Integrated Computational Materials Engineering of CMAS-resistant Thermal Barrier Coatings (TBCs)

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Agenda

- QuesTek overview
- CMAS infiltration background and approach
- Database extension
- Validation of database predictions
- Design approaches for CMAS resistant TBCs
Introduction to QuesTek
Background—QuesTek Innovations LLC

• Founded 1997 (Prof. Greg Olson, cofounder)
• 18 employees (12 with PhD, 4 with MS, 2 with BS)
• A global leader in computational materials design:
  – Our Materials by Design® expertise applies the Integrated Computational Materials Engineering (ICME) technologies and Accelerated Insertion of Materials (AIM) methodologies to design and deploy innovative, novel materials faster and at less cost than traditional methods
  – Aligned with the Materials Genome Initiative
• 7 US patents awarded (and 8 US patents pending)
• Create IP and license it to producers, processors, OEMs, end-users
• 4 computationally-designed steels are commercialized and deployed in demanding applications
• Designing novel Fe, Al, Ti, Cu, Ni, Co, Nb, Mo and W based alloys for government and industrial sectors
QuesTek’s *Integrated Computational Materials Engineering* approach
Computational materials design overview: 
*Systems design charts*

Design material as a system to meet customer-defined performance goals

*e.g. this “Design Chart” for *Ferrium* C64 was developed under a contract resulting from U.S. Navy Solicitation Topic #N05-T006.*
Approach
Turbine blade system design chart
TBC failure mechanisms

- Multiple variants of delamination mechanism directly related to CMAS attack
- Intrinsic mechanisms aggravated by higher bond coat temperatures in CMAS penetrated areas

Image courtesy of GE Aviation

Levi et al., MRS Bulletin Issue on Thermal Barrier Coatings, October 2012; adapted from A.G. Evans et al., JECerS 2008
Deposits and CMAS compositions from literature

Levi, Hutchinson, Vidal-Setif, Johnson
MRS Bulletin Issue on Thermal Barrier Coatings, October 2012
ICME Approach to Develop CMAS Resistant TBCs

- Databases extended using UCSB experimental findings (ThermoCalc and QT)
  - Full CMAS-YZ-Fe oxide system
  - All ternaries and binary phase diagrams evaluated and re-optimized (when necessary)
  - Apatite/Cuspidine phases identified for possible CMAS infiltration mitigation

- Validation with CMAS/YSZ experiments (UCSB)
  - Interactions of Yttria, 7YSZ, $Y_4Zr_3O_{12}$, and Zircon with $C_{33}M_{9}A_{13}S_{45}$, $C_{24}A_{17}S_{59}$, and $C_{15}A_{15}S_{70}$ compositions

- Design tools to predict CMAS infiltration (QT)
  - Interaction of CMAS compositions with 7YSZ, $\delta$-phase, eutectoid compositions

- Design heuristics exploration ongoing
  - RE systems—stabilize two phase tetragonal zirconia+RE Zirconate composition
Database Extension
Database Extension Activities

- Updated systems: CMASFe-YZ
  - Re-assessment of targeted phases: Al₂O₃-SiO₂-Y₂O₃, CaO-SiO₂-Y₂O₃, CaO-SiO₂-ZrO₂
  - Fe-based: Fe-Y-O, Fe-Zr-O, Fe-Mg-O, Al₂O₃-FeOₓ-MgO, CaO-FeOₓ-MgO, FeOₓ-MgO-SiO₂, Al₂O₃-CaO-FeOₓ-MgO, Al₂O₃-CaO-FeOₓ-SiO₂, Al₂O₃-FeOₓ-MgO-SiO₂, and CaO-FeOₓ-MgO-SiO₂

- Experimentally assessed at UCSB
  - CaO-SiO₂-Y₂O₃ (CYS)
  - CaO-Al₂O₃-SiO₂-Y₂O₃ (CAYS)
  - SiO₂-Y₂O₃-ZrO₂ (SYZ)

- Gd-based and other RE systems ongoing
  - CMASFe-YZGd
Apatite formation in CYS

Binary and ternary phases reported in literature

- Phase equilibria study at UCSB
  - Stable cuspidine stoichiometry
  - Anion and cation vacancies in apatite
- Apatite field terminates before YS binary

Crystallographically permitted apatite homogeneity range

Experimental Observations (1400°C)
Cuspidine Homogeneity Range (1600°C)

1600°C
- Synthesized Compositions
- Measured Cuspidine Composition
- Planned Additional Compositions

Oxygen Deficient
- Confirmed Stability Range
- Unexplored Compositions

Excess Oxygen

Ca$_2$Y$_{2-y}$Al$_{2-y}$O$_{2y}$

Y$_4$Al$_{2x}$Si$_{2x}$O$_{9+2x}$

Y$_4$Si$_2$O$_{10}$
Re-assessment of CYS system

• Cuspidine and apatite included
  – $Y_{0.5}$ solubility in cuspidine
  – Anion and cation vacancies in apatite
• Apatite field terminates before YS binary
• Solid agreement with experiment
Database Validation with CMAS experiments
CMAS/Oxide Stability Analysis (1300°C)

**Glass Compositions (Mol%)**

<table>
<thead>
<tr>
<th>ID</th>
<th>CaO</th>
<th>MgO</th>
<th>AlO$_{1.5}$</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMAS-I</td>
<td>33</td>
<td>9</td>
<td>13</td>
<td>45</td>
</tr>
<tr>
<td>CAS-1</td>
<td>35</td>
<td>--</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td>CAS-3</td>
<td>24</td>
<td>--</td>
<td>17</td>
<td>59</td>
</tr>
<tr>
<td>CAS-5</td>
<td>15</td>
<td>--</td>
<td>15</td>
<td>70</td>
</tr>
</tbody>
</table>

**Oxide Compositions**

<table>
<thead>
<tr>
<th>ID</th>
<th>YO$_{1.5}$</th>
<th>ZrO$_2$</th>
<th>AlO$_{1.5}$</th>
<th>SiO$_2$</th>
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</thead>
<tbody>
<tr>
<td>YZr</td>
<td>57</td>
<td>43</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>YSZ</td>
<td>7</td>
<td>93</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>YAP</td>
<td>50</td>
<td>--</td>
<td>50</td>
<td>--</td>
</tr>
<tr>
<td>Zircon</td>
<td>--</td>
<td>50</td>
<td>--</td>
<td>50</td>
</tr>
</tbody>
</table>

- 25mol% oxide added to each silicate
- Glass compositions:
  - CMAS=C$_{33}$M$_9$A$_{13}$S$_{45}$
  - CAS-3=C$_{35}$A$_{15}$S$_{50}$
  - CAS-3=C$_{24}$A$_{17}$S$_{59}$
  - CAS-5=C$_{15}$A$_{15}$S$_{70}$

**CMAS-1 (50h)**

<table>
<thead>
<tr>
<th>Ca</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Y</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>31.0</td>
<td>9.1</td>
<td>13.4</td>
<td>43.2</td>
<td>1.6</td>
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</tbody>
</table>

**CAS-3 (50h)**

<table>
<thead>
<tr>
<th>Ca</th>
<th>Al</th>
<th>Si</th>
<th>Y</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>25.5</td>
<td>18.7</td>
<td>52.0</td>
<td>1.9</td>
</tr>
<tr>
<td>ZS</td>
<td>0.1</td>
<td>0.1</td>
<td>49.9</td>
<td>1.8</td>
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</tbody>
</table>

**CAS-5 (200h)**

<table>
<thead>
<tr>
<th>Ca</th>
<th>Al</th>
<th>Si</th>
<th>Y</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>18.9</td>
<td>20.0</td>
<td>58.1</td>
<td>1.7</td>
</tr>
<tr>
<td>ZS</td>
<td>0.1</td>
<td>0.2</td>
<td>49.2</td>
<td>2.4</td>
</tr>
</tbody>
</table>
## TCOX6.0 calculated phases

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Composition (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CaO</td>
</tr>
<tr>
<td>7YSZ+CMAS1</td>
<td>Exp.</td>
<td>Glass</td>
</tr>
<tr>
<td></td>
<td>Cal.</td>
<td>Glass</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZrO$_2$</td>
</tr>
<tr>
<td>7YSZ+CAS3</td>
<td>Exp.</td>
<td>Glass</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZrSiO$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZrO$_2$</td>
</tr>
<tr>
<td></td>
<td>Cal.</td>
<td>Glass</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZrSiO$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZrO$_2$</td>
</tr>
<tr>
<td>7YSZ+CAS5</td>
<td>Exp.</td>
<td>Glass</td>
</tr>
<tr>
<td></td>
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<td>ZrSiO$_4$</td>
</tr>
<tr>
<td></td>
<td>Cal.</td>
<td>Glass</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZrSiO$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anorthite$^b$</td>
</tr>
</tbody>
</table>

- Compared to equilibrium phases at 1300°C
  - Results largely agree with predictions
- Anorthite not found in CAS5 interaction
  - <3 mol% predicted in by TCOX6 database
Design Tools to Predict CMAS Infiltration
CMAS-Y-Z: Apatite field reduces liquid in TCOX6

TCOX5: 1300°C

TCOX6: 1300°C

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MS&T 2015, Columbus, OH
8 October 2015
Lowest melting point CMAS

- NASA/Smialek composition \((C_{23}M_9A_{13}S_{55})\) melts at 1170°C
- Database predicted lowest melting point at 1161°C CMAS composition: \(C_{21.9}M_{5.9}A_{7.35}S_{57.5}\)
Lowest Melting CMAS: C_{21.9}M_{5.9}A_{14.7}S_{57.5}-Y-Z

TCOX6: 1300°C

CMAS

MOLE FRACTION ZRO2

YO_{3/2}

Apatite

Apatite+Cuspidine

Liquid+Apatite

Liquid presence

YSZ

Y_{4}Zr_{3}O_{12}
CMAS/YSZ Interaction in TCOX6 (1300°C)

- Range of CMAS compositions
- Not stable against liquid

Vary Fe

Vary Si

Vary Al

Vary Mg

Vary Ca

Liquid presence

CMAS/YSZ Interaction in TCOX6 (1300°C)
CMAS/δ-phase ($Y_4Zr_3O_{12}$) Interaction in TCOX6 (1300°C)

- Reduction in liquid region

Vary Fe

Vary Si

Vary Al

Vary Mg

Vary Ca

Liquid presence

CMAS/δ-phase ($Y_4Zr_3O_{12}$) Interaction in TCOX6 (1300°C)
CMAS/Eutectoid (δ-phase + Yttria) Interaction in TCOX6 (1300°C)

- Reduction in liquid region
- Similar to δ-phase

Vary Fe
Vary Si
Vary Al
Vary Mg
Vary Ca

CMAS-resistant Thermal Barrier Coatings (TBCs)
MS&T 2015, Columbus, OH
8 October 2015
Design Heuristics
Design considerations/heuristics

- **CMAS resistance**
  - More RE reduces CMAS infiltration by stabilizing solid reactants
  - Viscosity of molten CMAS

- **Low thermal conductivity (short wave phonon scattering)**
  - Heavy cation-based oxides
  - Defects/vacancies

- **High toughness**
  - Design for two-phase compositions with tetragonal reinforcement

- **Processability**
  - Similar vapor pressure of RE oxides needed for EBPVD
    - Columnar builds for lower thermal conductivity: preferred coating architecture
Design for two phase composition

- Possible binary RE regions
- Search for stable two-phase region at high temperature
  - δ-phase (Y-Zr.-based) and Pyrochlore (GdZr) have no 2-phase region with t-zirconia
  - Search for ternary additions that create stable tie-line with t-zirconia

* δ/pyrochlore decomposition temperature
Other RE systems

- LaZr-pyrochlore has 2-phase region with t-zirconia ~1900°C
- NdZr-pyrochlore has 2-phase region ~1200°C
Conclusions and Future Work

• Database developed to predict CMAS thermodynamics
  – Calibrated and validated with experiments at UCSB
  – Enables tools to predict lowest CMAS melting
  – Predicts YSZ interaction with all CMAS

• Initial design heuristics developed

• Future work
  – Additional RE extensions
  – Incorporate ICME tools to enable TBC design (modulus, TBC/bond coat compatibility, thermal conductivity, spallation resistance)
Thank you for your attention

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