Mechanical Degradation of Ferritic/Martensitic and Austenitic Steels in CO_2 Environment

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National Energy Technology Laboratory

Research and Innovation Center

- The Advanced Turbines Program at NETL conducts R&D for directly and indirectly heated supercritical carbon dioxide-based power cycles for fossil fuel applications.
- The focus is on components for indirectly heated fossil fuel power cycles with turbine inlet temperature in the range of 1300 - 1400°F (700 - 760°C) and oxy-fuel combustion for directly heated supercritical CO_2 based power cycles.
- Materials issues involve quantification of creep, fatigue, oxidation and other mechanical and chemical processes in sCO_2 and gaseous CO_2 environments.

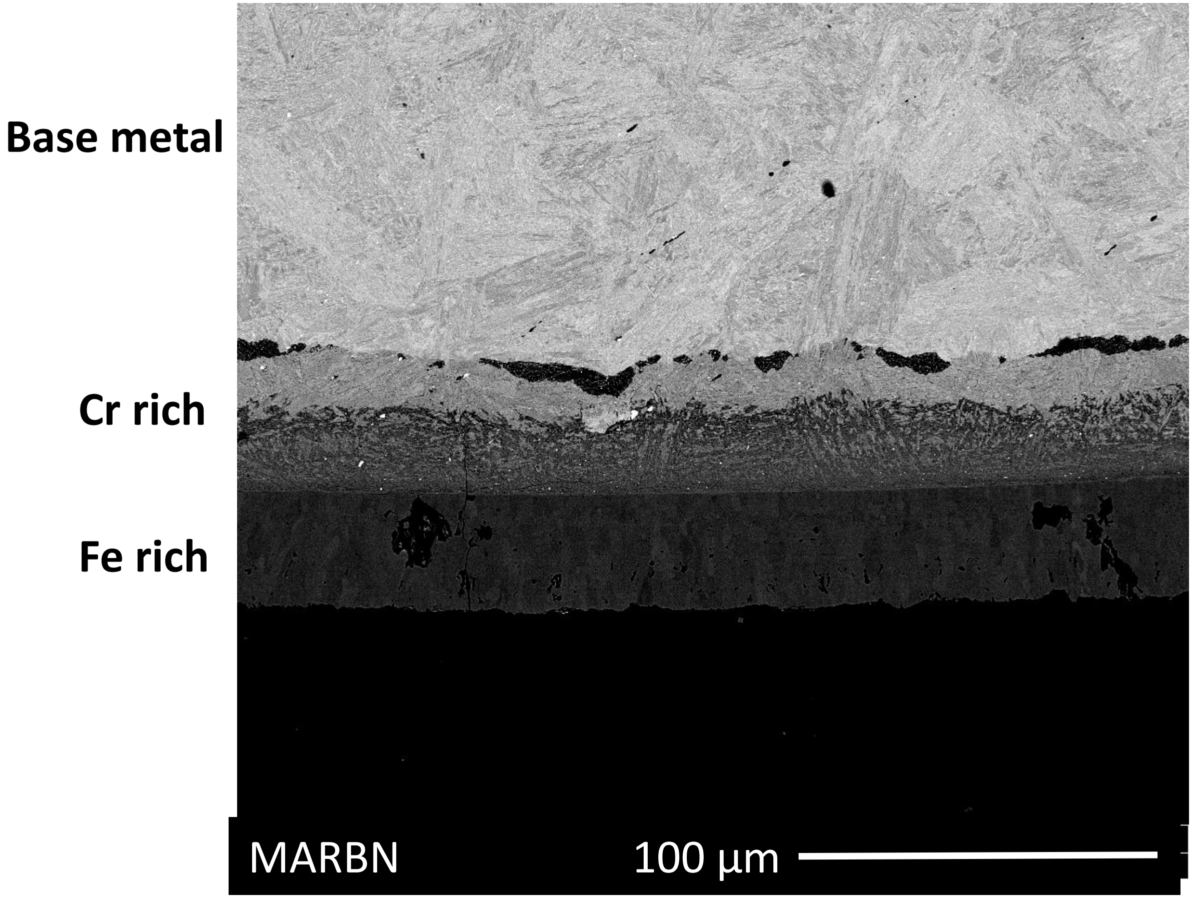
https://netl.doe.gov/onsite-research/materials

https://netl.doe.gov/node/7552

Introduction

Oxidation:

- **9% Wt. Cr steels under CO_2**
  - **Form duplex Fe-rich oxide scales following parabolic growth**
  - **Subject to enhanced carburization**
- **Austenitic Stainless (18-25% Wt. Cr.)**
  - **Protective Cr-rich scale is known to be interrupted in CO_2**



Introduction

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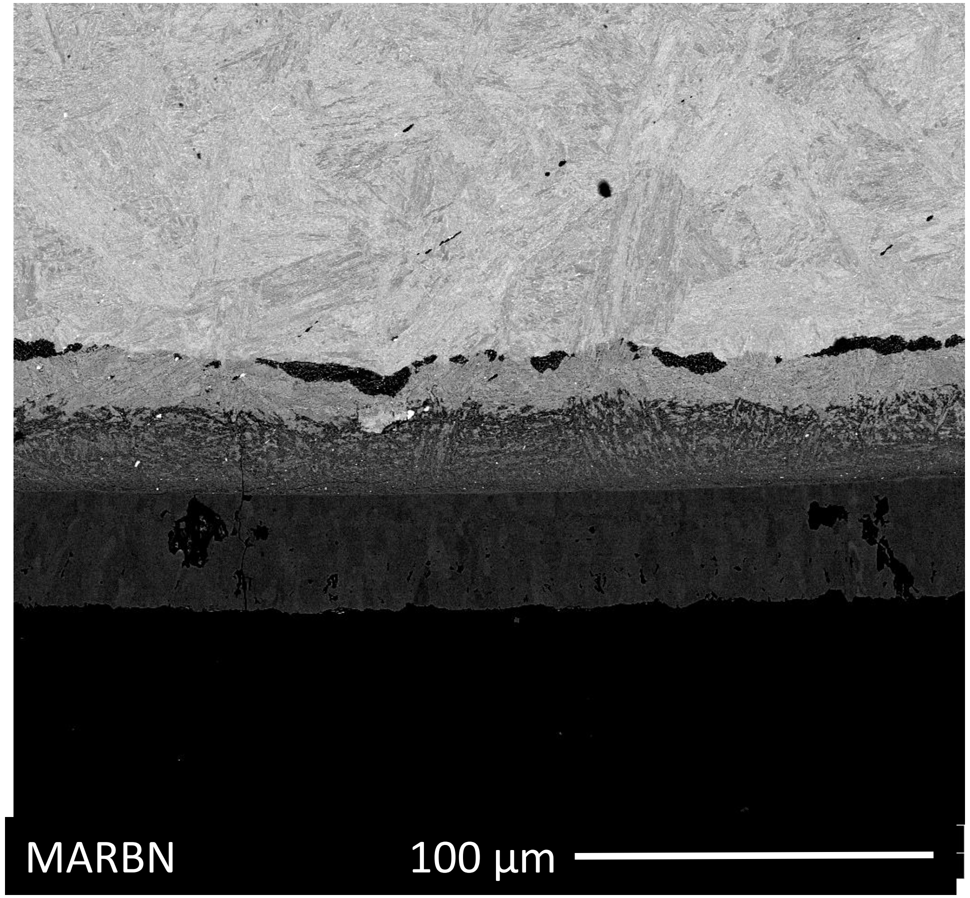
Mechanical Properties:

- *Exsitu* tests not showing difference after 500+ hour exposures, except in thin sections or with additions of H_2O, O_2 gases
  - Both steels and superalloys
- *Insitu* testing is more complex
  - Ethelene cracking experiments show severe carburization
  - Autoclave testing IN600 alloy only showed loss of creep life in sCO_2

Base metal

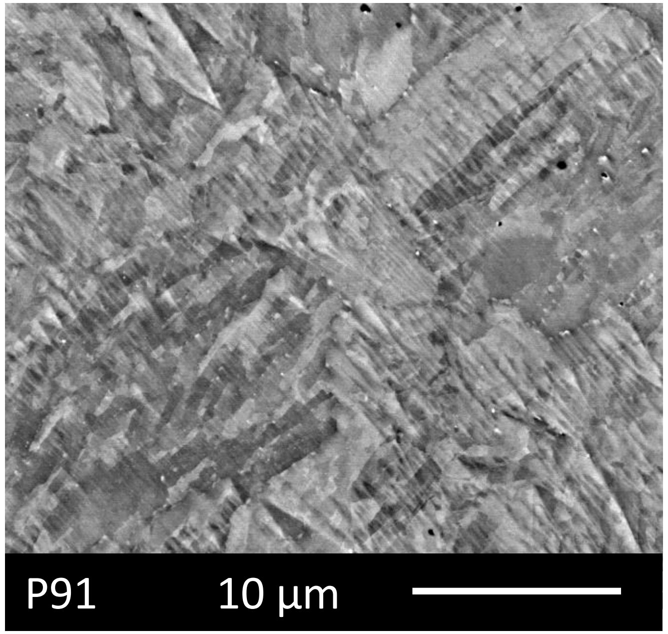
Cr rich

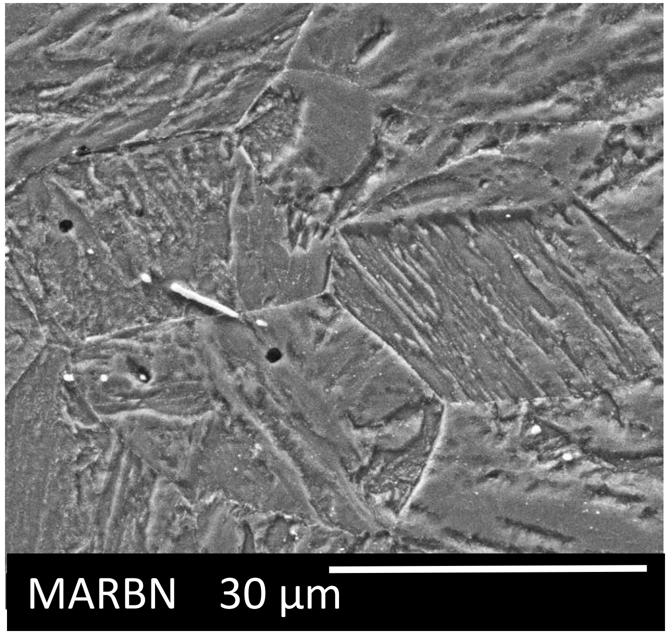
Fe rich

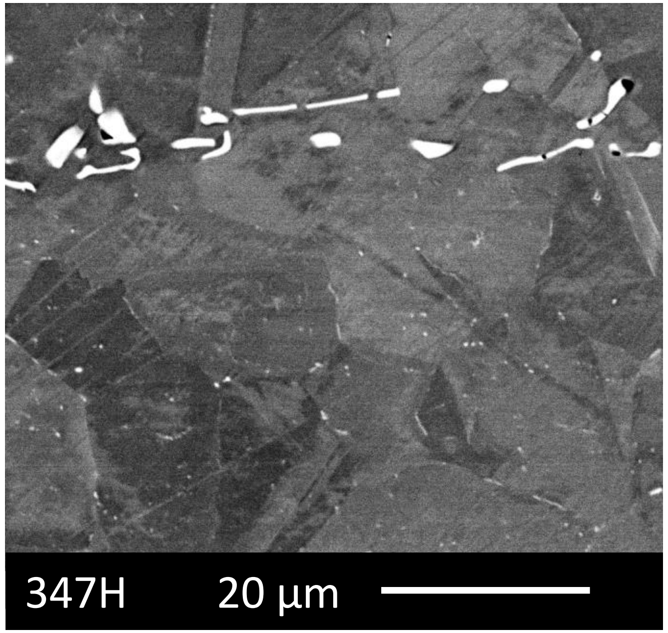


Materials

- **P91, 9% Cr steel, Martensitic / Ferritic**
- **MARBN, 9% Cr steel, Martensitic**
- **347H, 17.3% Cr stainless steel, Austenitic with Nb-rich carbides**

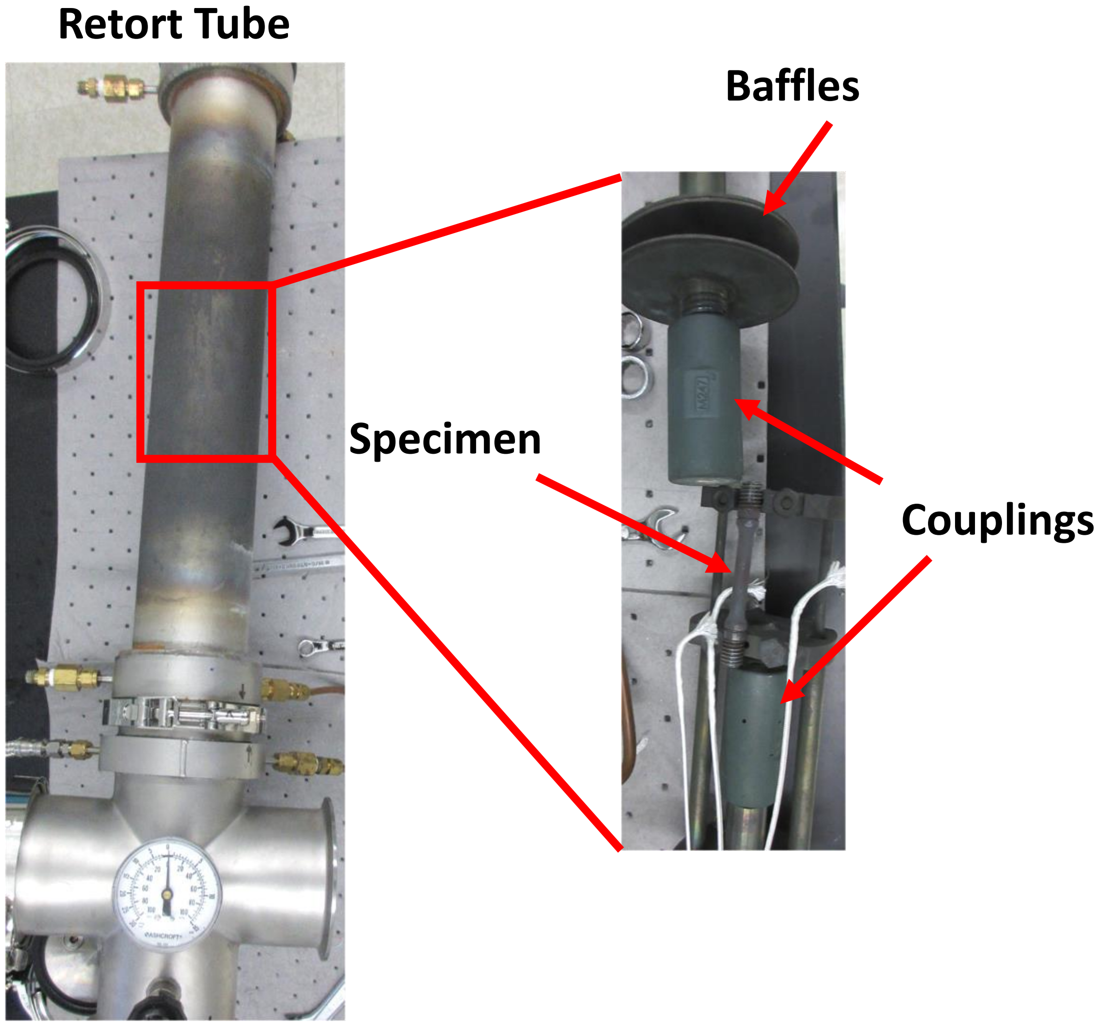






Methods

- Oxidation experiments performed in tube furnace
  - 2.54, 0.6 and 0.5 mm thick dogbone specimens
  - Surface finish of 600 grit
  - 650°C, CO_2 with 4% H_2O and 1% O_2 by volume.
  - 10^{-6} Torr Vacuum
  - 1000-hour exposure
- Tensile tests
  - 2.54, 0.6 and 0.5 mm thick dogbone specimens pre-exposed as above
  - ASTM E-8 test methodology
  - $3.3*10^{-5}$ / s strain rate to failure
- Creep testing
  - Cylindrical specimens
  - No pre-exposures
  - Retort tube controls environment at ambient pressures only
  - 207 MPa applied load at 650°C tested to failure



Pre-Exposure / Oxidation Results

- Tensile specimens were exposed to DF4 environment for 1000 h prior to testing
- P91 showed similar mass gain for both thicknesses
- Spallation led to reduction in mass gain for thin 347H specimen
- Thicker 347H specimen only had ~15% of the mass gain of P91 under the same conditions

Alloy	Specimen Thickness (mm)	Mass gain (mg/cm^2)
P91	0.50	29.0
P91	2.54	28.0
347H	0.60	-6.0
347H	2.54	4.6

Tensile Results

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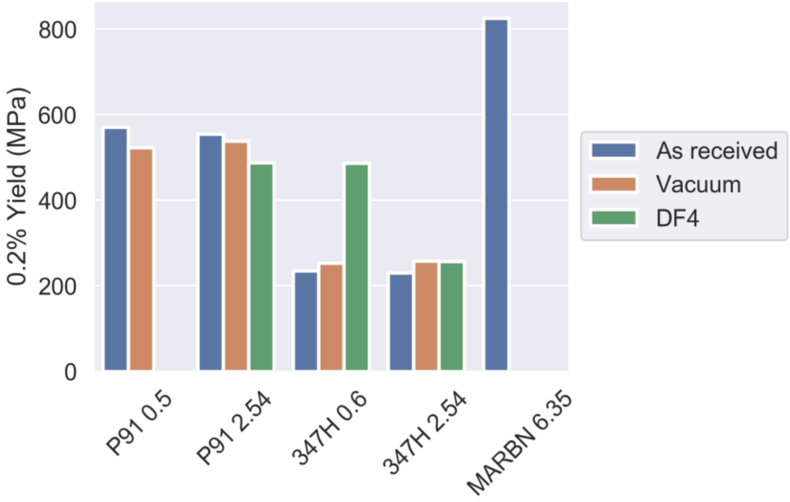
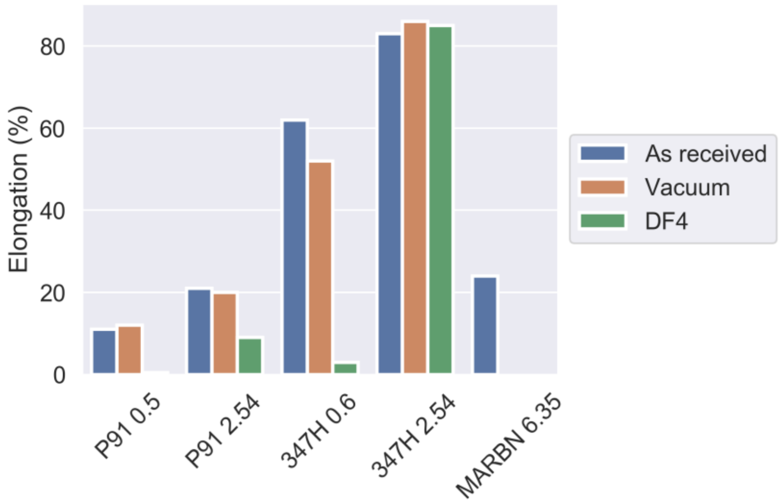
P91 Steel

- No significant changes noted from specimen thickness under vacuum exposures
- Thin specimen failed before yielding
- Thicker specimen's YS and UTS unchanged, but elongation was reduced by 57%

347H

- Only notable change from the thin section, which YS doubled and elongation severely reduced





Tensile Fracture Surfaces – P91

- Thick specimen showed
  - ~0.8mm enhanced carburization zone around the perimeter
  - No shear lip formation, suggesting embrittlement
- Thinner specimen showed
  - Severe embrittlement
  - Electron backscatter shows oxidation/carburization effected zone penetrating to ~0.2 mm (including oxidation scale)

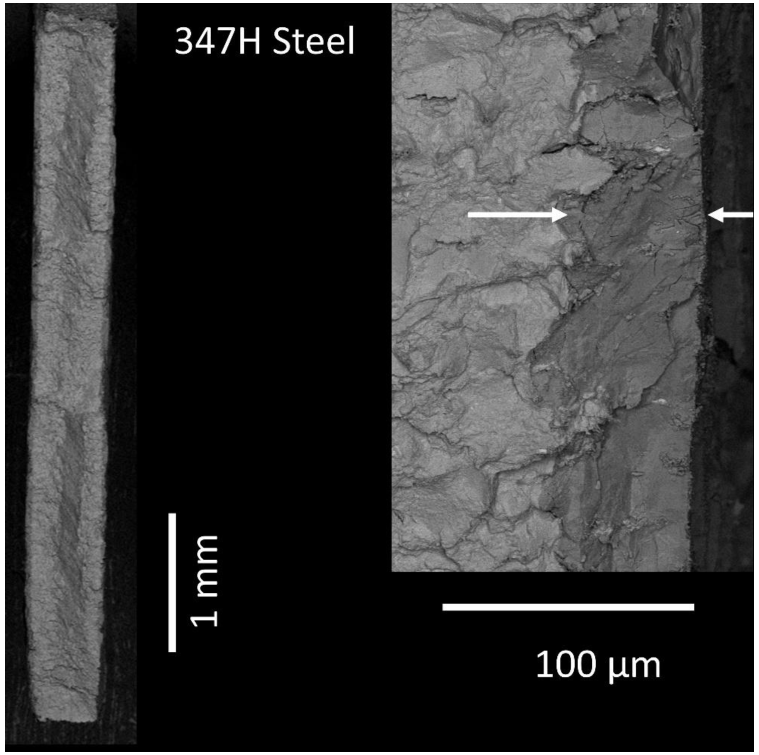
Thin specimen   Thick specimen

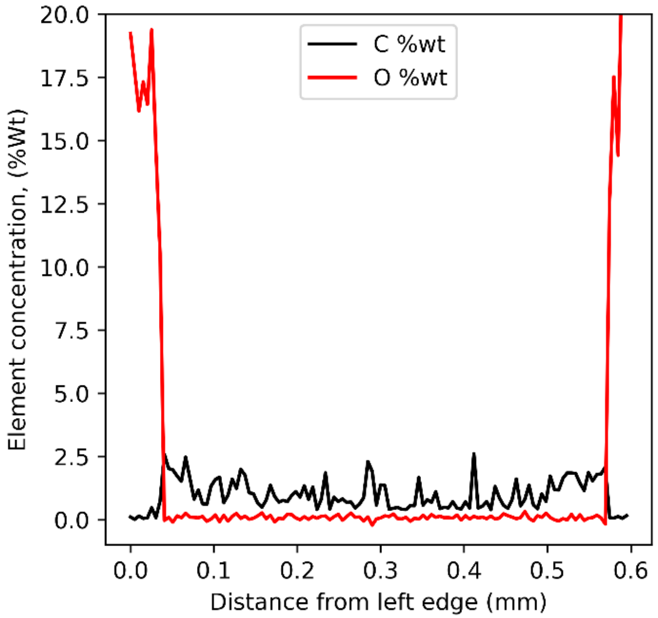
Tensile Fracture Surfaces – 347H

- Only Thin specimen featured
- Specimen failed at 45° incline plane, suggesting shear ductility
- High magnification shows phase contrast ~50 µm deep
- Microprobe analysis verifies this to be oxidation related

Thin specimen

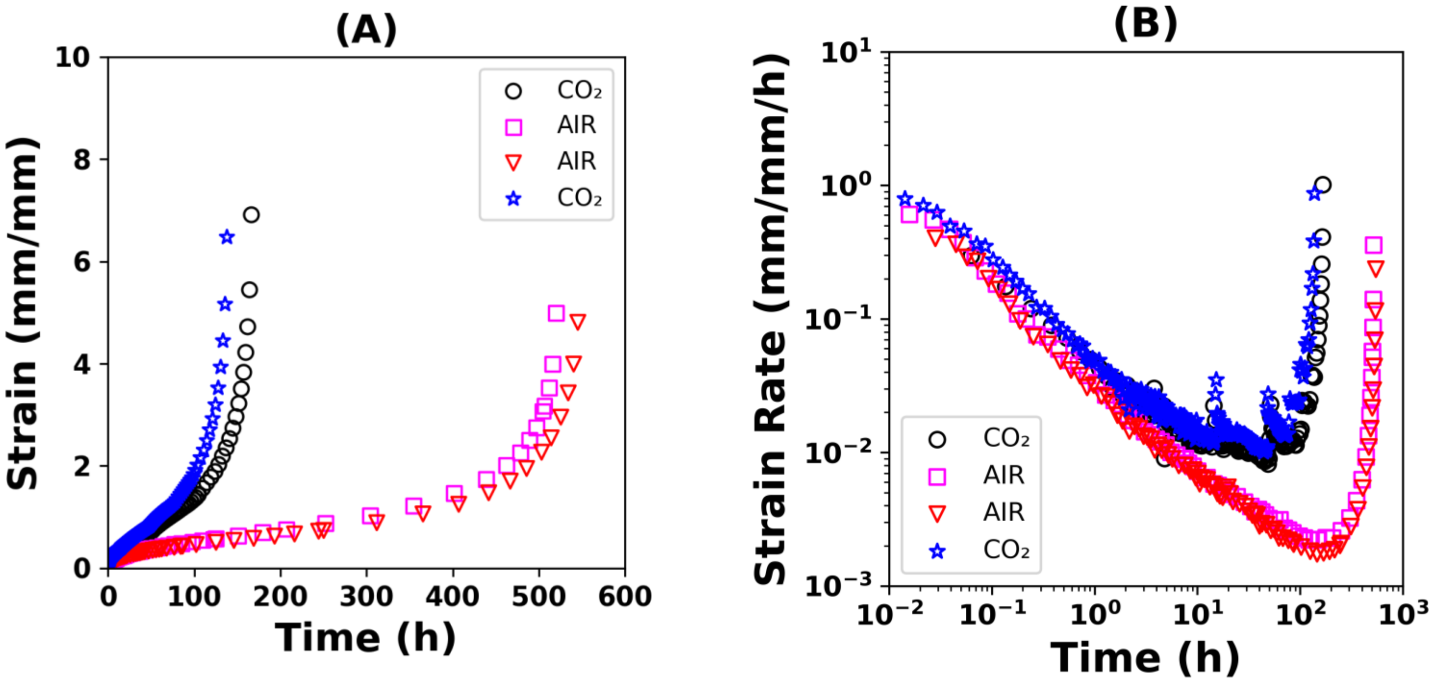
Thin specimen high magnification





Creep Results

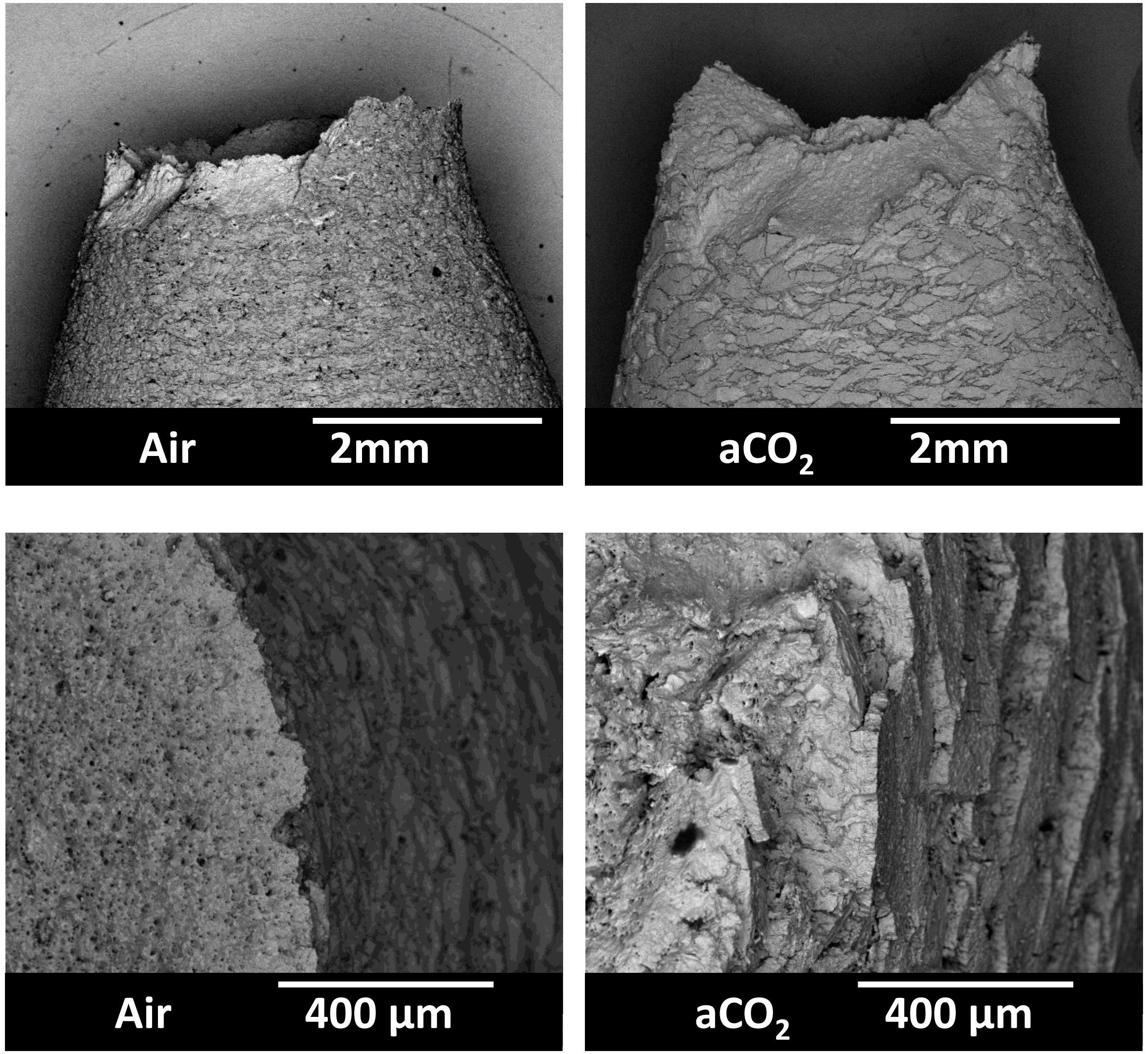
- MARBN and 374H tested to date
- Tests conducted in controlled environment retort tube
  - 100 sccm CO2, 650°C, ~207 MPa
- MARBN alloy showed
  - ~3.5X reduction in time to failure
  - ~1 decade faster MCR
- Faster MCR suggest mechanisms change



Alloy Designation	Test Temperature (°C)	Stress Level (MPa)	Time to Failure (h)	Elongation to Failure (%)	Reduction in Area (%)	Minimum Creep Rate (%/h)	Larson Miller Parameter, C=25
MARBN - Air	650	206.84	527	13.2	64.4	$2.21 \cdot 10^{-3}$	25586.18
MARBN - Air	650	206.84	545	12.6	69.9	$1.74 \cdot 10^{-3}$	25605.15
MARBN - CO_2	650	206.84	169	16.1	67.3	$8.20 \cdot 10^{-3}$	25129.21
MARBN - CO_2	650	206.84	140	14.7	58.3	$1.00 \cdot 10^{-2}$	25054.18

Fracture Surfaces - MARBN

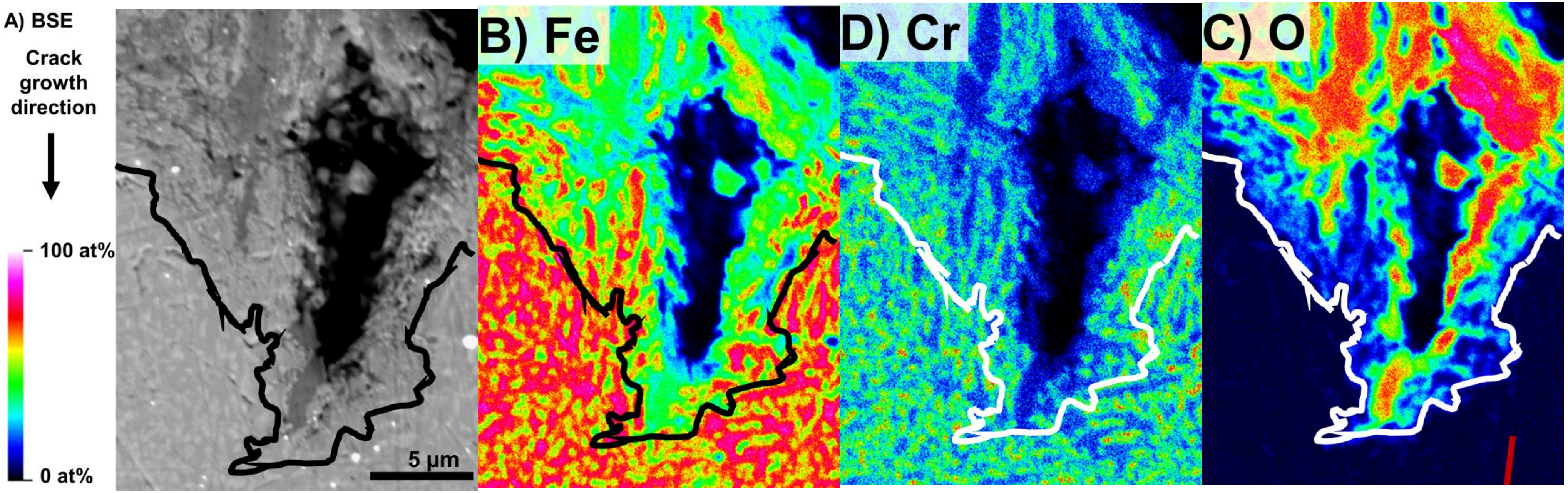
- Left images are from air, right from gaseous CO_2
- Brittle failure near specimen edge
- Cross sectioned samples
  - Hardness and etching revealed carburized zone penetrated ~200 µm deep



Rozman et al., 2021, Mat Sci Engr A, 826, #141996

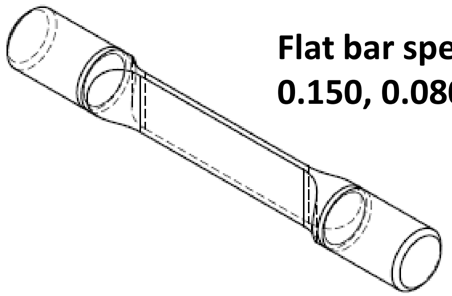
Cross Sections - MARBN

- Found complex interactions between oxide growth and enhanced carburization
- Carburization tied up Cr
- Less Cr to form protective chromia scale
- Feed back mechanism to enhance environmentally assisted cracking
- As evidenced by microprobe analysis and change in MCR

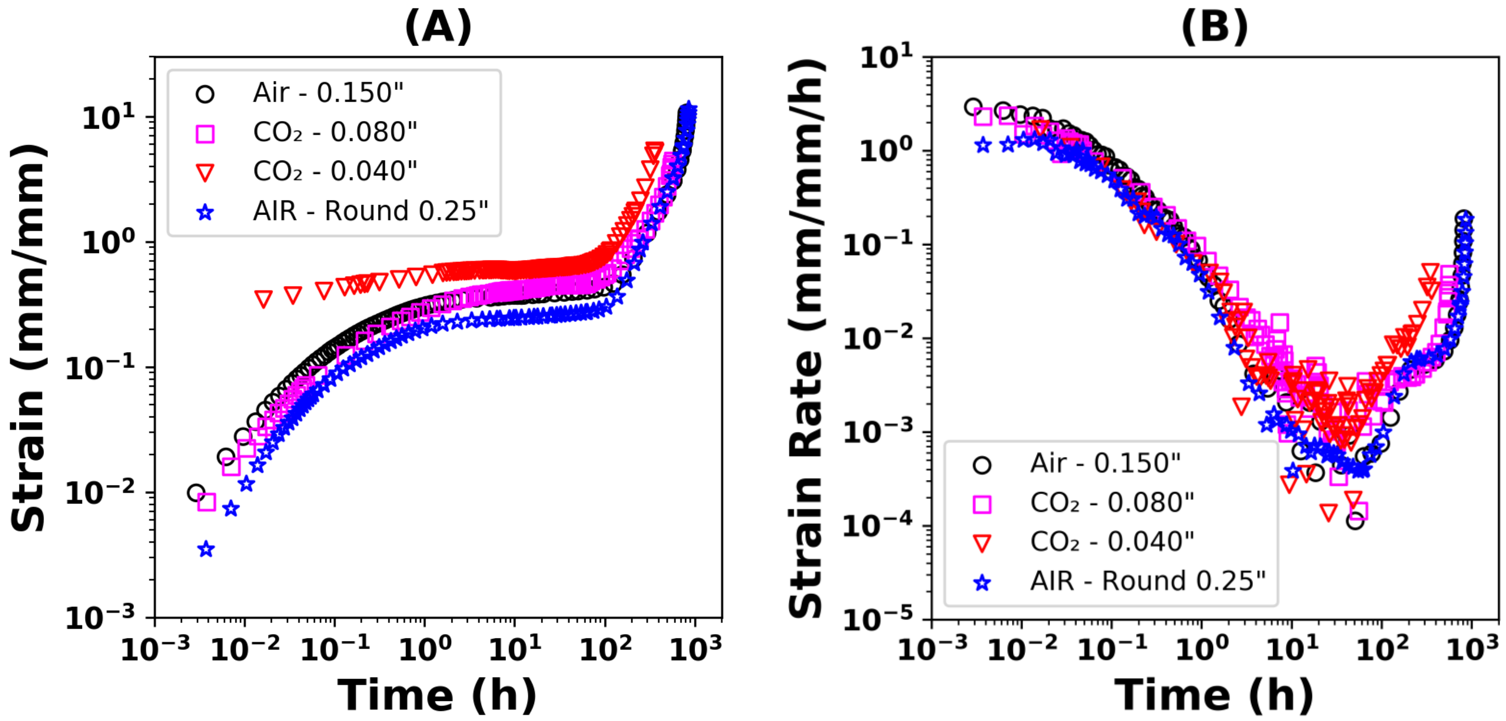


Creep Results – 347H

- Creep tests on going
  - 650C, 197 MPa
  - Evaluating both effect of thickness and environment
- To date no change NETL has found
  - Reduced creep life
  - Slight increase in MCR
  - Suggests no mechanism change



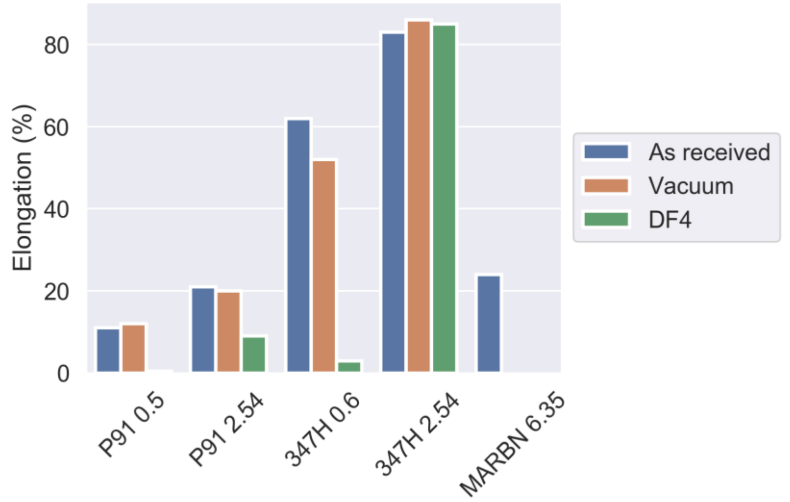
Flat bar specimen to maximize surface area
0.150, 0.080, 0.040, 0.020 inch thicknesses



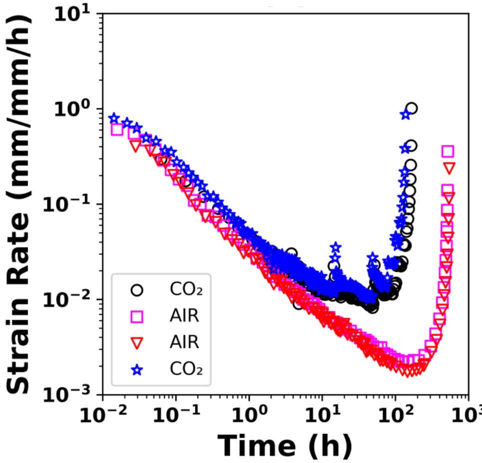
Conclusions

<u>9%Wt Cr steels</u>

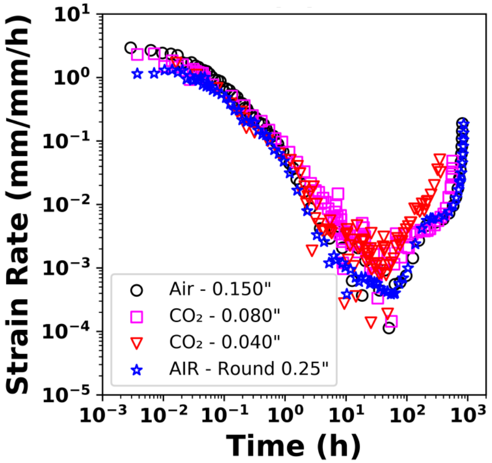
- **Carburization strongly effects mechanical properties**
- **Strategies to mitigate carburization are necessary if used in sCO_2 applications**
- **Thin sections subject to severe degradation**
- **Creep lifetimes reduced ~3.5X**



MARBN



347H



Conclusions

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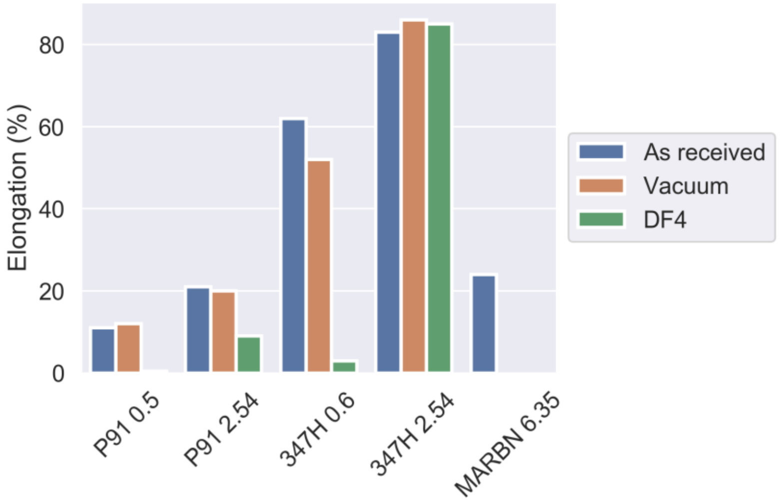
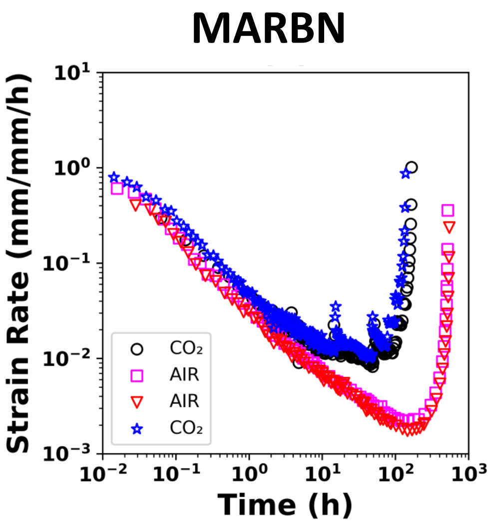
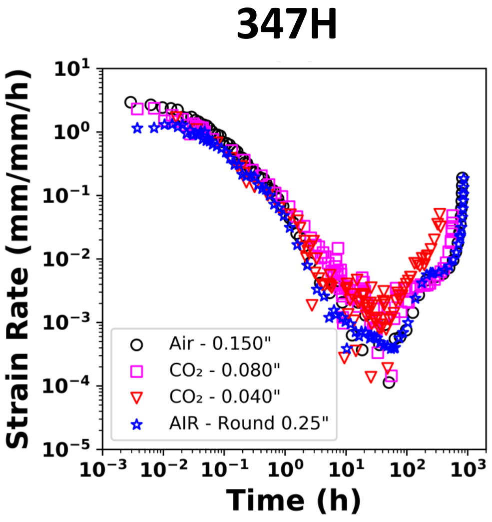
Austenitic steels – 17%Wt Cr

- Generally better resistance to environmental effects in sCO_2
- Thin sections showed brittle behavior (reduction in ductility and increase in yield stress)
- Creep experiments are on going
- Preliminary results show reduction in lifetimes but no change in MCR
- Suggests they may be resistant to environmentally assisted cracking







Thank You

Questions?

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