challenging**, yet important for evaluating coating performance.

Burner rigs

- ✓ High gas velocity
- ✓ Thermal gradient
- × Atmospheric pressure
- × Temperature limitations

Steam-jet furnace



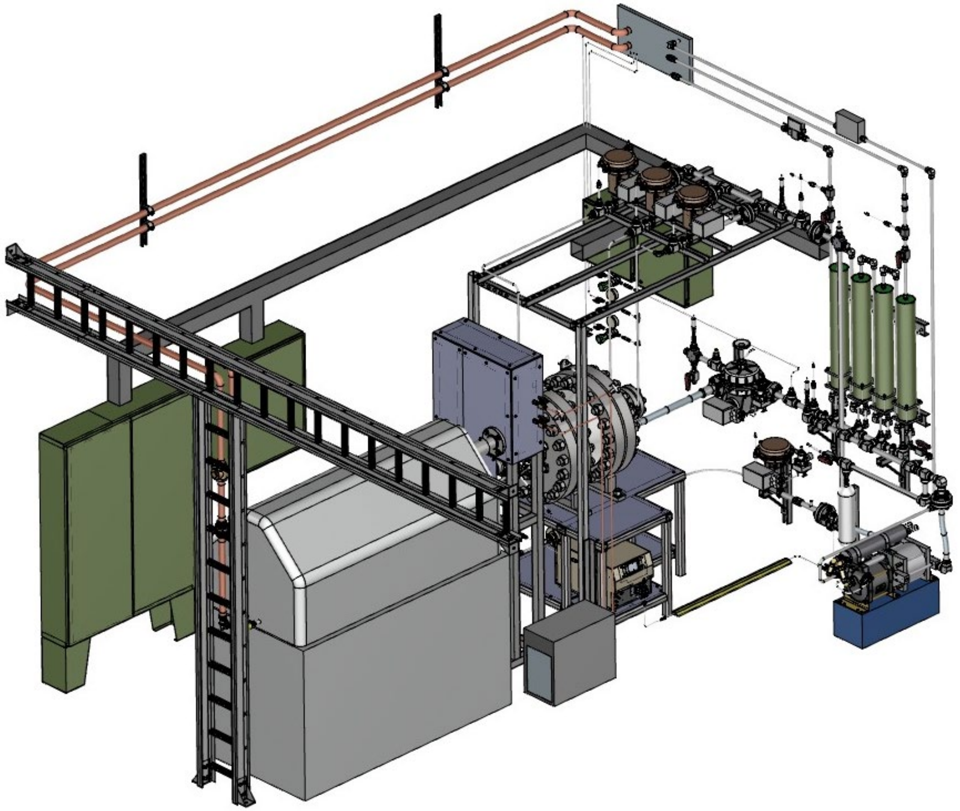
- ✓ High gas velocity
- × Fixed environment
- × Atmospheric pressure
- × No thermal gradient

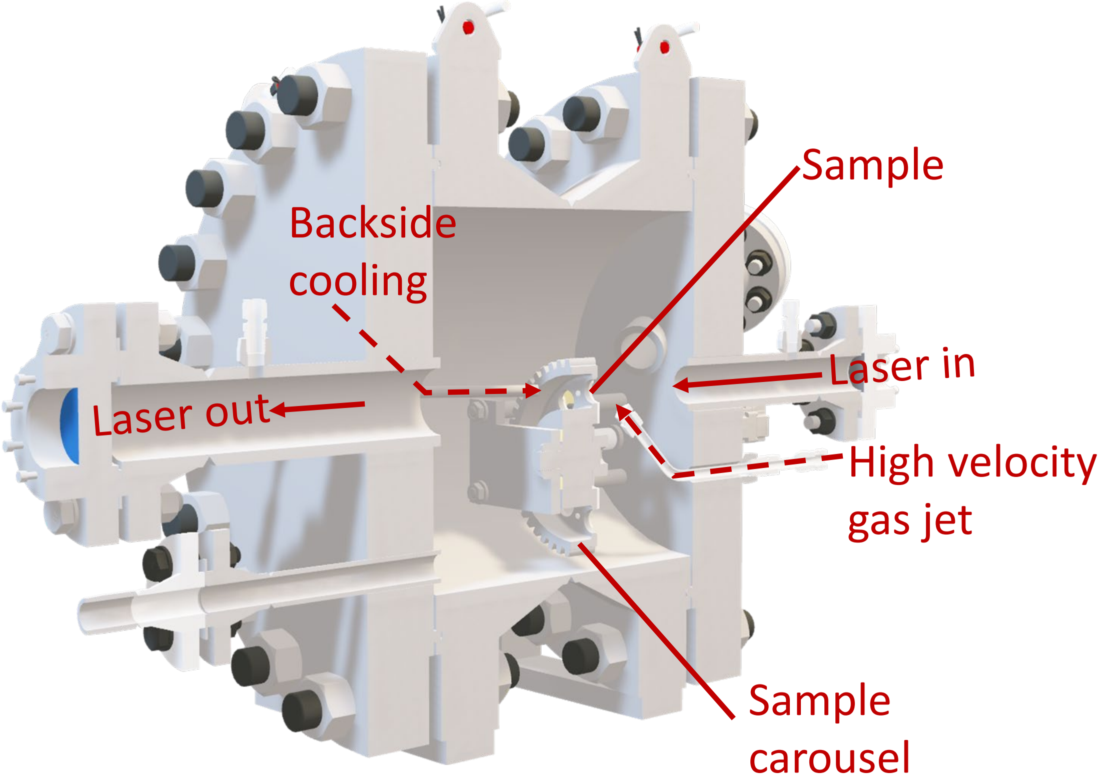
Furnace testing

- ✓ Controllable environment
- × Low gas velocity
- × Atmospheric pressure
- × No thermal gradient
- × Sample contamination

NETL Gas Turbine Combustion Simulation Rig

A new capability for environmental performance testing of T/EBCs, CMCs, and other high temperature materials





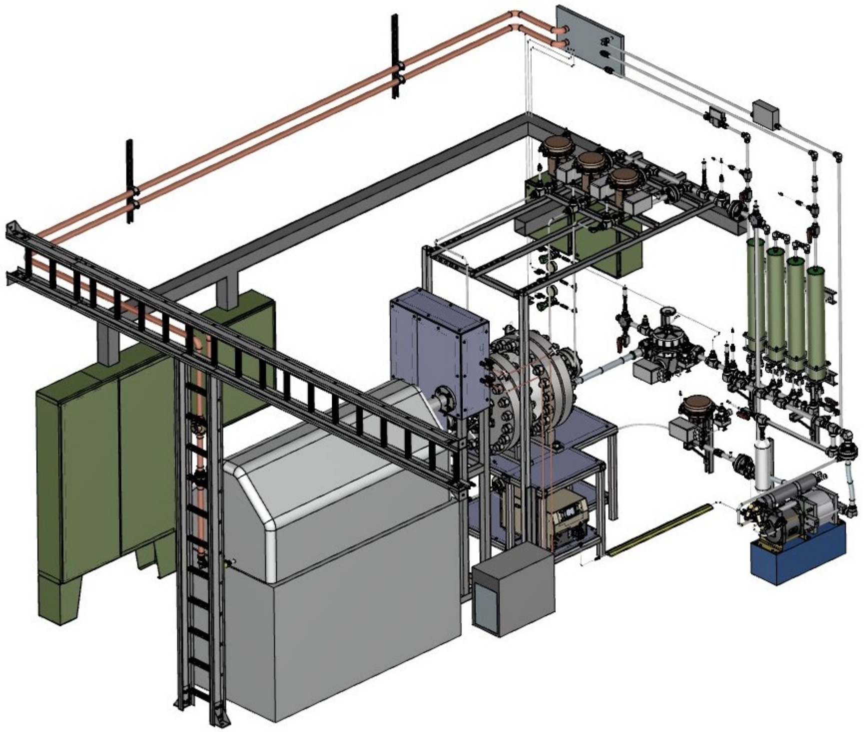
- ✓ Ultrahigh surface temperatures
- ✓ High gas velocity
- ✓ High pressure
- ✓ Complex gas mixtures
- ✓ Backside cooling (thermal gradient)
- ✓ Long exposure times (unattended operations)

→ **Realistic gas turbine environments**

NETL Gas Turbine Combustion Simulation Rig

Summary of main features

- **Temperature**
  - 2 kW CO_2 laser → **T >1600 °C** surface temperatures.
  - Backside cooling → **temperature gradient**.
  - Fast **thermal cycling** → simulate startups/shutdowns.
- **Samples**
  - Accommodates 1”×1” square samples.
  - Uniformly heated ½” diameter circle in sample center.
- **Environment**
  - Controllable pressure up to **20 atm**.
  - **Controllable gas composition** (simulated combustion of hydrogen, natural gas, and their mixtures).
  - **Long duration testing** (unattended operations).
  - **High velocity gas** jet impinging on sample:
    - Gas jet via 3-mm converging nozzle
    - 45° impingement angle
    - Jet velocities up to 200 m/s
    - Jet pre-heated to 650°C

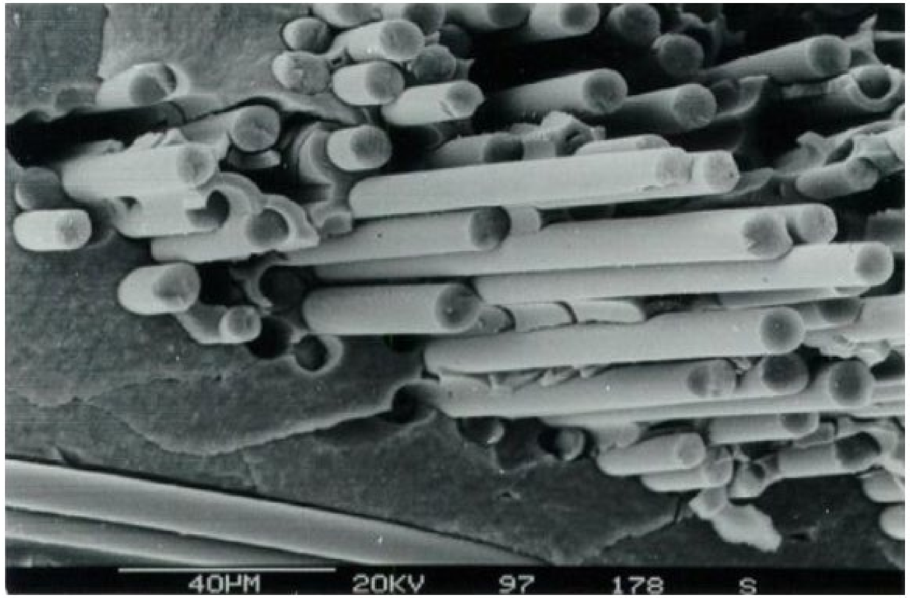


Rig commissioning expected summer 2024

Phase Field Damage Modeling of CMCs

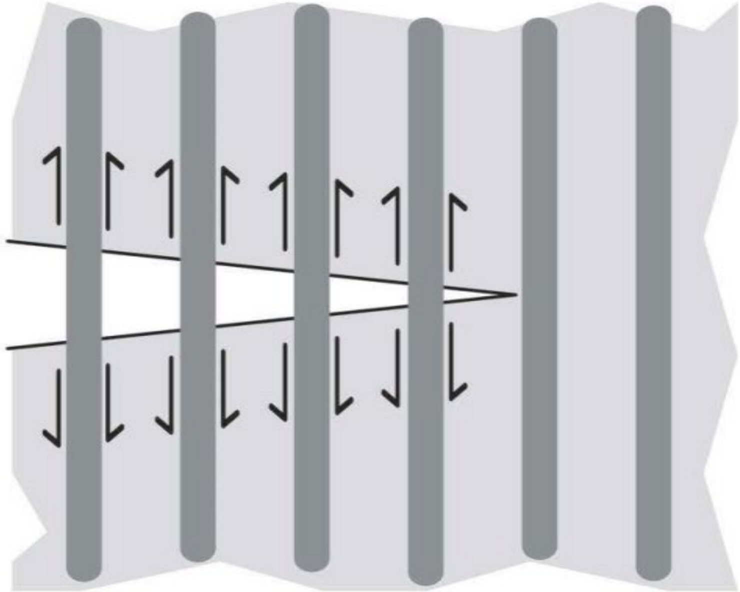
Understanding effect of microstructure on fracture behavior

Fracture surface of a SiC CMC



Int J Res Sci Innov 2, no. 28 (2015): 10-13140.

Fiber bridging with interface sliding



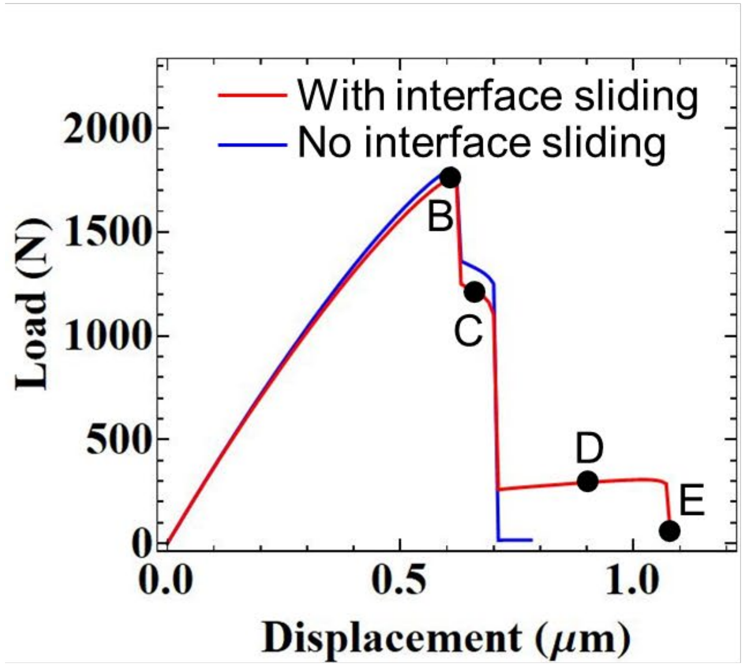
Anderson, Ted L. *Fracture mechanics: fundamentals and applications*. CRC press, 2017

Fiber bridging and fiber pull-out mechanisms are the keys to the superior property of CMCs

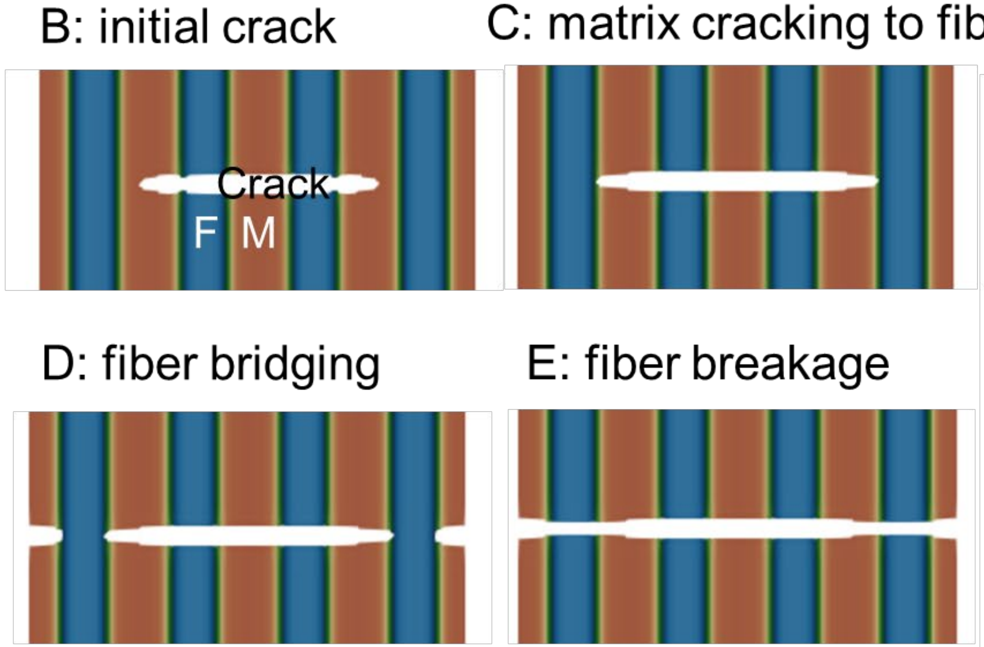
See poster Wednesday night!

Phase Field Damage Modeling of CMCs

Understanding effect of microstructure on fracture behavior



2D cross section

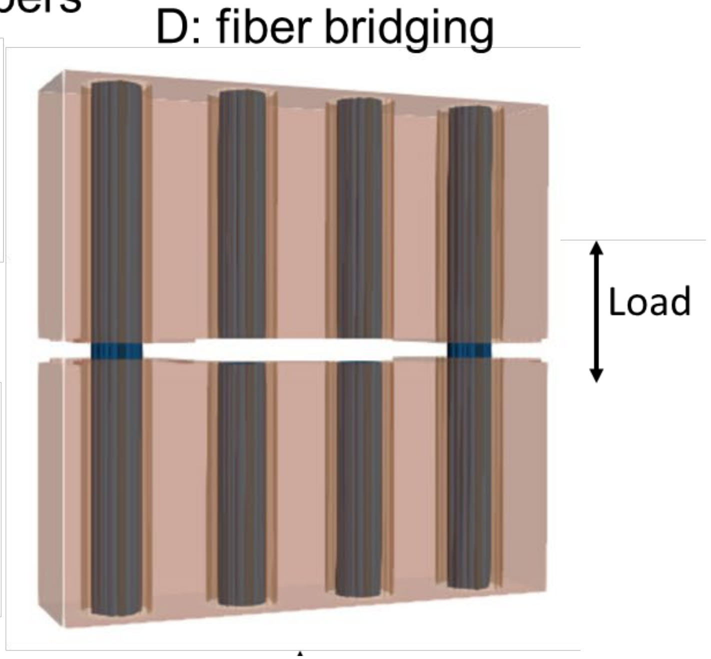

B: initial crack

C: matrix cracking to fibers

D: fiber bridging

E: fiber breakage

3D plot


D: fiber bridging

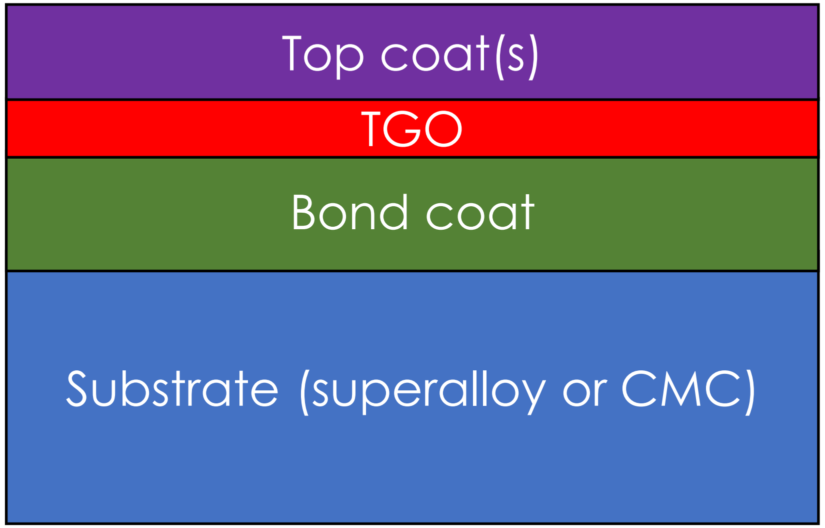
A phase field model incorporating interface sliding was developed to describe **crack growth in SiC/SiC CMCs**. The model successfully reproduces fiber bridging, and is used to gain insight into **effect of fiber geometry and distribution** on CMC performance.

See poster Wednesday night!

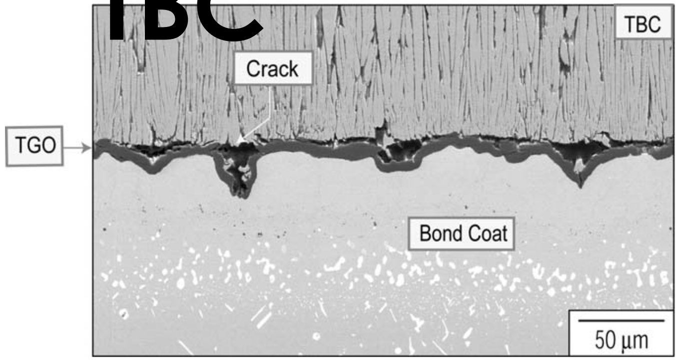
Phase Field Damage Modeling of EBCs

A micro-mechanical model incorporating large inelastic deformation

Like thermal barrier coating (TBCs) on superalloys, **a primary failure mode in EBCs has been linked to the growth of the thermally grown oxide (TGO) layer**.

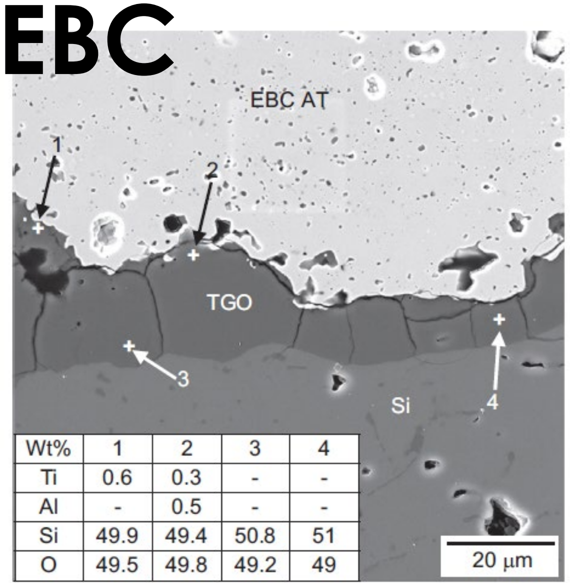


TBC



(Balint, D.S., et al. 2006. Acta Mater. 54, 1815

EBC



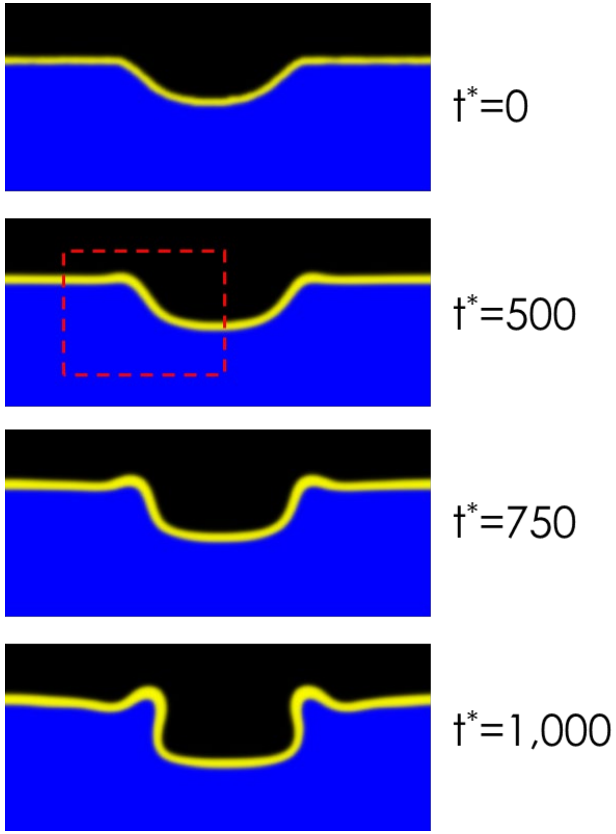
Wt%	1	2	3	4
Ti	0.6	0.3	-	-
Al	-	0.5	-	-
Si	49.9	49.4	50.8	51
O	49.5	49.8	49.2	49

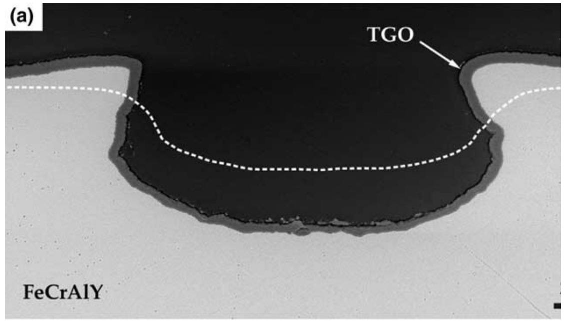
K. N. Lee, J. Am. Ceram. Soc. 102, 1507 (2019).

See poster Wednesday night!

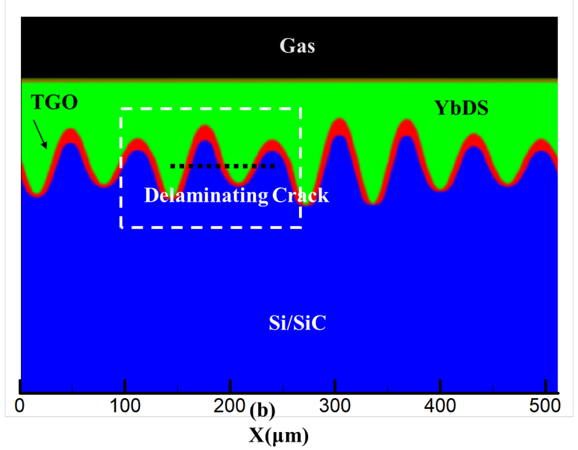
Phase Field Damage Modeling of EBCs

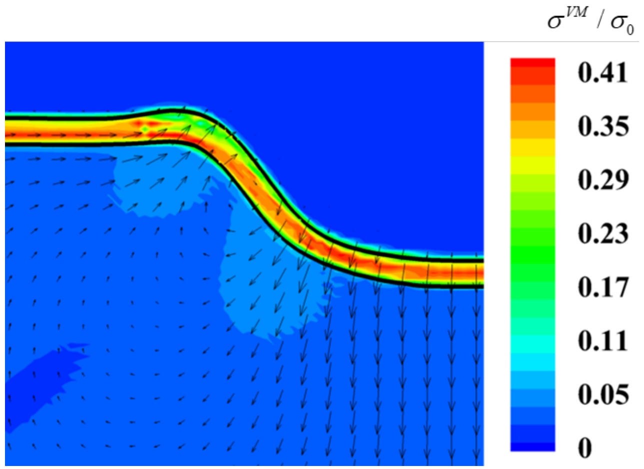
A micro-mechanical model incorporating large inelastic deformation





(Davis, A., Evans, A., 2005. Acta Mater. 53, 1895-1905)





- Developed a multi-phase-field model focused on TGO growth and associated stresses.
- The model successfully captures evolving morphology of the interface induced by TGO growth.

See poster Wednesday night!

Summary and Future Work

- Ongoing efforts to enable use of ceramic matrix composite (CMC) materials in high efficiency **hydrogen turbines**, with an emphasis on developing the **thermal/environmental barrier coatings (T/EBCs)** required to protect these materials.
- Promising new T/EBC materials in the **multicomponent $RE_2Si_2O_7$ system** were designed using DFT based methods. Future work includes further optimizing coating properties + experimental validation.
- **State of the art gas turbine combustion simulation rig** coming online summer 2024. Newly designed NETL T/EBCs will be deposited and tested alongside existing EBCs to evaluate performance in hydrogen turbine environments.
- Phase field approaches are being used to **model damage evolution in both EBC and CMC materials**.

NETL RESOURCES

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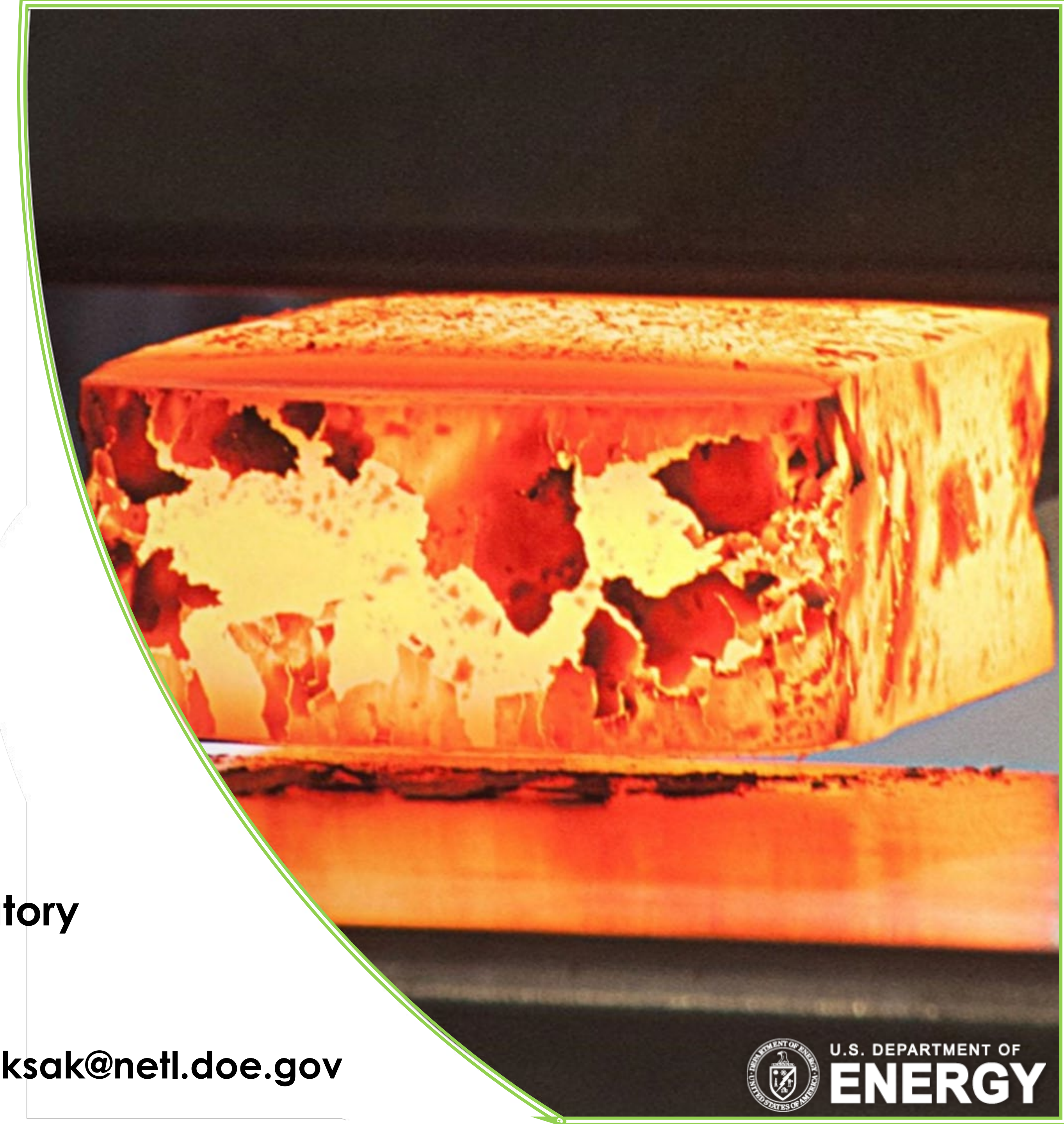

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