Coating Issues in Coal-Derived Synthesis Gas/Hydrogen-Fired Turbines

B. A. Pint
Materials Science and Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6156

Research sponsored by DOE, Office of Coal and Power R&D
Office of Fossil Energy (B. White, project monitor)
Acknowledgments

I. G. Wright - architect of ORNL syngas project (2005)
Task leaders: J. A. Haynes - coatings (Y. Zhang, Tenn. Tech.)
                      K. Unocic - characterization (TEM, etc.)
K. Cooley - coating fabrication
G. Garner, M. Stephens - oxidation experiments
T. Lowe - characterization
D. W. Coffey - TEM specimen preparation, FIB
H. Longmire, T. Jordan - metallography
D. Leonard - EPMA

Ken Murphy, Howmet - X4 superalloy substrates
Jacqui Wahl, Cannon-Muskegon - CMSX7,X8 substrates
Anand Kulkarni, Siemens - 1483 superalloy substrates
Ben Nagaraj, GEAE - N515 alloy, EB-PVD YSZ deposition
S. Sampath, Stonybrook U. - HVOF,APS coatings

12MWh/yr per U.S. resident

From where? coal? how?

Integrated gasification combined cycle (IGCC):
- similar to NGCC
- control NO$_x$, SO$_x$, Hg...

Kemper County, MS (Southern Co.)
$2.67$ billion, $\sim 60\%$ CO$_2$ capture (oil recovery)
550MW, Siemens turbines, 2014 start

Edwardsport, IN (Duke Energy)
$2.88$ billion (Carbon capture ready)
618MW, GE Energy turbines, 2012 start
De-rating of syngas turbines

Current project: more durable coatings
- coal-derived synthesis gas or syngas
- syngas turbines operating ~100°F(C?) less
- eliminating de-rating will improve efficiency

Reasons for de-rating*:
- higher water vapor content (fuel+diluent)
  (~10vol.%H₂O for natural gas vs. 30-60%)
- higher S levels (imperfect syngas cleanup)
- increased deposits
- syngas lower caloric value: higher fuel/air
  5-10X more fuel, magnifying impurities

TBC requires “perfect” scale adhesion

Spallation of the scale has catastrophic effect (loss of YSZ)

scale is key to extending coating performance/reliability

Failure assumption:
- Many possibilities but when other problems corrected the “weak link” will be the metal-scale interface
- Thinner scale more “strain tolerant” – less strain energy

Focus on alumina scale growth and adhesion
Outline

FY10 (initiated 3 related “pre-competitive” tasks)
   Task 1: water vapor effects
   Task 2: superalloy dopant effects
   Task 3: characterization

FY12
   Task 1: repeating results from first 2 groups
      Two issues: Dry vs. Wet and Wet vs. Wetter
   Task 2: Completed, no significant benefit in X4
   Task 3: dopant & H₂O effects on alumina scale
   Task 4: New compositions and processes
      - model bond coating (NiCrAlX) alloys
      - low Re superalloys

FY13
   Future directions
Recent Presentations

8th Int. Charles Parsons Conf. (Sept. 2011, UK)
- Effect of water vapor content on TBC lifetime
  (publication in *Materials Science and Technology*)

ICMCTF (April 2012, San Diego)
- Effect of Water Vapor on the 1100°C Oxidation Behavior of
  Plasma-Sprayed TBC’s with HVOF NiCoCrAlX Coatings
- Effect of Water Vapor on Thermally Grown Alumina
  Scales on Bond Coatings
  (publication in *Surface & Coatings Technology*, Dec. 2012)

*Advanced Materials and Processing* (May 2012 issue)
- Effect of water vapor content on TBC lifetime

*Microscopy & Microanalysis* (August 2012, AZ)
- Microstructure and Chemistry of the Oxide Scale and Pt-
  containing Coatings Deposited on Superalloy N5

*Superalloys 2012* (Sept. 2012, PA)
- The Effect of Water Vapor and Superalloy Composition
  on Thermal Barrier Coating Lifetime (Proceedings)
Several TBC groups investigated
(3 YSZ samples per condition + 1 without YSZ)

<table>
<thead>
<tr>
<th>Group</th>
<th>Alloy</th>
<th>Bond coating</th>
<th>Top coating</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N5</td>
<td>Diffusion $\beta/\gamma+\gamma'$</td>
<td>EB-PVD</td>
<td>“quick start”</td>
</tr>
<tr>
<td>2</td>
<td>X4±RE</td>
<td>HVOF $Y\pm$Hf</td>
<td>APS</td>
<td>RE/H$_2$O effect</td>
</tr>
<tr>
<td>3</td>
<td>N5/N515</td>
<td>Diffusion $\beta/\gamma+\gamma'$</td>
<td>EB-PVD</td>
<td>repeat/low Re</td>
</tr>
<tr>
<td>4*</td>
<td>1483/X4</td>
<td>HVOF YHf</td>
<td>APS</td>
<td>rougher,1483</td>
</tr>
</tbody>
</table>

* 5 YSZ samples per condition + 1 without YSZ

HVOF: High velocity oxygen fuel (plasma spraying)
EB-PVD: electron-beam physical vapor deposition
APS: Air plasma spraying
N5 - GE SX (single crystal) ~3 wt.%Re; N515 - 1.5%Re
X4/1483 - Siemens recommended
Does water vapor explain de-rating?

Motivation for Task 1 on water vapor:
- Experiments done in dry O\textsubscript{2} or air - convenience
- All turbines contain some H\textsubscript{2}O
  Natural gas - 10-15 vol.\%
  Syn. gas - \textasciitilde30\%
  Hydrogen - \textasciitilde60\%
  higher levels with diluent
- Recent literature discussion on H\textsubscript{2}O effect on TBC
  Anomaly of testing without H\textsubscript{2}O
  Negative effect on lifetime when H\textsubscript{2}O added

Syngas-firing question:

What is difference in TBC lifetime when H\textsubscript{2}O increased from 10\% to 30\%-50\%? (not dry vs. wet, but wet vs. wetter)
Well controlled coating procedures

16mm disks: single crystal substrates (all at.%):
N5: 13.3Al,8Co,8Cr,0.9Re,70Y-17S-540Hf-132Zr
X4: 13.0Al,10Co,8Cr,0.9Re,1.2Ti,17S-270Hf

ZrO$_2$-Y$_2$O$_3$ coated (1 side)
1. N5, Pt diffusion/EB-PVD
   β: CVD at ORNL (7µm Pt)
   γ-γ': 7µm Pt, 2h, 1175°C
2. X4, HVOF/APS
   MCrAlY & MCrAlYHfSi:
   41Ni,18C0,16Cr,23Al,0.4Y
   or 0.4Y, 0.07Hf, 0.65Si

Oxidation testing: 1h cycles (10min cooling)
1150°C or 1100°C: dry O$_2$, air + (10,50,90%) H$_2$O

Characterization: Laser & optical profilometry ($R_q$)
Metallographic cross-sections, EPMA, PSLS...
TBC Group 1: more effect on $\beta$ life

1h cycles, 1150°C, air with 10-90 vol.% $\text{H}_2\text{O}$

$\beta$-NiAl bond coating: >50% decrease with 10%$\text{H}_2\text{O}$

$\gamma$-$\gamma'$ Pt diffusion: no statistical change in life
Higher $\text{H}_2\text{O}$: not what I expected
1h cycles, 1150°C, air with 10-90 vol.% $\text{H}_2\text{O}$

$\beta$-NiAl bond coating: expected more $\text{H}_2\text{O}$ resistance
$\gamma$-$\gamma'$ Pt diffusion: lower Al, expected $\text{H}_2\text{O}$ problem
β coatings have non-uniform scale

Backscattered SEM, 1-h cycles at 1150°C

dry O₂, 900h
10%H₂O, 400h

Images from: 4th specimen in each group without YSZ

50%H₂O, 900h
90%H₂O, 800h

Difficult to assess thickness/roughness differences
More quantitative method needed to compare
Thicker oxide beneath YSZ
Average of 40 measurements from SEM images

Failed TBC specimens plotted versus exposure time
Standard deviation shown
Thicker oxide with 10% H$_2$O
Average of 40 measurements from SEM images

Similar thicker oxide formed with and without YSZ
Rate similar in both cases
Higher $\text{H}_2\text{O}$ - no further trend
Average of 40 measurements from SEM images

Oxide not thicker with higher water vapor content
Box plots better represent data
Box of same 40 measurements from SEM images

Not much statistical difference between two cases
TBC Group 3: in depth repeat
1h cycles, 1150°C, air with 0 & 10 vol.% H$_2$O

New: Superalloy composition (X4 1%Ti, N515)
- similar lifetime with X4 substrate, no Ti debit
- higher Hf (2000 ppma) in N515 increased lifetime
- observed higher life with and without Pt
New data: no H₂O roughness effect

β coating: 4th (no YSZ) specimen cut in half

Previously: Observed large difference with H₂O for β Specimens from different batches, test in 2 rigs No mechanistic reason for such an effect Both X4 (NiPtAl) and N515 (NiAl) showed little effect
Effect of lower temperature
1h cycles, 1125°C, air with 10 vol.% H₂O

1125°C: reduced temperature to lower rumpling
- 4.5X higher life than 1150°C
- Pt increased life by 40%
1125°C: did not eliminate rumpling
4th (no YSZ) specimen cut in half (in progress)

Specimens stopped after 1000 cycles (TBC 1400-1950h)
- similar roughness for NiAl and NiPtAl on N5
- somewhat lower roughness in dry air vs. wet air
Group 3: stress measurements too
Residual stress in alumina by PSLS

Same specimen used for roughness (no YSZ, cut in half)
1150°C - NiAl on N515 (high Hf): little H₂O effect
- NiPtAl on X4: lower stress in dry air
1125°C: no effect of Pt on stress
In progress: alumina residual stress by PSLS

Same specimen used for roughness (no YSZ, cut in half)
1125°C - N5 with NiAl/NiPtAl: same stress
Data still being crunched for 1125°C dry air exposure
Next gen. stress measurements

PSLS measurement as a function of location

NiAl on N515 after 5h at 1150°C in dry air

stress in single grain
PSLS identified alumina phase

Theta map: 1h 5h

1150°C wet air
X4 NiPtAl

1150°C dry air

Water vapor stabilized faster growing $\theta$-$\text{Al}_2\text{O}_3$

1125°C wet air
N5 NiPtAl
Initial $\theta$-$\text{Al}_2\text{O}_3$ explains thickness

Alumina thickness measured from SEM images

Increase due to initial faster-growing $\theta$-$\text{Al}_2\text{O}_3$ formation
3D microscopy links stress/location
Keyence examined same location as PSLS

- Can link stress and deformation as a function of time
- Similar analysis done for wet and dry air
- Supports hypothesis that coating grain size affects rumpling (Dryepondt): small grains “shrink and sink”
- Last step: microstructure at key locations (FIB)
Are doped superalloys a solution?

Motivation for Task 2 on doped superalloys:
Difficult to develop/commercialize new alloy/coating
  - is there a solution available?
Cannon-Muskegon has commercial CMSX4+Y,La
  - reported to increase TBC lifetime by 2-3X
  - little independent verification
  - little mechanistic understanding
  - Proposed Impurity flux mechanism for S,RE:

```latex
\begin{align*}
\text{gas} & \quad J_0 \quad \text{PO}_2 \approx 0.2 \\
\text{YSZ} & \quad J_{\text{Al}} \quad \text{PO}_2 \approx 0.2 \\
\text{alumina bond coating} & \quad J_{\text{RE(bc)}} \\
\text{superalloy} & \quad J_{\text{RE(sx)}} \quad \text{PO}_2 \approx 10^{-30} \text{ bar (Al/Al}_2\text{O}_3 \text{ equil.)} \\
& \quad J_{\text{Ni, Cr, Co, Hf, Ta}}
\end{align*}
```
Three alloys & one coating examined
CMSX4: 6-7 at.% Cr-9-13Al-1Re-10Co-2W-2Ta-1Ti

Baseline:

X4: 13.0Al-270Hf-17S

disks: 16 x 2mm thick

MCrAlYHfSi (PWA286) by high-velocity oxygen-fuel
41 at.% Ni-18.4Co-16.2Cr-22.9Al-0.39Y-0.07Hf-0.65Si

1h cycles:
1100°C
flowing, dry O₂ or
air + 10, 50% H₂O

100h cycles:
1100°, air+10% H₂O
Group 2: no Y/La benefit in X4
Two bond coatings on CMSX4 + APS YSZ

30% drop in lifetime in 10% H₂O for both bond coats
No increase in lifetime with Y/La addition to CMSX4
100h cycles increased lifetime
1100°C: two bond coatings on X4-1 + APS YSZ

FY12 Milestone

Cycle more representative of land-based turbine
100h cycles in tube furnace with slow heat/cool

Results support 1h accelerated testing
HVOF characterization: few trends
Interdiffusion and oxide thickness on both sides

FY12 Milestone

Subset of large number of HVOF specimens
Since many specimens fell within scatter, not all specimens were examined
Conclude doped superalloy task:

- No evidence of Y/La benefit in these tests
- Y+Hf bond coat more effective benefit
  Increased lifetime compared to MCrAlY
- Perhaps, Y+La benefit clearer with higher S
  Low S superalloys are now more common
  Also, Howmet X4 contained higher Hf, which may overshadow Y and La effects
  Expect more effect with diffusion coatings
Characterization helps understanding

Motivation for Task 3 characterization:
- Developing mitigation strategies is very difficult without understanding the role of dopants & H₂O
- Strong interest in the alumina scale but typically <10µm in thickness
- Imaging from light microscopy to SEM to TEM
- Also PSLS and roughness

FY12 tasks:
- complete TBC Group 1 characterization
- complete TBC Group 2 characterization
- broader characterization on Group 3 (PSLS...)
- continue characterization of model alloys
TEM: variable scale thickness on $\beta$

After 900 1-h cycles at 1150°C

Martensitic $\beta$ apparent

Only minor changes in microstructure
TEM: thicker oxide on $\gamma$-$\gamma'$ in $\text{H}_2\text{O}$

After 1500 1-h cycles at 1150°C

Columnar grains typical of $\gamma$-$\gamma'$ coatings

Thicker oxide, otherwise few differences
TEM: model NiCrAl+La,Hf
Oxidized 100h at 1100°C in dry O₂

α-Al₂O₃

200nm

Hf
La

NiCrAl-La,Hf

250nm
Task 4 focused on solutions for syngas

Motivation for task:
- Other tasks concern understanding
- This task added to develop solutions
- Also to investigate new coating technologies
  (often difficult to get specimens)

FY12 work:
- more oxidation resistant MCrAlY coatings:
  initial work on model NiCrAlX cast alloys
  invention disclosure filed
- different superalloys (N515, 1483)
  N515, X7, X8: lower Re
  1483: higher Cr (hot corrosion resistance)
Cast NiCrAl show benefit of “X”
1h cyclic oxidation testing at 1150°C

after 200 cycles:

- YTi
- "YTiX"
- YHf
- YHfX
- YHfTi
- LaHf
- LaHfTi

Specimen Mass Change (mg/cm²)

0.11%Y
0.29%Ti
0.12%Y
0.30%Ti
0.01%Y
0.13%Hf
0.03%Y
0.14%Hf
0.03%Y
0.14%Hf
0.05%La
0.05%X
0.16%Hf
0.07%X
0.06%X
0.14%Hf
0.30%Ti

air + 10%H₂O

Higher temperature used for short time evaluation
Bar graphs at 200 cycles do not reflect behavior

Next step is to make powder/spray coatings
Bare superalloy tests in progress
1h cyclic oxidation testing at 1050°-1150°C

Comparison of low Re alloys with conventional 2nd generation single crystal alloys

1050°C example
All similar, little Re effect
1483 poor (low Al)
FY13 directions

FY10 (initiated 3 related “pre-competitive tasks)
   (1) water vapor effects
   (2) superalloy dopant effects
   (3) characterization

FY13

   Task 1: Broadening environment effects
           Including CO₂ and SO₂ (late FY13 or FY14)
   Task 2: Effect of superalloy composition
           Higher Cr and lower Re effects (market pull)
   Task 3: Characterization (continue key role)
   Task 4: New bond coatings/processes
           Validate model alloy performance in coating
           Work with industry for new directions
           - OEM/utilities, S-rich deposits, new processes
Summary–take away points

Higher water vapor does not appear to explain de-rating although H$_2$O effect is detrimental
- continue to study role of H$_2$O on TBC life
- more relevant/better understanding

Doped superalloys do not appear to be a solution
- conventional SX alloys may have improved

Co-doped (Y+Hf) bond coatings appear to be very effective and should be further explored

Promising solution for new bond coating

Scope evolving to include performance of new superalloys and effect of CO$_2$ and SO$_2$
CLEAN COAL.
COOL.
TBC Group 4 in progress

Coatings (w/YSZ) received from Stonybrook
- mostly 1483 substrate, some X4 to compare
- only HVOF NiCoCrAlYHfSi bond coatings
- APS top coating on one side
- increased roughness compared to Group 2
- closer to industry standard
- 5 specimens per condition (3 for Group 2)

Experiments (complete Task 1 on H₂O effect)
- 1h cycles 1100°C: 0%, 10%, 50%H₂O
  (compare to previous work)
- 100h cycles 1150°C: 0%, 10%, 50%H₂O
  (increased temperature to reduce test time)
- 1h cycles 1150°C: 0%, 10%
  (link experiments)
1100°C used for MCrAlY coatings
Thermal expansion difference among coating classes

MCrAlY bond coatings (industry standard)
X4: 13.0Al, 10Co, 8Cr, 0.9Re, 1.2Ti, 17S-270Hf
MCrAlY & MCrAlYHfSi: 41Ni, 18Co, 16Cr, 23Al, 0.4Y
or 0.4Y, 0.07Hf, 0.65Si

\[ \text{stress} = f(\Delta \alpha_{M-O}) \]
\[ W \propto \xi_{\text{oxide}} \]
\[ \xi^* \propto (\Delta T \Delta \alpha)^{-2} \]

\( \xi \) strain energy
\( \xi^* \) thickness at spallation

MCrAlY & MCrAlYHfSi: 41Ni, 18Co, 16Cr, 23Al, 0.4Y
or 0.4Y, 0.07Hf, 0.65Si
Morphology of HVOF MCrAl

Epoxy-mounted polished cross-sections after failure

Relatively small $\beta$ denuded zone
Low roughness of $R_a \sim 5.5$, not industrial standard
Scale on HVOF MCrAl

Epoxy-mounted polished cross-sections after failure

Rougher areas: more alumina scale + YSZ attached

~100% APS YSZ spallation leaves little to analyze
\( \gamma + \gamma' \) coatings: more uniform scale

Backscattered SEM, 1-h cycles at 1150°C

dry \( \text{O}_2 \), 1,500h  
10\%\( \text{H}_2\text{O} \), 1,500h  
50\%\( \text{H}_2\text{O} \), 1,500h  
90\%\( \text{H}_2\text{O} \), 1,500h

Relatively uniform oxide formed on \( \gamma + \gamma' \) coatings

More variation for scale formed in 0\% \( \text{H}_2\text{O} \): spall?
Coated X4-2 - found Ti in scale
Oxidized for 100h at 1100°C in dry O₂

Demonstrates that Ti diffused through coating
(No Ti in MCrAlYHfSi coating, 1% in X4-2)
50% H$_2$O: no effect on TBC life
1100°C: two bond coatings on X4-2 + APS YSZ

Similar to diffusion coatings, higher water vapor content did not reduce TBC lifetime.
Characterization in progress
FY12-13 milestones

FY2012
- Complete TBC lifetime testing at two different cycle frequencies. (Met).
- Complete characterization of the coated CMSX4 variants (with and without dopants) (Met).
3. Complete initial assessment of model alloy oxidation results (Progressing, 9/30/12).

FY2013
1. Complete oxidation evaluation of bare superalloys with higher Cr or lower Re (12/31/2012)
2. Complete TBC lifetime testing and characterization in the presence of CO$_2$ and H$_2$O (5/31/2013)
3. Fabricate bond coatings with new composition and complete initial cyclic oxidation evaluation (9/30/2013)
Model alloys show benefit of “X”
1h cyclic oxidation testing at 1100°C

Testing in dry and wet air
La/Hf compositions also worked well without X
Path forward for MCrAlY+X

Invention disclosure filed in June 2012
   - patent review being conducted
   - more data needed to file strong patent

Next steps:
   Identify vendor, obtain non-disclosure agreement
   Make two powders, spray coatings (FY13 funds)
   Test coatings, compared to current coatings
Change in $\text{Al}_2\text{O}_3$ morphology on $\gamma-\gamma'$

Plan view SEM, all 1,500, 1-h cycles at 1150°C

dry $\text{O}_2$ (0% $\text{H}_2\text{O}$)  \hspace{1cm} 10%$\text{H}_2\text{O}$

1$\mu$m

50%$\text{H}_2\text{O}$  \hspace{1cm} 90%$\text{H}_2\text{O}$

Spinel(?) at surface except 0% -> spall at 0%(?)
EPMA: no clear differences
Line traces from specimens without YSZ

\( \gamma - \gamma' \) coatings (1500h)  \( \beta \) coatings

No apparent effect of water vapor on interdiffusion
\( \beta \) coatings exposed for different times at 1150°C