

The Use of Glow Discharge Optical Emission Spectroscopy to Quantify Internal Carburation from Exposure to Supercritical CO₂

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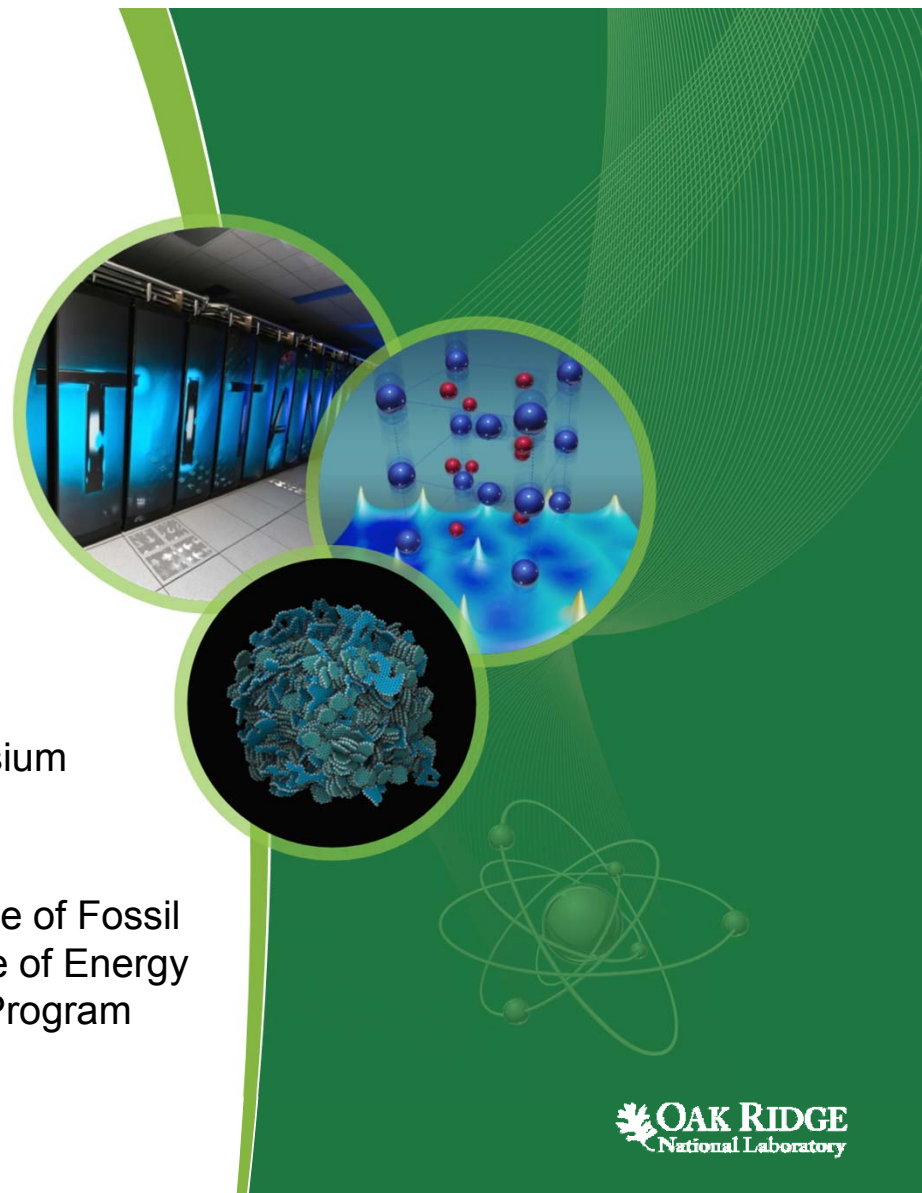
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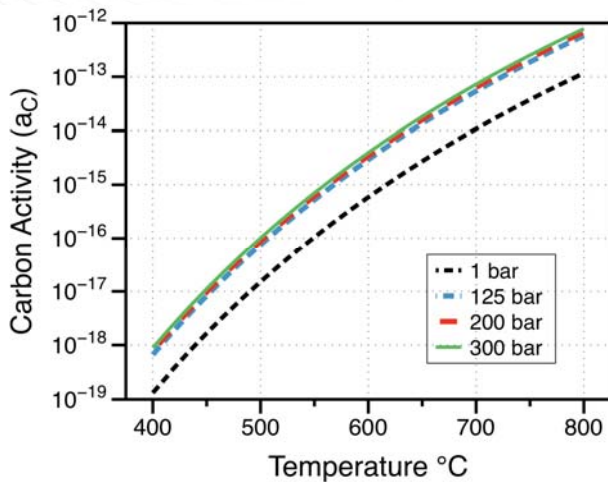
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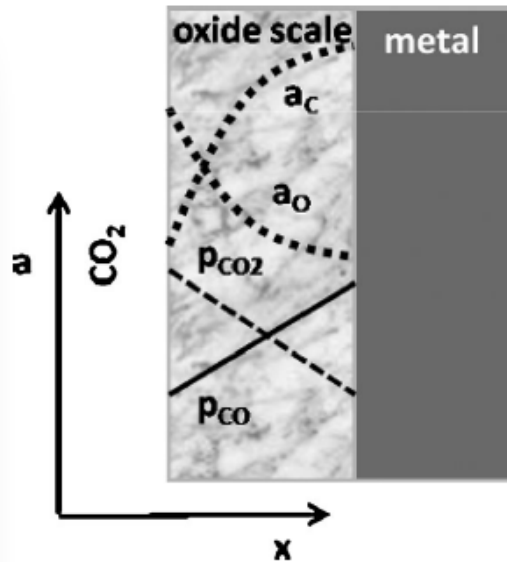


sCO₂: Thermodynamic calculations suggest that internal carburization is possible

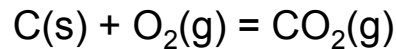
Factsage a_c calculations:
low C activity in RG sCO₂



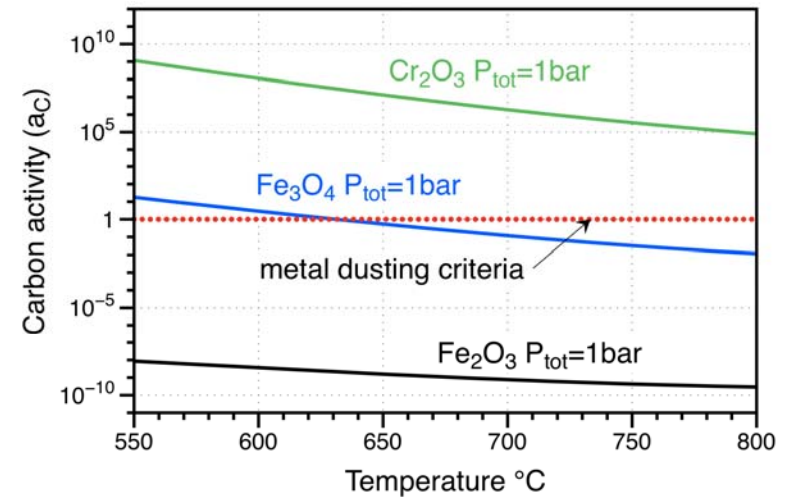
Young 2011
schematic



Fujii and Meussner 1967
identified the same issue



At interface: C is a concern



High carbon activity at P_{total} = 1 bar

Up to 25% Chromium carbides in the alloy after 20kh at 600°C for AGR

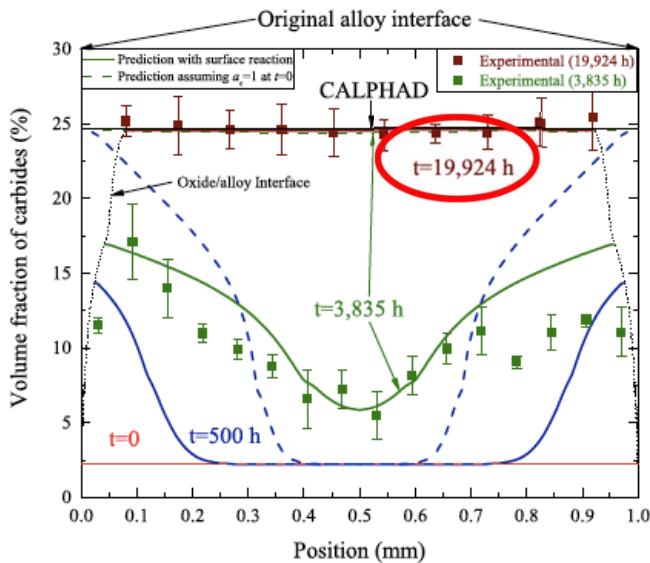


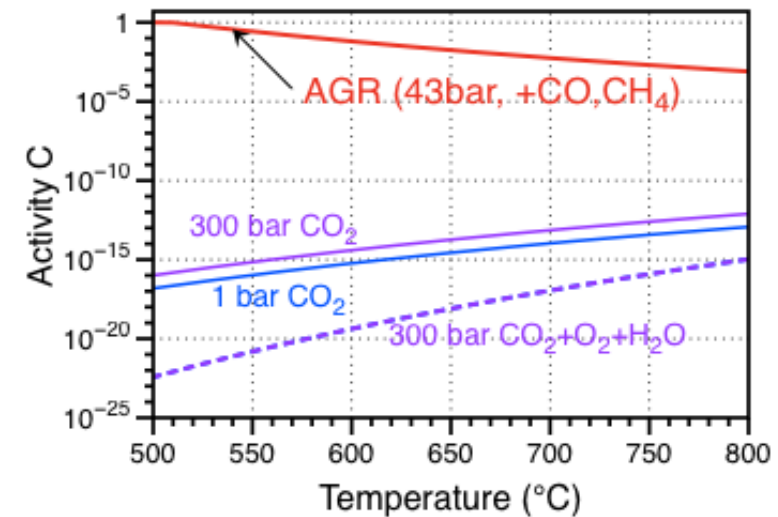
Fig. 8. Predicted profiles of volume fraction of carbides for a 1 mm fin exposed to experimental gas conditions at 600 °C at 0, 500 h, 3835 h and 19924 h, in comparison with measurements corresponding to black box marked in Fig. 1(b); simulations were conducted by 1D-DiCTra as described in § 3.2 treating migration of oxide/alloy interface and non-steady state carburization with $\alpha_{\mu,C} = 1.2 \times 10^{-12} \text{ mol m s}^{-1} \text{ J}^{-1}$ (solid lines) or fixed $a_C = 1$ at the oxide/alloy interface (dashed lines).

Gong, Young...Reed,
Acta Mater. 2017



Grade 9 steel fins:
Fe-9Cr-1Mo

But the 600 psi CO₂ in
AGR is very carburizing

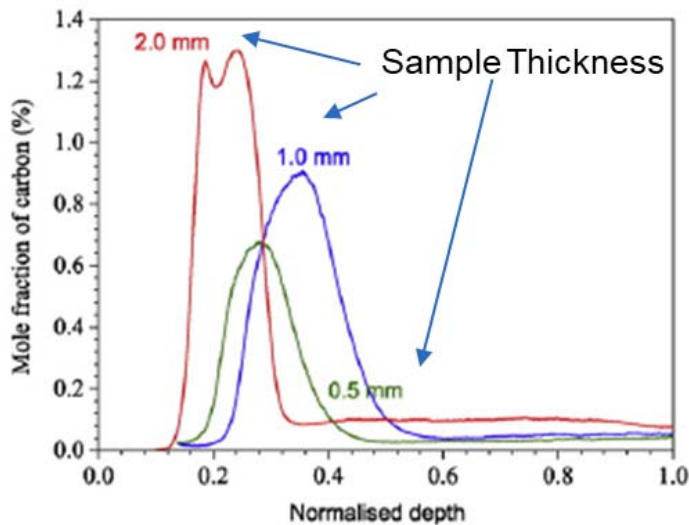


- Can GDOES be used to detect the onset of carburization under milder conditions?

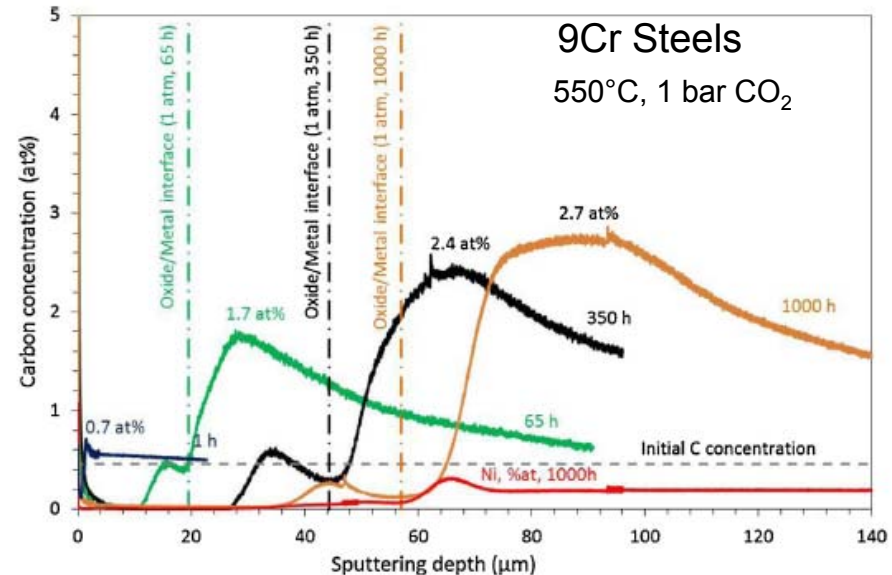
Glow discharge optical emission spectroscopy (GDOES) has been successfully used to study carburization following exposure to sCO₂

Jülich: Pillai, R., A., et al. (2016)

CEA: Rouillard, F. and T. Furukawa (2016)



- Carbides were detected in the interdiffusion zone following aluminization of a SX Ni base alloy.



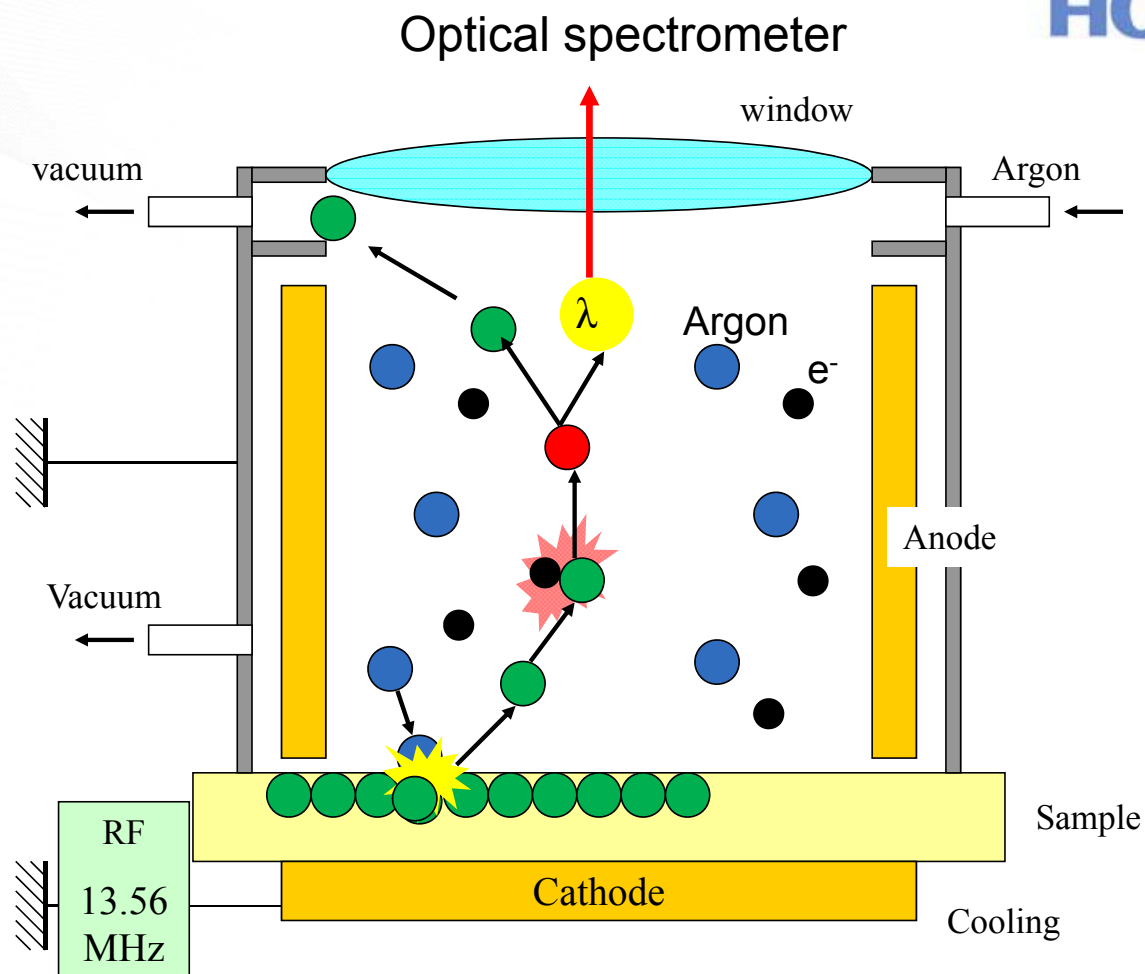
- Carburization increases with CO₂ pressure above 500 °C.
- C was detected in the spinel layer as well.

Key Points about Glow Discharge Optical Emission Spectroscopy (GDOES)

- Light elements (H, D, He, Li, Be) can be quantified. Carbon detection limit <30 ppm (Shimizu, K., et al. 2003).
 - **KEY STRENGTH** over electron-based x-ray spectroscopy (EPMA) which has poor detection limits for light elements.
- Technique relies on the sputtering of materials using a plasma and the analysis of emission lines through an optical spectrometer.
- High dynamic range PMTs allow concentrations to be measured from ppm to 100%
- Fast sputtering rate (2-150 nm/s) – much faster than XPS or SIMS.
- Thin and thick films can be measured (nm to ~200 μm). Depth resolution is nm scale.
- Lateral spot diameter is 1 – 7 mm, but typically 4 mm.
 - **KEY WEAKNESS** compared to electron-based techniques: only 1D profiles, not 2D mapping.
- 40 elements are measured simultaneously plus one more using a monochromator.
- Depth is directly measured during sputtering using laser interferometry.

Principle of Glow Discharge Optical Emission

HORIBA JOBIN YVON



2 separate processes :

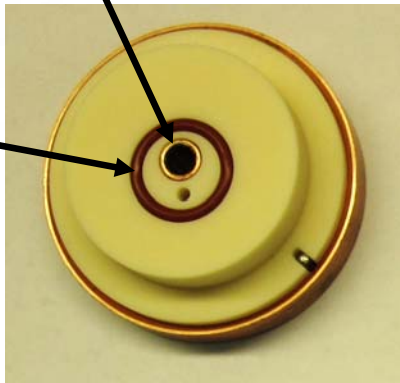
1) Erosion (sputtering)
Ion bombardment
Particle erosion

2) Excitation (emission)
Collision and excitation
Photon emission

Sample placement on the GDOES instrument

4 mm anode

o-ring

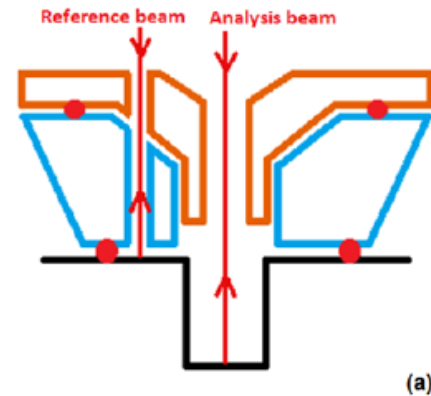


Sample

Cathode (cooled)

- The sample must form an air-tight seal against the o-ring
- Very large samples can be measured. Small samples require more sample preparation.
- Scans take around 10 minutes.

Differential Interferometry Profiling (DiP) measures sputtering depth directly



(a)



(b)

- Two laser beams hit the surface within and outside of the sputtered area.
- Interferometry is used to convert sputter time in seconds to sputtered depth in nm.
- Measurement occurs at the same time as the concentration profile.

CO₂ compatibility was evaluated in two ways at 700°-800°C

**Autoclave: 300 bar sCO₂
500-h cycles**



Correct temperature and pressure

**Automated cyclic rig:
10-h cycles, 1 bar CO₂**



Simulate the CSP duty cycle

Baseline of industrial grade (IG) CO₂: 18±16 ppm H₂O and ≤ 32 ppm O₂

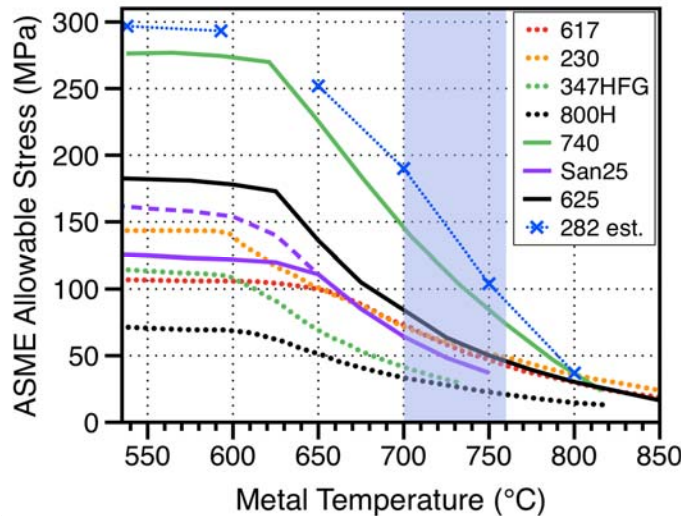
Four alloys selected for SunShot study

- Composition analyzed by ICP-OES and combustion analyses

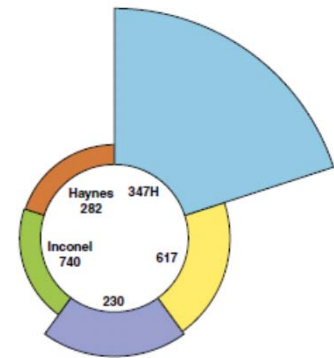
| Alloy | Fe | Ni | Cr | Al | Co | Mo | Nb | Ti | Mn | Si | Other |
|--------------|------|------|------|------|------|-----|-----|------|------|------|---|
| Sanicro 25 | 42.6 | 25.4 | 22.3 | 0.03 | 1.5 | 0.2 | 0.5 | 0.02 | 0.5 | 0.2 | 3.5W, 3.0Cu, 0.2N, 0.068 C (Sandvik) |
| Haynes 282 | 0.2 | 57.1 | 19.6 | 1.6 | 10.6 | 8.6 | < | 2.2 | 0.02 | 0.04 | 0.059 C (Haynes International) |
| Inconel 740H | 0.1 | 49.7 | 24.5 | 1.4 | 20.6 | 0.3 | 1.5 | 1.4 | 0.3 | 0.2 | 0.027 C (Special Metals) |
| 625 | 4.0 | 61.0 | 21.7 | 0.12 | 0.1 | 8.8 | 3.5 | 0.2 | 0.2 | 0.2 | 0.06W, 0.09Cu, 0.016 C (Industry selection) |

ASME Boiler & Pressure Vessel Code allowables:

Precipitation-strengthened (γ') Ni-base alloys



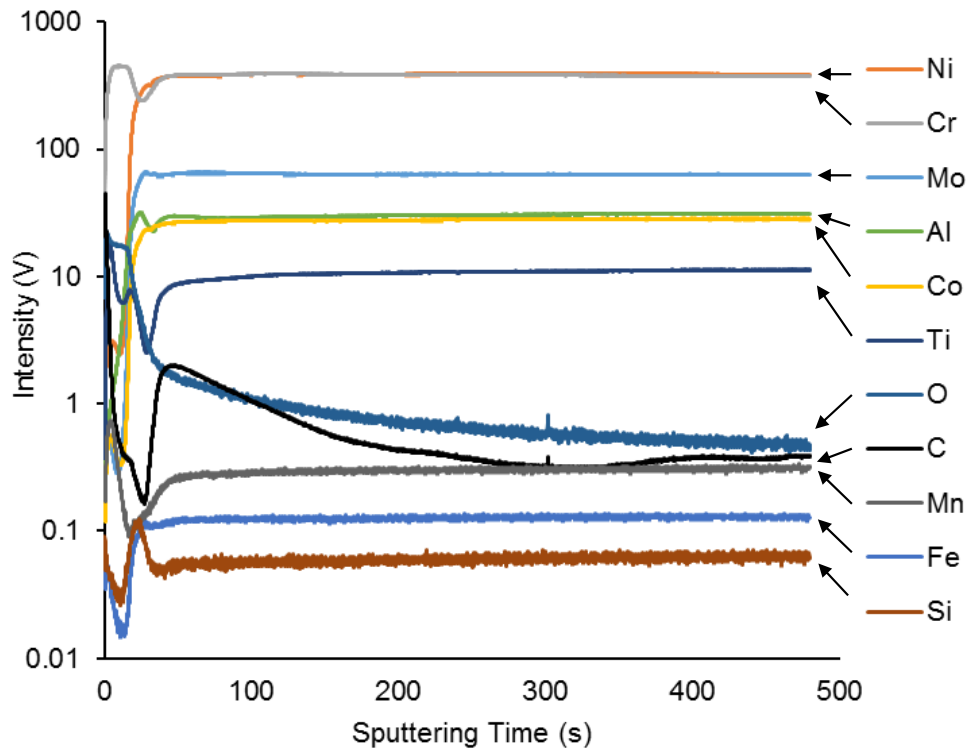
Required Wall Thickness



Shingledecker ~2011



GDOES Raw Data from 282 exposed to 300 bar CO₂ at 700 °C for four 500-h cycles



- A Horiba GD Profiler 2 with Argon pressure at 850 Pa and the power of 50 W for all measurements.
- The anode diameter was 4 mm which is also the size of the region measured across the sample surface.

Conversion of GDOES light intensity to atomic %

- Following the procedure of Nowak (2017) from Jülich, the base alloy below the depletion zone is used to calibrate the carbon signal.
- Relative sensitivity factors (RSF) is the concentration of the element (c_x) in the base alloy divided by the average light intensity (I_x) during the final minute of sputtering. Each sensitivity factor is then normalized to the sensitivity factor for the base element (Ni):

$$RSF_x = \left(\frac{c_x}{I_x}\right) / \left(\frac{c_{Ni}}{I_{Ni}}\right)$$

- The RSF for oxygen was estimated by averaging light intensity for O and Cr in a region of the scale that is composed almost entirely of Cr_2O_3 :

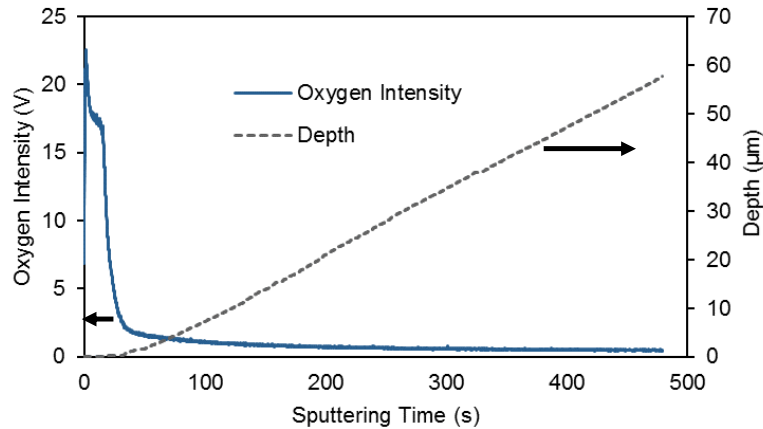
$$RSF_O = \left(\frac{I_{Cr} * RSF_{Cr}}{I_O}\right) \left(\frac{3}{2}\right)$$

- Concentration for each element at each depth ($c_{x,depth}$) is then calculated in atomic percentage:

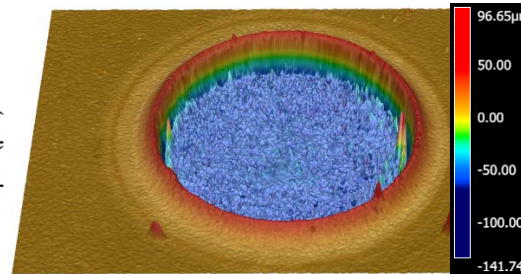
$$c_{x,depth} = \frac{I_{x,depth} * RSF_x}{\left(\sum_{i=1}^n I_{i,depth} * RSF_i\right)}$$

Differential Interferometry Profiling (DiP) failed to work on the oxide scale

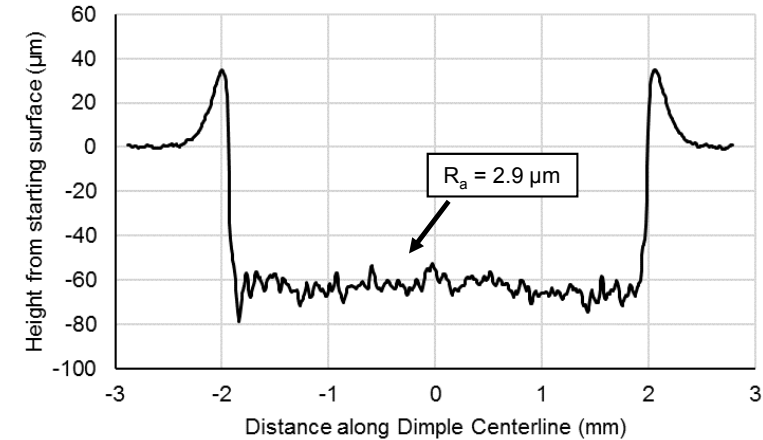
Measured depth profile and oxygen signal



Sputtered dimple



Line profile across dimple

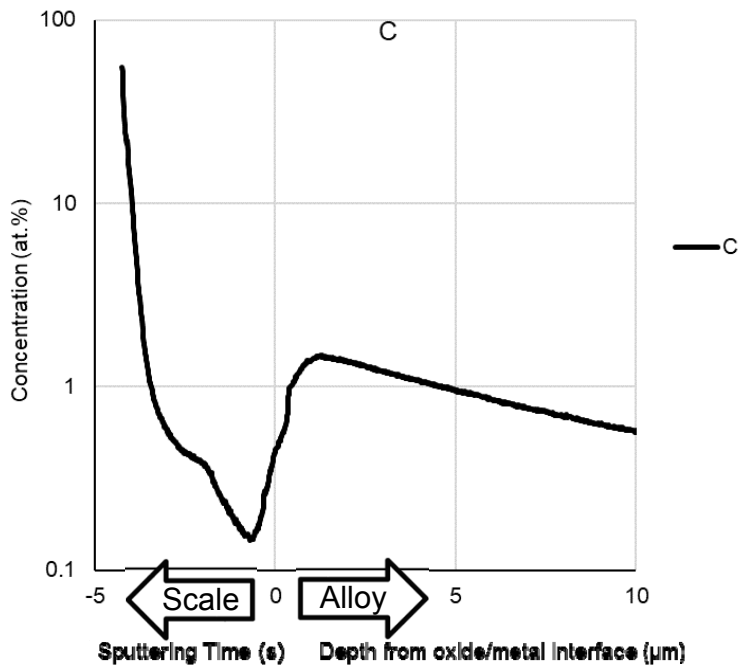


- The DiP signal only works after the oxide scale has been removed.
- The difference between the final sputtered depth measured by DiP and by optical profilometry was $\sim 6 \mu\text{m}$ which was the scale thickness including internal oxidation.
- The average roughness (R_a) of the sputtered surface which was $2.9 \mu\text{m}$ which is the effective depth resolution of the technique under these operating conditions.

GDOES measurements match EDS elemental maps

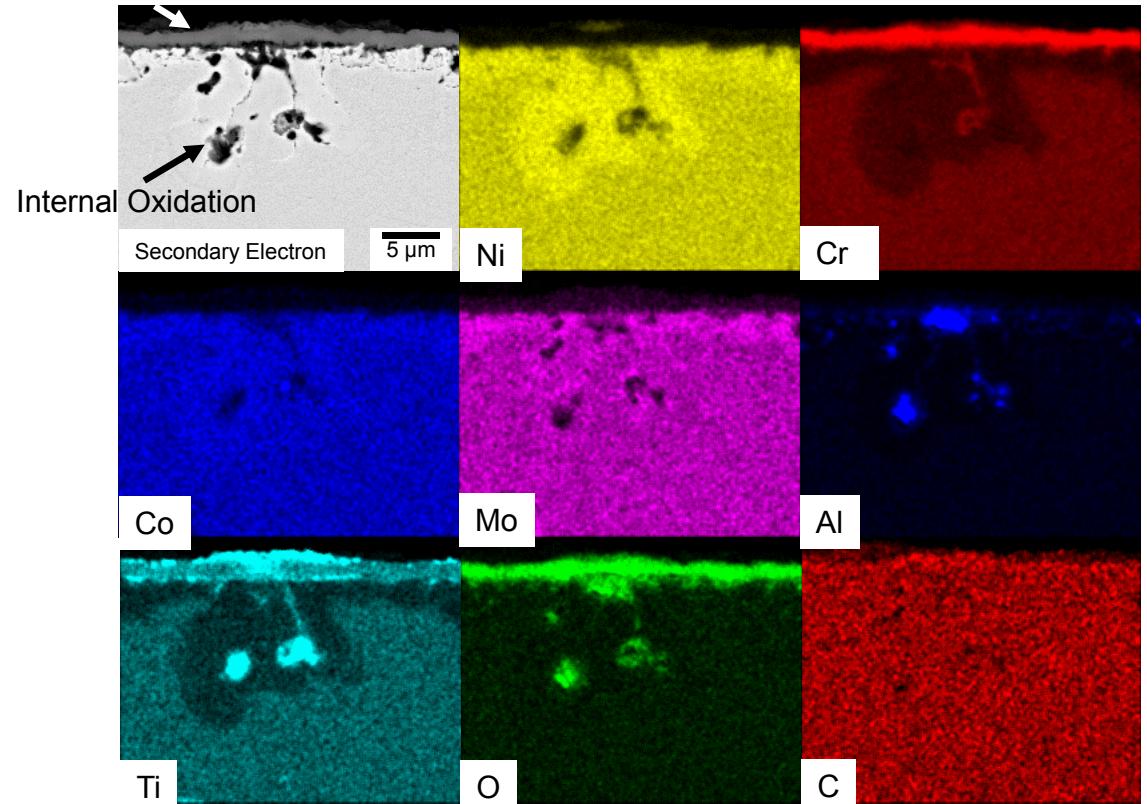
EDS Elemental Maps

Calibrated GDOES Concentration Profiles



282 exposed to 300 bar of CO₂ at 700 °C for four 500-h cycles

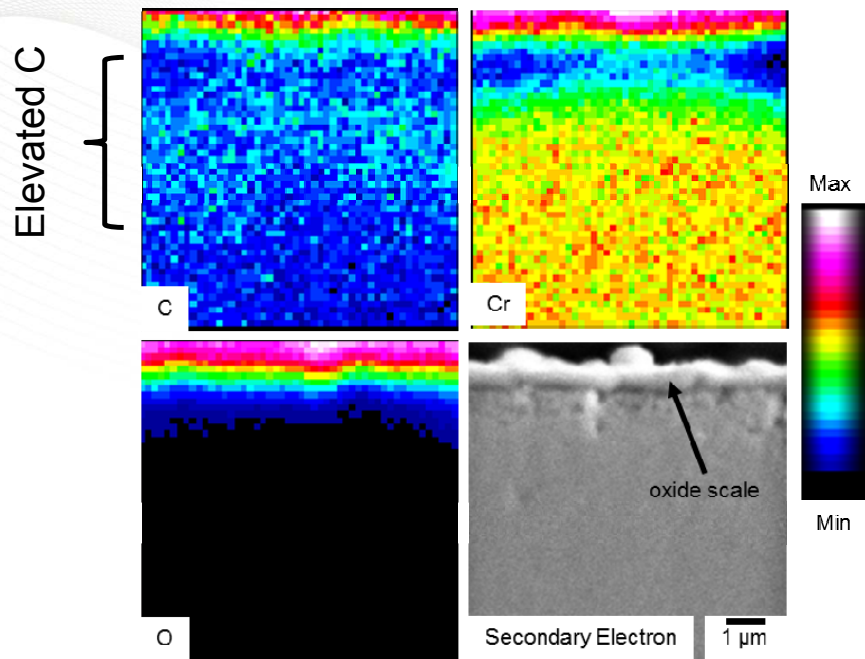
Oxide Scale



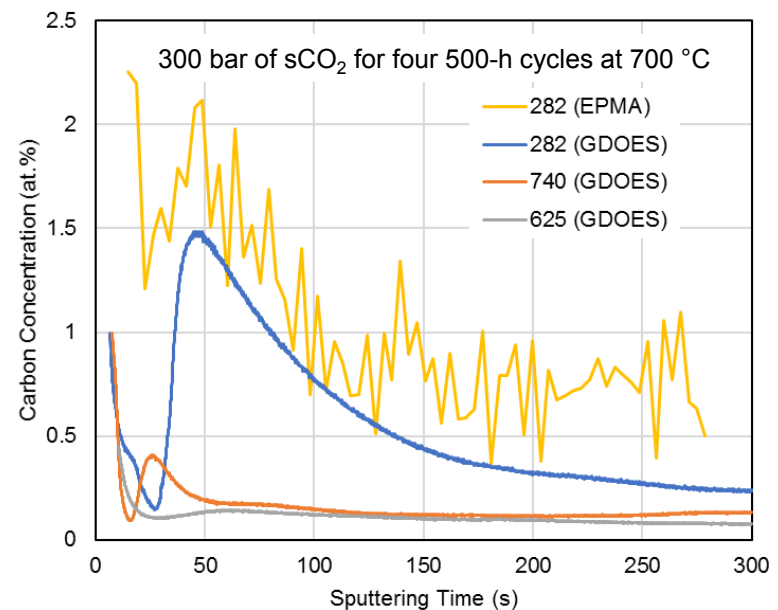
Carbon was from the sample prep not the sample

GDOES is more sensitive to C concentration than Electron Probe Microanalysis

EPMA Elemental Maps



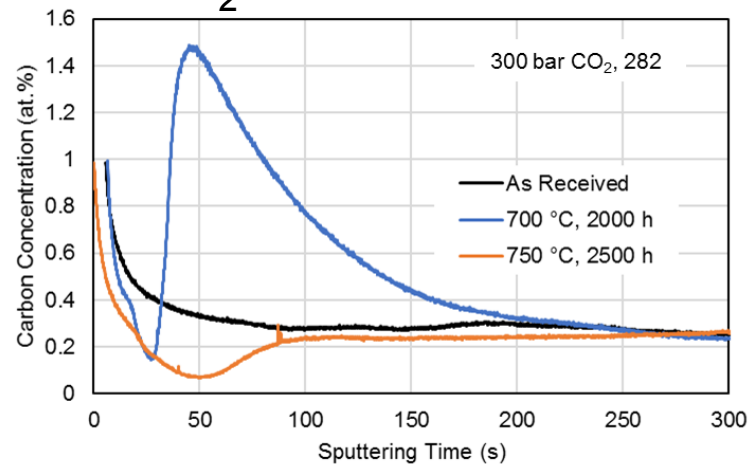
Calibrated GDOES Concentration Profiles



- Since GDOES collects data across a 4-mm diameter spot, the analytical volume is orders of magnitude larger than that of EPMA and so the GDOES measurement will be more accurate with less noise.
- The degree of carburization was highest for 282 followed by 740 and then 625.

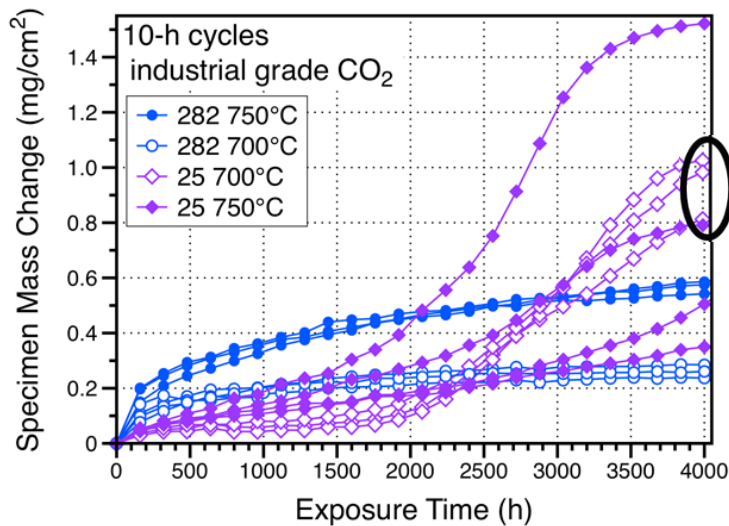
The 282 specimen exposed to the lower temperature showed carburization

C concentration profiles for 282 exposed to 300 bar sCO₂ at 700 °C and 750 °C.

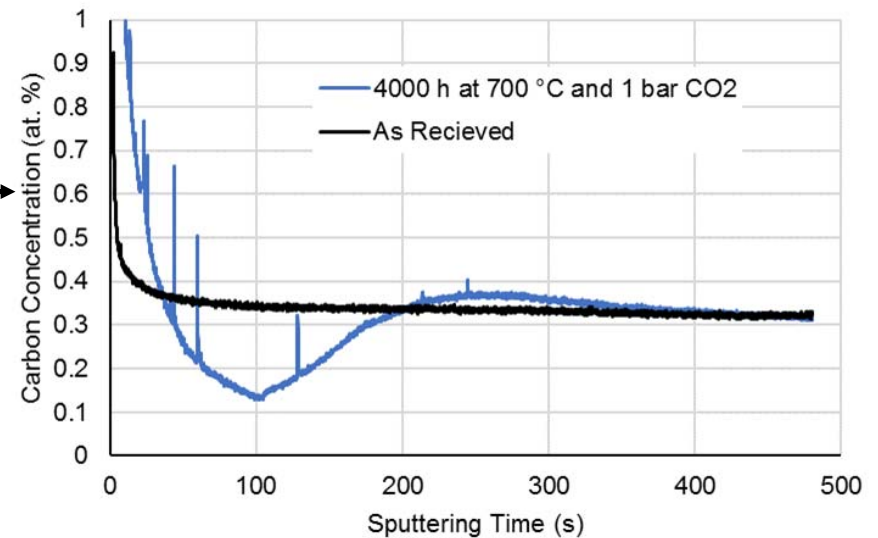


- The thicker oxide formed at the higher temperature may provide a better barrier to C ingress.
- C concentration declines beneath the oxide scale due to the loss of chromium carbides

Fe-based alloy 25 specimens all showed accelerated (i.e. non-parabolic) mass-gain behavior

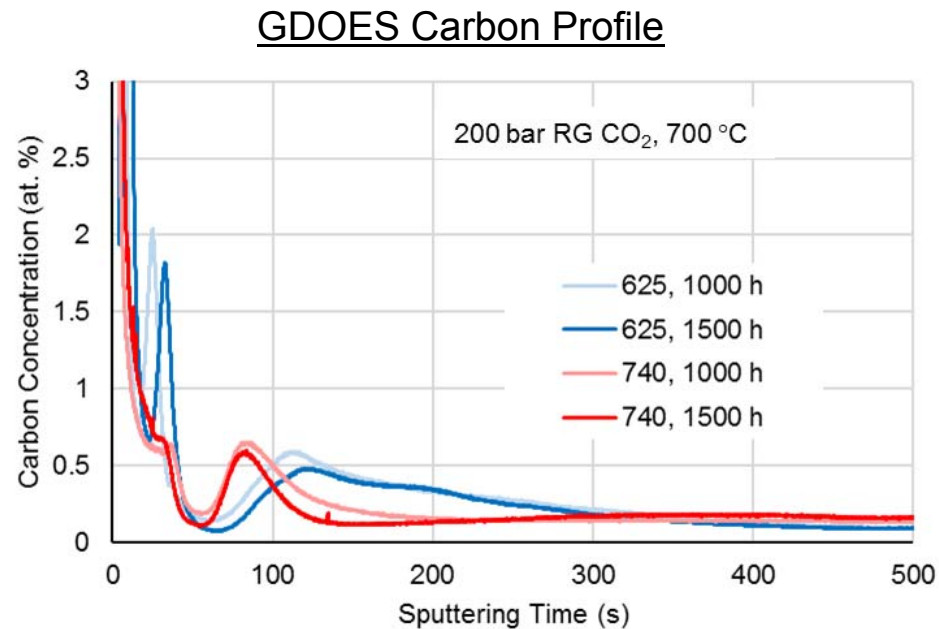


GDOES Carbon Profile in Fe-based 25



- Fe-based alloys may be more susceptible to C ingress because of the higher affinity of C for Fe than Ni.
- However, GDOES shows that there is no strong evidence that the accelerated attack was caused by C ingress.

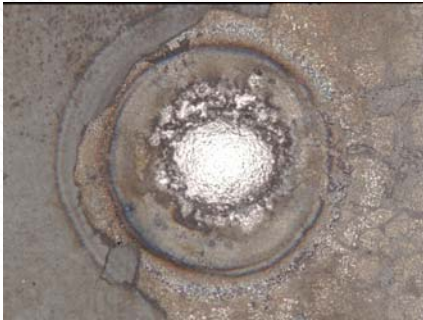
Round robin samples showed higher mass gains than expected which may have been caused by a dead leg



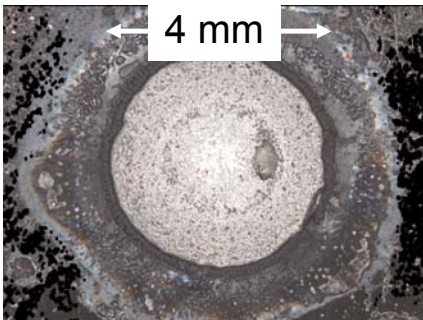
- On both alloys and after both exposure times, two regions of C are observed; the first occurs within the oxide scale at ~30 s of sputtering time and the second below the oxide scale.

T91 Fe-9Cr at 500h @ 550°C & 200bar RG sCO₂ results in a scale thicker than the maximum depth range of GDOES

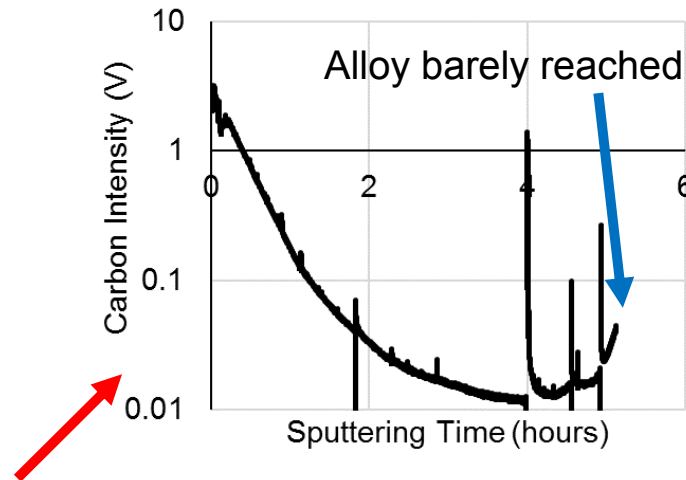
Continuous Sputtering



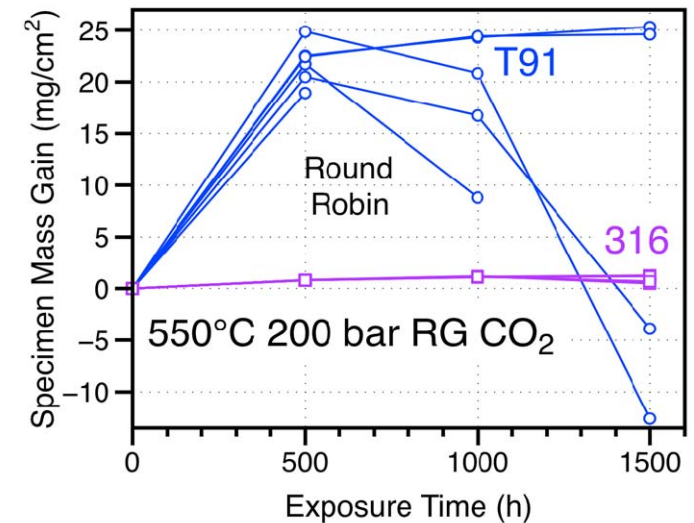
Pulsed Sputtering



GDOES C Profile



Mass Gain



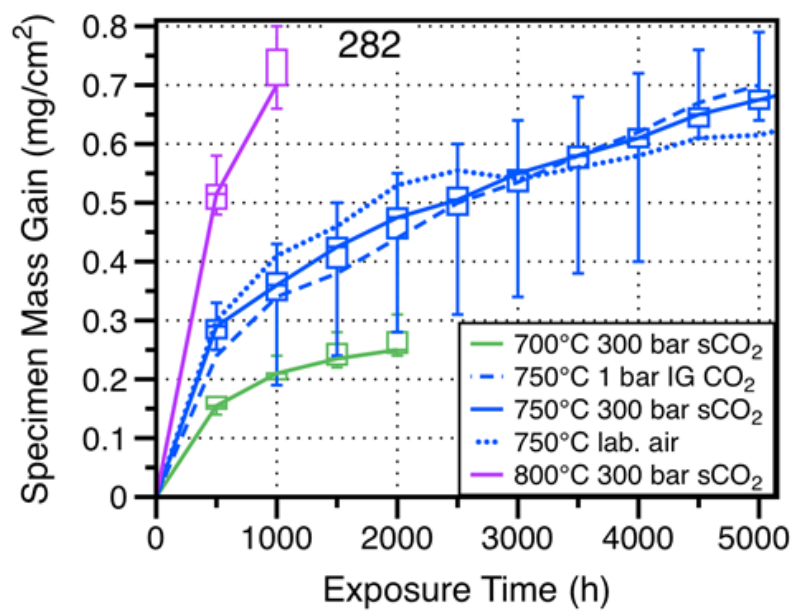
- The scale was >200 μm thick which is thicker than the depth profile range of GDOES.
- Pulsed sputtering prevented cracking of the scale and resulted in a more uniform dimple. However, ~5 hours of sputtering.
- In the future we will scrape the scale off prior to GDOES.

Summary

- GDOES was used to measure carbon profiles in four different alloys exposed to $s\text{CO}_2$ under varying conditions.
- The sensitivity of GDOES to carbon was found to be superior to EPMA.
- Profiles showed a C depletion zone under the oxide scale due to consumption of chromium carbides followed by carburization deeper into the alloy.
- The extent of this carburization varied depending on the alloy and the exposure condition with the alloy 282 exposed at 700 °C and 300 bar of $s\text{CO}_2$ having the highest degree of carburization.

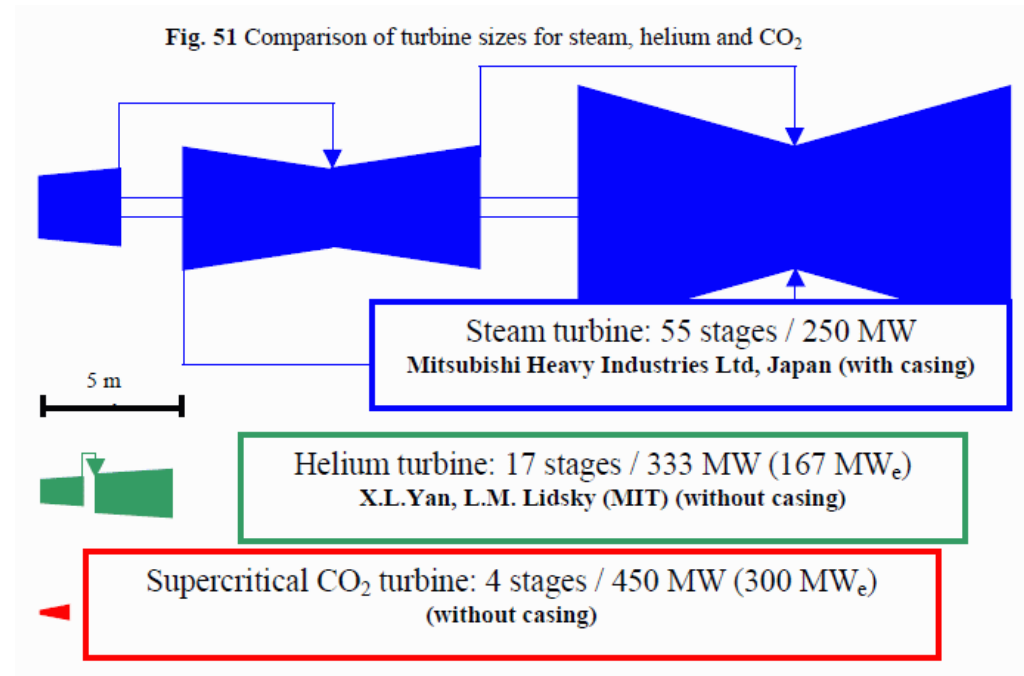
Additional Slides

Fig. 5 Sample Mass Gain 282

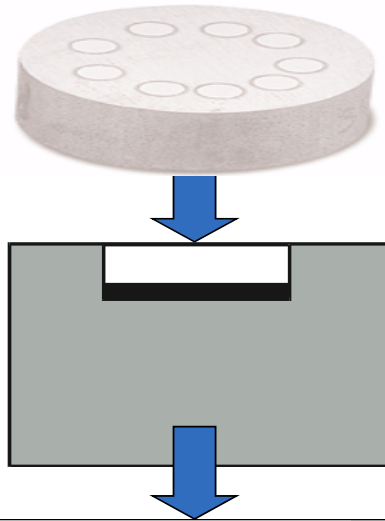


Supercritical CO₂ (sCO₂) Power Cycles Are A Current Crosscut Area at the Department of Energy

- sCO₂ as a working fluid is of interest for many power generation systems: fossil (coal or gas), nuclear, and concentrated solar power
- Advantages of sCO₂ are:
 - low critical temperature and pressure (31 °C/73.8bar)
 - single phase over a wide temperature and pressure range
 - high thermal capacity and density leading to much smaller turbomachinery
 - low work for recompression (e.g., compared to He)
- ORNL has materials R&D lead for fossil sCO₂ technology

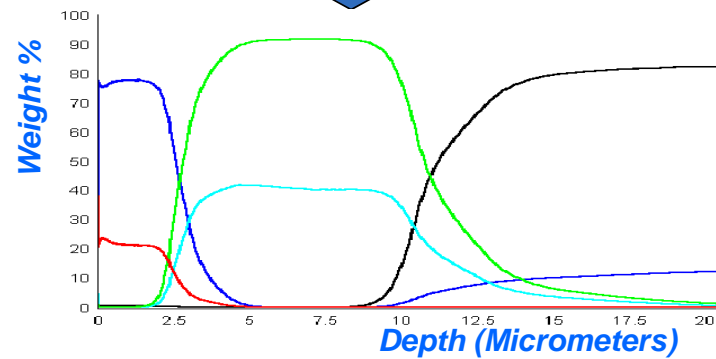
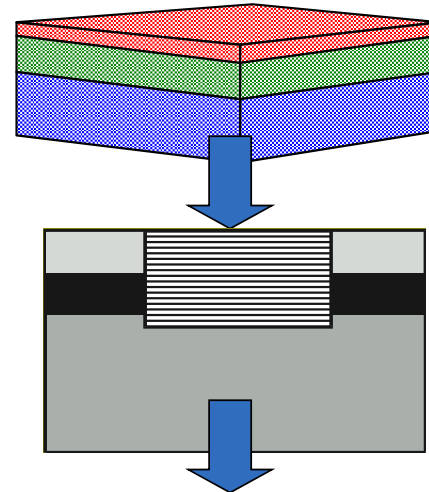


Bulk Analysis



| | Burn 1 | Burn 2 | AVG |
|-----------|----------------|----------------|----------------|
| C | 0.159 | 0.160 | 0.160 |
| P | 0.00469 | 0.00470 | 0.00470 |
| S | 0.00451 | 0.00466 | 0.00460 |
| Si | 0.0112 | 0.0113 | 0.0112 |
| Mn | 0.0287 | 0.0286 | 0.0286 |

Depth Profiling



GDOES was been successfully used to carburization following exposure to sCO₂

CEA: Furukawa, T. and F. Rouillard (2015)

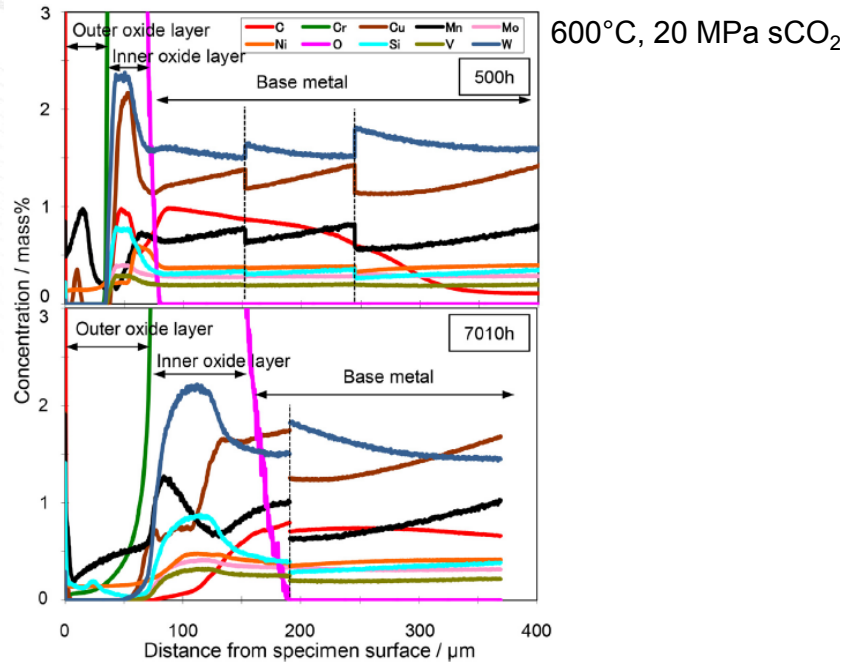
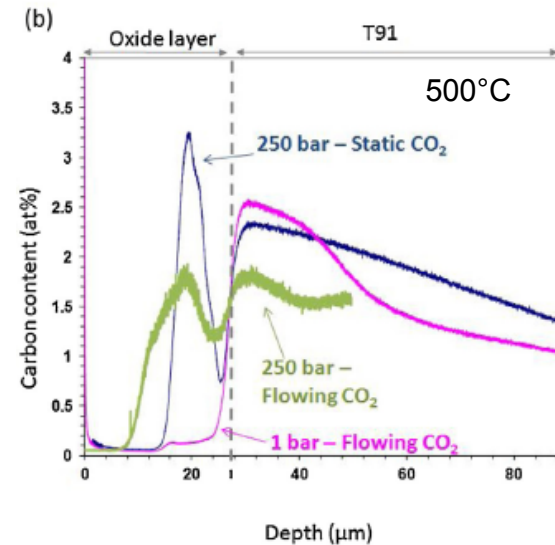


Fig. 8. GDOES results for 12Cr-steel specimens tested at 600 °C and 20 MPa.

- In the base metal near the oxide layers, only carburizing was observed, and no contamination of other elements.
- Carburizing was saturated at approximately 1 wt% in this steel, and further carburizing progressed with diffusion into the matrix.

CEA: Martinelli, L., et al. (2015)



- Carbon was detected in the Fe-Cr spinel layer grown on T91 Fe-9Cr steel at much higher levels at 250 bar CO₂ than at 1 bar and is related to the formation of carbides in the spinel in sCO₂.

Samples and Furnace Cycle Testing

- Coupons with dimensions of ~10 x 20 x 1.5 mm were polished to a 600-grit finish using SiC paper and ultrasonically cleaned in acetone and methanol prior to exposure.
- For the 500-h cycles in 200 or 300 bar CO₂, the exposures were conducted in an autoclave fabricated from alloy 282. The fluid flow rate was ~2 ml/min.
- The specimens were slowly heated to temperature over several hours (~2 °C/min) in sCO₂, held at temperature ±2 °C and then cooled in sCO₂ to room temperature by lowering the furnace and using a cooling fan on the autoclave.
- For the 500-h cycles at 1 atm CO₂, the coupons were placed in an alumina boat in an alumina reaction tube with end caps. The specimens were heated in argon to 750 °C over 4 h to minimize oxidation of the sample prior to exposure to CO₂, held for 500 h in CO₂ and cooled in argon to room temperature. Gas flow rates were ~300 cc/min.
- For 10-h cycles, samples were hung from alumina rods with platinum wire and exposed in automated cyclic rigs for 10 h in the hot zone followed by 10 min cooling in laboratory air to <30 °C after being automatically pulled from the furnace. Exposures at 700, 750 and 800 °C were conducted in industrial grade (IG) CO₂ at 1 bar, with <60 ppm O₂ and <32 ppm H₂O. Gas flow rates were ~100 cc/min or ~0.1 cm/s flow rate.

| Alloy | Fe | Ni | Cr | Co | Mo | Al | Ti | Si | Mn | Nb | W | Cu | V | Zr | C | O |
|-------|-------|-------|-------|-------|------|-------|-------|------|-------|------|------|-------|-------|-------|--------------|-------|
| 740 | 0.11 | 47.54 | 24.47 | 19.64 | 0.18 | 2.89 | 1.62 | 0.30 | 0.26 | 0.89 | 0 | 0 | 0.009 | 0.014 | 0.126 | 0.002 |
| 282 | 0.17 | 56.04 | 21.74 | 10.36 | 5.16 | 3.49 | 2.63 | 0.07 | 0.021 | 0 | 0 | 0 | 0.011 | 0 | 0.283 | 0.003 |
| SN25 | 43.30 | 24.55 | 24.39 | 1.43 | 0.12 | 0.053 | 0.028 | 0.31 | 0.54 | 0.29 | 1.07 | 2.68 | 0.059 | 0 | 0.322 | 0.009 |
| 625 | 4.22 | 61.67 | 24.85 | 0.13 | 5.50 | 0.27 | 0.28 | 0.33 | 0.17 | 2.19 | 0.02 | 0.084 | 0.022 | 0 | 0.079 | 0.004 |

All compositions are in atomic percentage measured by ICP-OE and Combustion analysis