Understanding Corrosion Mechanisms in Oxy-Fired Systems

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T. Lowe - SEM, image analysis
D. Leonard - EPMA
Where will it come from? coal? how?

Conventional: “USC”
-PC Turk, AR, 595°C

Gasification:
-IGCC Kemper Co., MS
-IGCC Edwardsport, IN

Oxy-firing:
-FutureGen 2.0 (?)
FutureGen 2.0: U.S. demo of oxy-firing

Germany: 30MW oxy-fired pilot plant (Alstom)

maybe Ni-base alloys

Fe-Cr

Austenitics

Air

Particle removal

CO$_2$ 15 59%
H$_2$O 10 32%
O$_2$ 2.5 1.9%
SO$_2$ 0.13 0.46%

flue gas recirculation

hole in the ground

Several studies published by Alstom (Bordenet)

Oxy-firing literature tends to focus on worst case
Current Tasks & Timeline

Goal: Mechanistic understanding to enable accurate oxy-fired corrosion modeling

1. Steam/gas corrosion (no ash)
2. Fireside corrosion (with ash)
3. Environment-mechanical property effect
   - effect of steam on creep (Dryepondt)
4. Coatings
   - fabrication and model (TTU subcontract)
   - effect on mechanical properties (Dryepondt)

A. ~600°C ferritic/martensitic steels (FY10-12)
B. ~650°-700°C austenitic steels (FY11-13)
C. ~700°-750+°C Ni-base alloys
   - creep testing at 800°C (FY11-12)
   - ash testing 600°-800°C (FY12)
What’s different here?

Many previous & current studies of oxy-firing & CO₂
- Complicated: boiler OEMs have advantage
- CO₂ effect: Jülich, U. Pitt & Australia (Young)

Issues with fireside corrosion experiments:
Different experimental conditions (if published)
  1000h vs. 10 x 100h (ash re-supply)
  Ash/gas/temp. variables
  Use of Pt catalyst (SO₂/SO₃)
* Evaluate experimental parameters (FY12)

Typically, only commercial alloys evaluated
  Prior work showing Cu-containing alloy attacked
  Was it an effect of Cu or other element(s)?
* Model alloys to better understand composition
Not just commercial alloys
Model alloys: better composition understanding

Cr Content (wt.%)

<table>
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<tr>
<th>Ni Content (wt.%</th>
<th>0</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>45</th>
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<td>15</td>
<td>X</td>
<td>(new 347mods)</td>
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<tr>
<td>16</td>
<td>O O O O o o o o (2001 set)</td>
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<tr>
<td>18</td>
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<tr>
<td>20</td>
<td>X O O O o o o o</td>
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<td></td>
</tr>
<tr>
<td>25</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>X</td>
<td>(overlay coatings) 622,625</td>
<td></td>
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<tr>
<td>35</td>
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</tr>
<tr>
<td>40</td>
<td>X</td>
<td>chromizing</td>
<td></td>
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</table>

Alloy 33

Cast 400g, hot-roll to 8mm: cut coupons & rods
Corrosion testing w/o ash
Determine effect of higher CO$_2$, H$_2$O, SO$_2$...

- Gas only, no ash
- H$_2$O only
- Ar-50%CO$_2$*
- H$_2$O-50%CO$_2$* (*CO$_2$+1500ppmO$_2$)

Synthetic ash: 30%Fe$_2$O$_3$-30%Al$_2$O$_3$-
30%SiO$_2$-5%Na$_2$SO$_4$-5%K$_2$SO$_4$
Gas: N$_2$-CO$_2$-H$_2$O-O$_2$-SO$_2$
Temperature: 600°C
Time: 500h (1 cycle)

Continuing to establish methodology + procedure
- Current focus on characterization process
Summary: Gas only exposure

1. 600°C:
   a. steam 1 bar  FY11, 2kh
   b. Ar-50%(CO$_2$-0.15O$_2$)(buffer)  FY11, 2kh
   c. 50%(CO$_2$-0.15O$_2$)-50%H$_2$O  FY11, 5kh
   d. 50%CO$_2$-50%H$_2$O(no buffer)  FY12, 2kh
   e. Ar-10%(CO$_2$-0.15O$_2$)-50%H$_2$O  FY12, 2kh
   f. Ar-50%H$_2$O  started

2. 650°C:
   a. steam 1 bar  FY11-12, 5kh
   b. 50%(CO$_2$-0.15O$_2$)-50%H$_2$O  started
   c. Ar-50%(CO$_2$-0.15O$_2$)  next

3. 800°C steam 17bar: A-USC follow on, started

4. 550°C steam 1bar (compare 17bar)  started
600°C: CO₂ content and buffer
Followup on H₂O-50%(CO₂-0.15O₂)

FY11 results

Mass gain after 2,000h
Worst case (fastest rate):
O₂ buffered
50%H₂O-50%CO₂

Most other groups do not use buffer, what is its role?
Little effect of $\text{C(CO}_2\text{)}$ & buffer

600°C, 4 x 500h cycles, 1bar

FY11 results

FY12 results

No buffer: 50%$\text{H}_2\text{O}$-50%$\text{CO}_2$

Lower $\text{CO}_2$: Ar-50%$\text{H}_2\text{O}$-10%(CO$_2$-0.15O$_2$)

Both: little effect on 2,000h mass change

Need to complete metallography comparison
Model 347 alloys: 650°C steam
Cast, hot rolled Fe-Cr-Ni-1.5Mn-0.4Si-0.8Nb-0.09C

5,000h 1bar exposure completed in March 2012
Higher (12%) Ni content very beneficial
2000h 17bar completed April 2012 (no effect)
Concern: model alloys better than 347HFG & S304H
Summary: Ash exposure

1. 600°C: (oxy-fire retrofitting current plants)
   air/oxy-firing (hot gas recirculation) (done)
   low $\text{H}_2\text{O}/\text{low SO}_2$ (done)
   FY12: low $\text{H}_2\text{O}/\text{low SO}_2$ (cold gas recirculation)

2. 650°C: (current USC plants)
   air/oxy-firing (run/awaiting metallography)

3. 700°C:
   air/oxy-firing (later this year)

4. 750°C: (A-USC range)
   air/oxy-firing (run/awaiting metallography)

5. 800°C: (A-USC range)
   air/oxy-firing (later this year)
Little effect of gas at 600°C
Synthetic coal ash, 500h exposures in 4 gases

Higher CO$_2$ environments not detrimental
Expected the lower SO$_2$ environment to lower attack
- same synthetic ash used in all cases
Little effect of gas at 600°C

Synthetic coal ash, 500h exposures in 4 gases

Higher CO$_2$ environments not detrimental
Expected the lower SO$_2$ environment to lower attack
- same synthetic ash used in all cases
310-740 differences accurate?

Highest alloyed examples with minimal attack

Sometimes focus on deepest penetrations
Need more images at “medium” magnification
Metal loss from 6mm diameter rod is minimal
Reanalyzed: 310HCbN < 740
High Ni-content alloy not most protective at 600°C

More accurate distributions from new images
Ash experiment issues

Experiments:
- air/oxy: worst case comparison
- “milder” oxy-firing: lower $H_2O$ or $SO_2$
- add cold recirculation: low $H_2O$/low $SO_2$

Test protocols to be evaluated:
- use of Pt catalyst
- crucible (covered sample) vs. ash slurry
- cycle frequency 10 x 100h vs. 500h x ?
- goal: “actual” rate or accelerated?

Metal loss measurement
- box plots capture variable attack
- scale thickness (not rod diameter)

Ash composition: how changed by oxy-firing?
Summary: Creep in steam

1. 800°C:
   completing work on Ni-base
   740 (Ni-23Cr-20Co); 230 (Ni-22Cr-14W)
   air vs. steam
   in-situ vs. ex-situ
   anneal (thermal effect)

2. 650°C:
   Grade 91 (9Cr-1Mo)
   air vs. steam
   coated vs. uncoated

   two in-situ creep rigs
800°C: 230/740 limited steam effect
Creep rupture tests in air and 1 bar steam

230: no effect of in-situ or ex-situ steam
740: microstructural reason for decreased life?
   - alloy/oxide characterization in progress
   - task will conclude this summer with paper
Grade 91: higher lifetime in steam
650°C 100MPa in air and 1 bar steam

Two concerns:
- temperature
- load transfer

Verified similar oxide formed on coupon in steam

Grade 91: Fe-9Cr-1Mo
650°C, 500h, 1 bar steam
Milestones

FY11

Done - Procure coatings for creep testing (12/10)
Done - Initial assessment of CO\textsubscript{2} role (6/11)
Done - Complete 600°C coal ash testing (6/11)

Delayed (9/11) - In-situ 650°C creep testing
(Resource delays/followup on results)

FY12

Done - Report CO\textsubscript{2}-H\textsubscript{2}O effects (12/11)
Done - Complete 600°-650°C steam tests (3/12)
- Complete in-situ Ni-base creep testing (6/12)
- Complete 700°C coal ash characterization (9/12)
Summary

Four tasks: gas only, with ash, creep, coatings

Gas only: further work on 600°C CO₂ effect
650°C steam testing complete

Coal ash corrosion:
- further data analysis of 600°C results
- Oxy-firing no worse with same ash
FY12 focus on temperature series
add “cold” oxy-firing conditions

Creep: T91 work at 650°C in progress
Ni-base: completing characterization

Coatings: final work on model/creep effects
CLEAN COAL.
COOL.
800°C model Ni-22Cr alloys
17bar steam, 2,000h exposure

Model alloys: simulate Al, Ti effect on internal oxidation

Ni-18Cr alloys (282) fabricated (2)

Future: quantify depth of attack, continue to 5,000h expose to coal ash

Specimen Mass Gain (mg/cm²)

After 2kh at 800°C, 17bar steam

Model alloys: 1Al+2Ti, 2Al+1Ti

Commercial alloys: 617 (1.3Al, 0.4Ti), 282 (1.5Al, 2.2Ti)

Cr₂O₃, TiO₂, Al₂O₃
Fe-xCr model binary alloys
1 and 17bar steam, 1-2 kh exposures

Here, model alloys perform worse than expected
Need to fill in with additional temperatures
Next question is about ternary additions (Mn, Si...)

[Graph showing mass gain vs nominal alloy Cr content and critical Cr content vs temperature for Fe-Cr model alloys]
Coating commercialization (slow)
- No industry interest in coating 8-11%Cr steels. Peak application is \( \sim 600^\circ C \) - no interdiffusion.
- More interest for austenitics (304, 347, etc.). Boiler application limited to \( \sim 650^\circ C \). Phase boundary will limit interdiffusion.
304H/347H tube explosions created interest.
EPRI funding for coating demonstration:

Vapor slurry coating
900°C steam
5,000h
Fe-9Cr in Steam vs. Humid Air
comparison of mass gain and reaction products
650°C, 1202°F

Similar attack in steam and wet air (10±1 vol.% H₂O)
Define failure: must have environment that attacks substrate
Prior work in lab. air could not define coating lifetime
Effect of temperature on $C_b$ 
$\sim 40 \mu m$ coatings on Fe-Cr at 650°-800°C in H$_2$O

Six failures of thin coatings, one higher Al activity coating
Agüero: 650°C slurry coating failed at $\sim 60$kh in steam
If temperature relationship is understood, this data set forms the basis for a comprehensive lifetime model
Creep Testing of P92 (Fe-9Cr-2W)

Effect of as-deposited coating thickness

- Specimen with thin coating has better creep resistance
- Effect of coating can be modeled as if coated layer absent
- Suggests that thin coatings are preferable

650°C, 1202°F; gage: 2 x 2 mm

Specimen with thin coating has better creep resistance
Effect of coating can be modeled as if coated layer absent

Suggests that thin coatings are preferable

Unusual Ti distribution in scale
Cast alloy 282 after 5kh in steam at 800°C

Electron probe analysis:
Typical internal Al + Ti oxidation
Ti “layer” at both gas & metal side

Scale after 5kh lab air:
\~12\%Cr needed at 550{\degree}C
For protective behavior at 17bar steam

Surprisingly, little difference in 2.25-11\%Cr steels
5,000h cross-sections in progress
800°C steam follow up work
Alloy 282: 5kh in 17bar steam or lab. air

Ni~20Cr
Al+Ti→γ’
Synergy
Al-Ti?

Model alloys: Ni-22Cr + Al +/- Ti in steam
New coal ash tests: H$_2$O added

Air- and Oxy-firing conditions: 600°C, 500h

Modified gas train to add H$_2$O to test
Mass gain: not a strong effect of H$_2$O
Change to oxy-firing had strongest effect on high Cr
Evaluated weld-overlay coupons
Air- and Oxy-firing conditions: 600°C, 500h

Nominal composition wt.%

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>other</th>
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<tr>
<td>309L</td>
<td>60</td>
<td>14</td>
<td>23</td>
<td>1Mn, 1Si</td>
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<td>8020</td>
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<td>20</td>
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<td>33</td>
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<td>31</td>
<td>33</td>
<td>2Mo, 1Cu</td>
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<td>72</td>
<td>57</td>
<td>43</td>
<td></td>
<td>0.3Ti</td>
</tr>
<tr>
<td>C22</td>
<td>3</td>
<td>58</td>
<td>23</td>
<td>13Mo, 3W</td>
</tr>
</tbody>
</table>

Rectangular coupons: removed overlay from tube
~1mm thick
- face adjacent to substrate has some dilution
- mass change data meaningless
Box plots to quantify attack
Air- and Oxy-firing conditions: 600°C, 500h

40 data points taken from 500X pictures including scale + internal oxidation
high Ni coating more oxidation resistant
attack not increased in oxy-firing conditions
Ex-situ testing: anneal vs. steam

2kh anneal to account for thermal effect

230: no effect of 2kh in steam at 800°C

740/617: decrease life after 2kh steam

larger decrease with 800°C 2kh anneal (?)
Coating results at 600°C
Low Al content chemical vapor deposition coating

Conclusions:
Coating prevents thick oxide formation in steam
Coating less effective on low Cr substrates
CO$_2$-H$_2$O is most aggressive environment