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Exploring Materials Options for Ultra-High Temperature Supercritical CO_2 Applications

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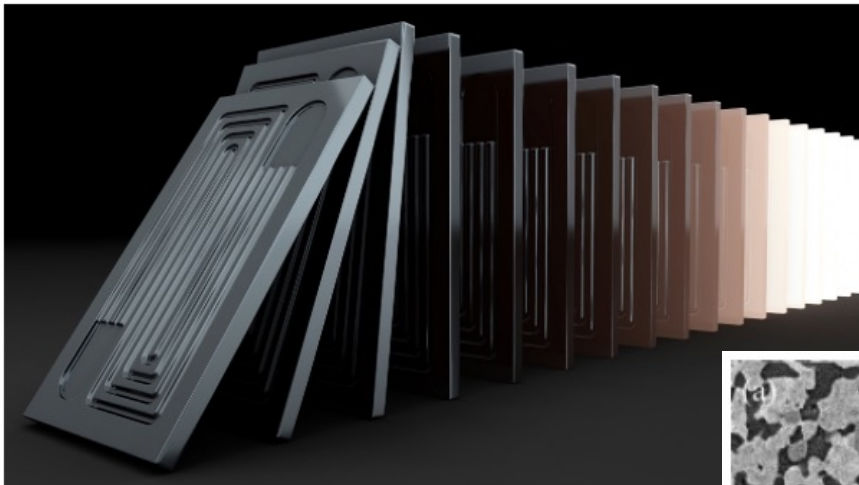
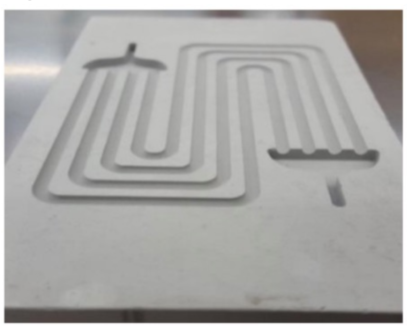
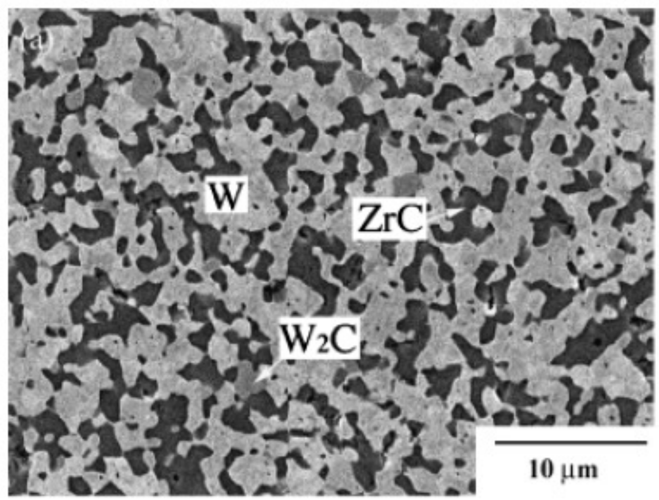
Recent project on cermet heat exchangers has pushed interest in sCO_2 above 800°C



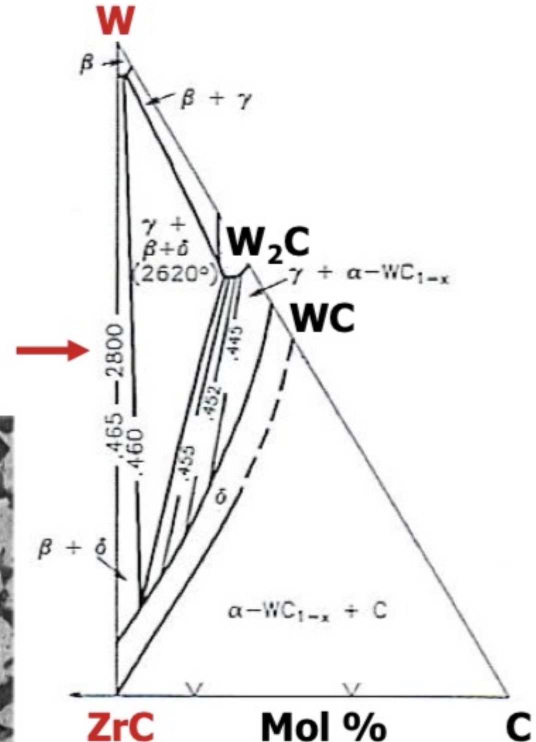
Heat exchanger cermet plates for diffusion bonding

K. Sandhage, Purdue





Zhang et al. 2007 J. Am. Ceram. Soc.

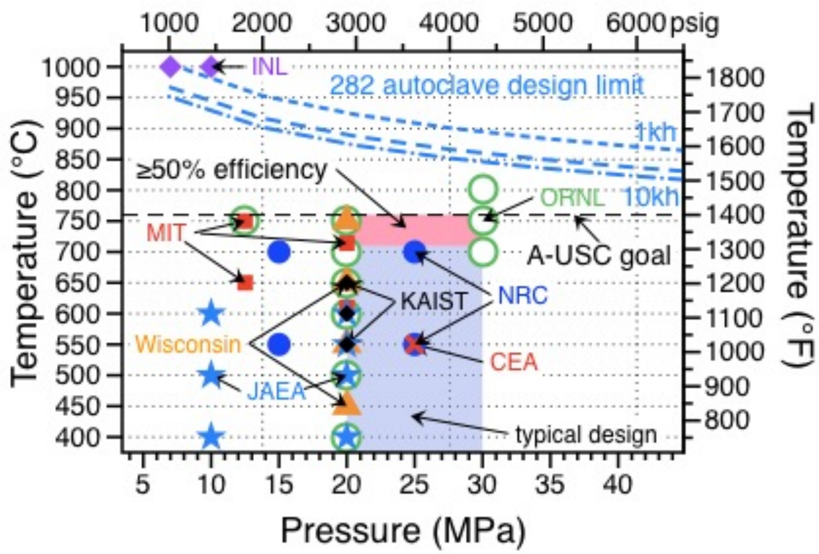


Displacement reaction:
WC + Zr(Cu) -> ZrC + W

Dickerson 2002 J. Am. Ceram. Soc.

However, we can't do supercritical pressure above 800°C

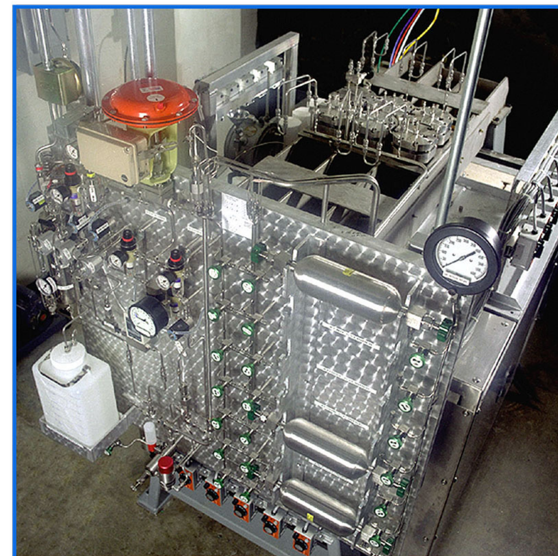
Autoclave: 300 bar sCO_2
500-h cycles



Correct temperature and pressure

4-5 cm^2 alloy coupons

"Keiser" rig:
500-h cycles, 1-43 bar CO_2



Study CO_2 at >800°C

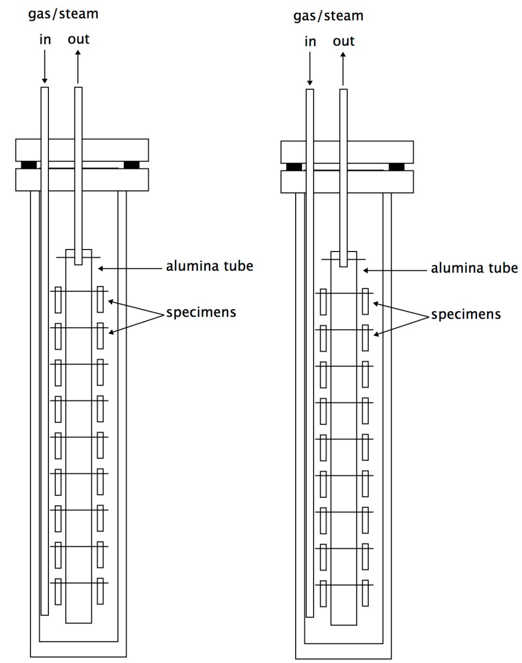
Baseline of research grade (RG) CO_2: ≤ 5 ppm H_2O and ≤ 5 ppm O_2
industrial grade (IG) CO_2: 18±16 ppm H_2O and ≤ 32 ppm O_2

Screening experiments: not a deep mechanistic study

Basic test matrix

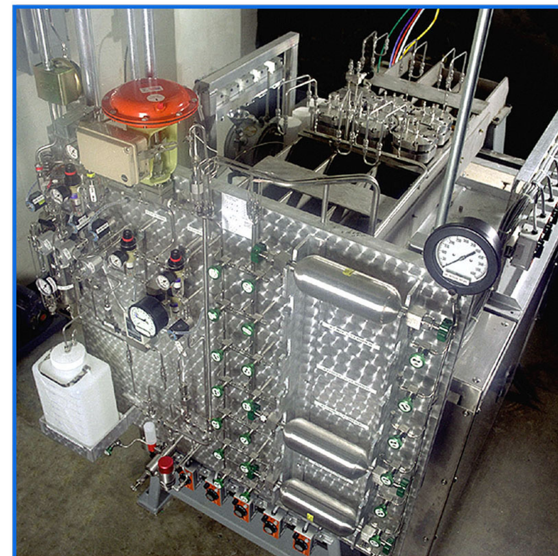
- 1-3 coupons of each material
  - Polished to 600 grit finish
- 20-500 h exposures to 20-1000 h
- 1000° and 1200°C
  - 900° & 1100°C for HITEMMP (ARPA-E)
- Flow ~0.1cm/s RG CO_2
- Mass change: ±0.04 mg
  - or ~0.01 mg/cm^2
- Characterization
  - Polished sections
  - SEM/EDS

SiC (Hexoloy) tubes



1 bar CO_2   **20 bar CO_2**

"Keiser" rig:
500-h cycles, 1-43 bar CO_2

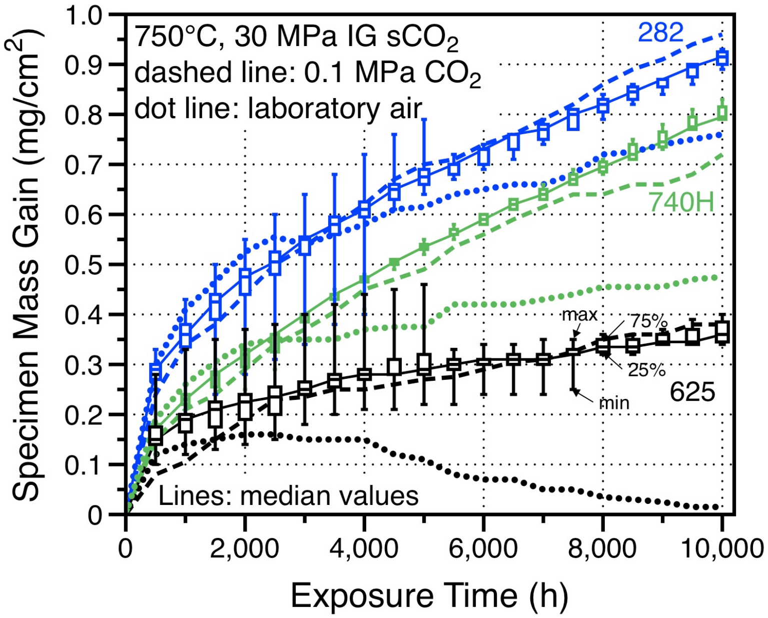


Research grade (RG) CO_2: 4.1±0.7 ppm H_2O and ≤ 5 ppm O_2

industrial grade (IG) CO_2: 18±16 ppm H_2O and ≤ 32 ppm O_2

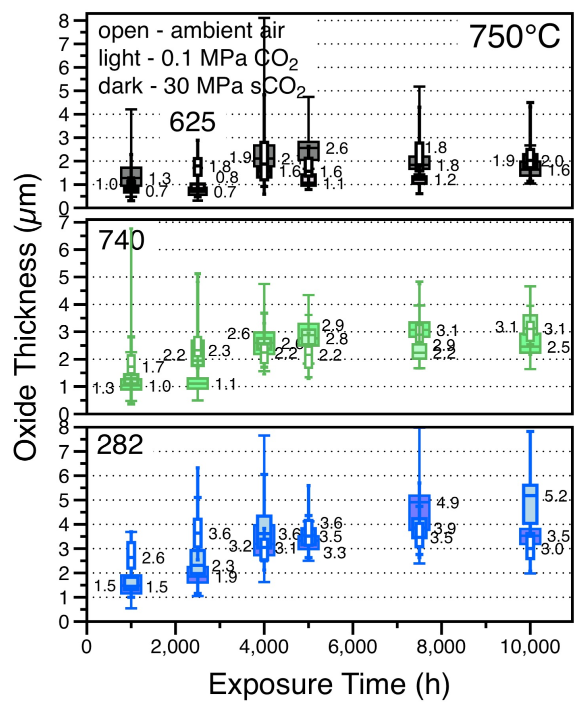
Prior conclusion: 700°-800°C Ni-based alloys are sCO_2 compatible–similar rates in air, ambient CO_2 and sCO_2

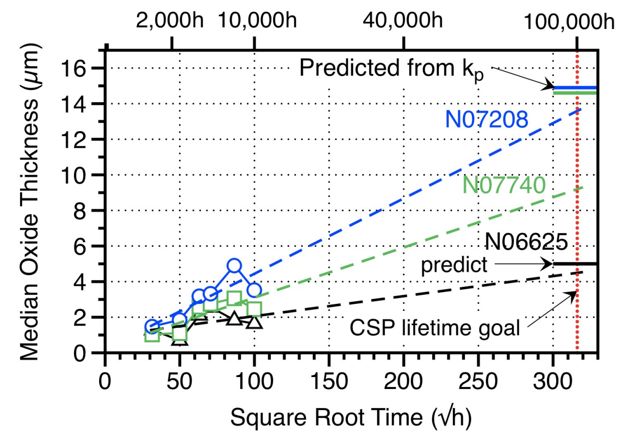
500-h cycles: three different environments



All 750°C, 1382°F

Quantification of scale thickness in three environments:





Extrapolation: minimal reaction in sCO_2 after 100,000 h

Pint, et al. Oxid. Met. 94 (2020) 505
DOE SETO Final report: DOI: 10.2172/1515655

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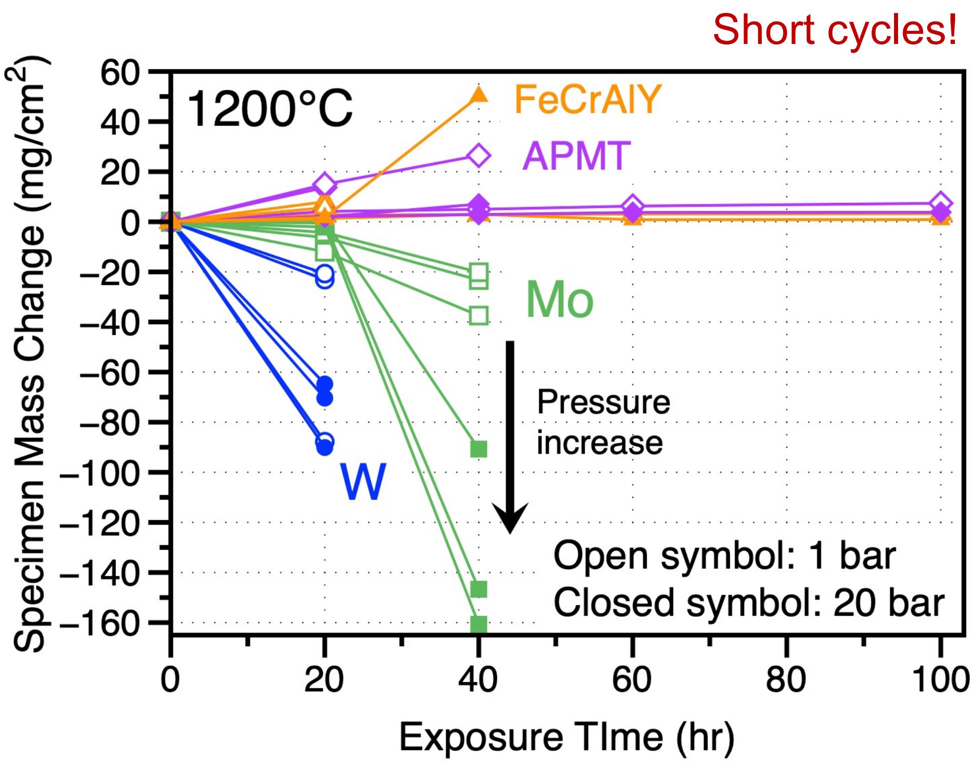
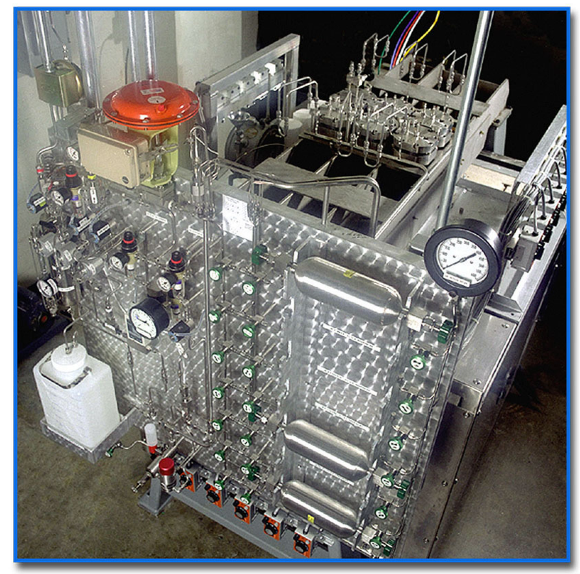
1200°C,1+20 bar: Metal specimens did not perform well

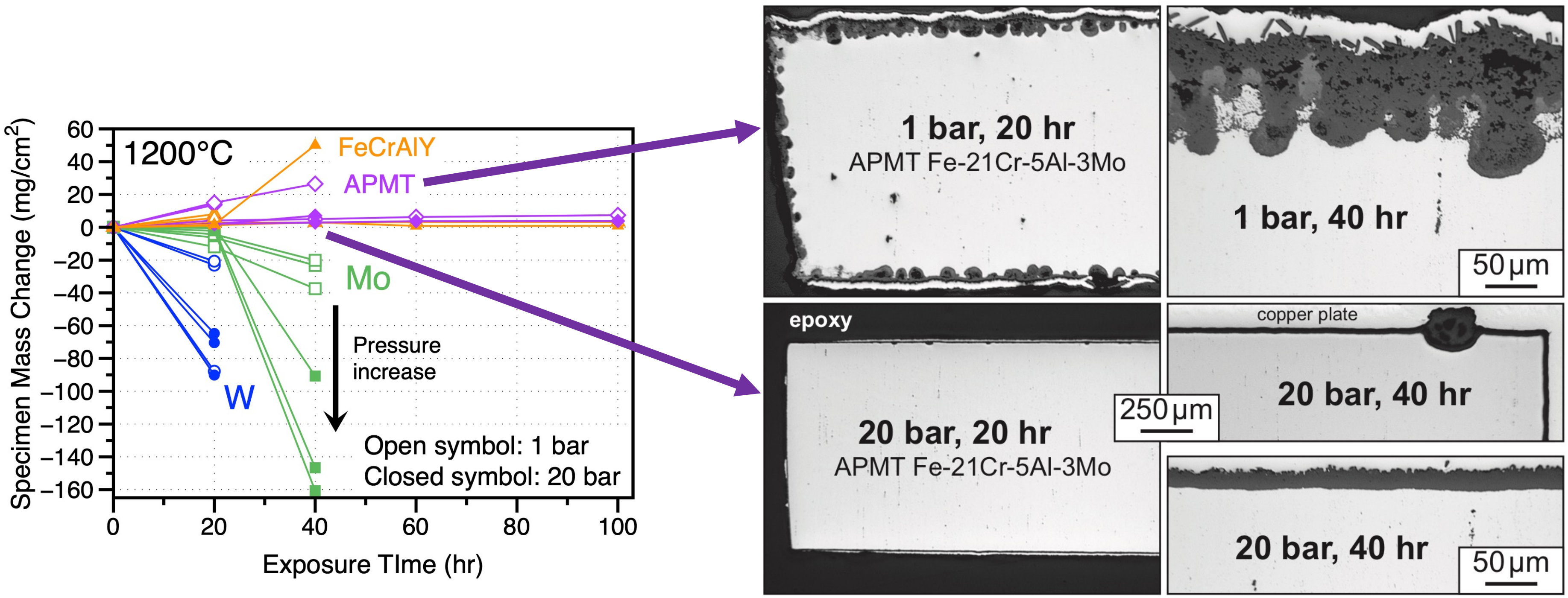




Two SiC reaction tubes: 1 and 20 bar RG CO_2

- Mo and W as possible cermet matrices
- FeCrAlY & APMT (FeCrAlMo) **Al_2O_3**-formers (Al_2O_3 good C barrier?)
- Did <u>not</u> test any Ni-based alumina-forming alloys at 1200°C

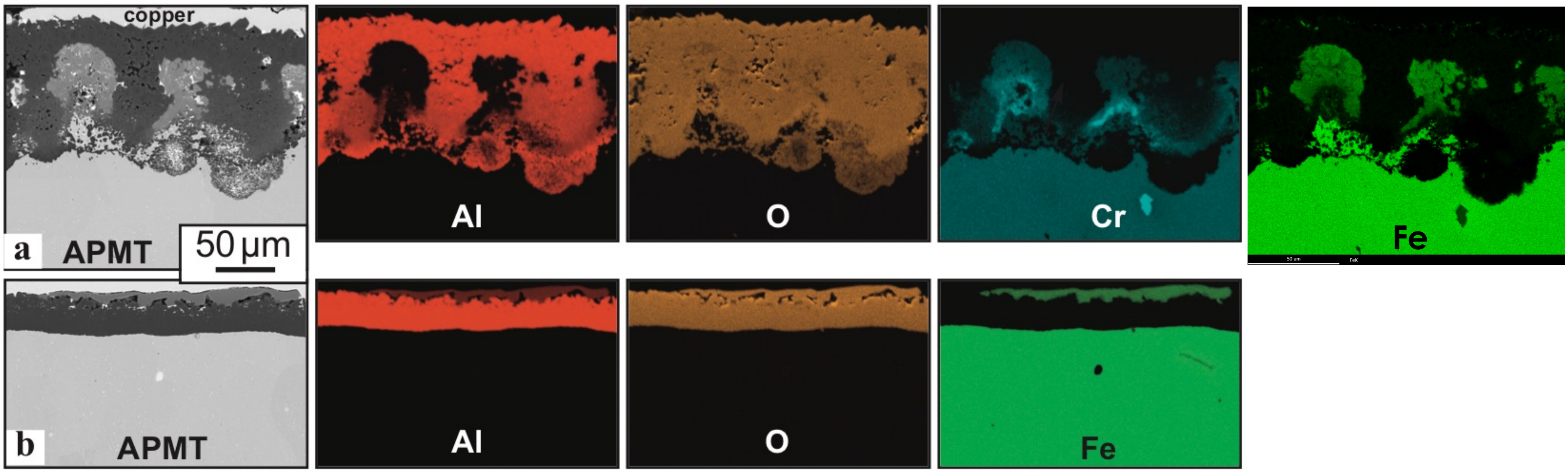
Pressure effect: Higher mass losses for Mo and W with P
But, reduced attack of FeCrAl with higher P (?)



Much thicker oxide forming in 1 bar CO_2

1200°C/40 h: Significant pressure effect

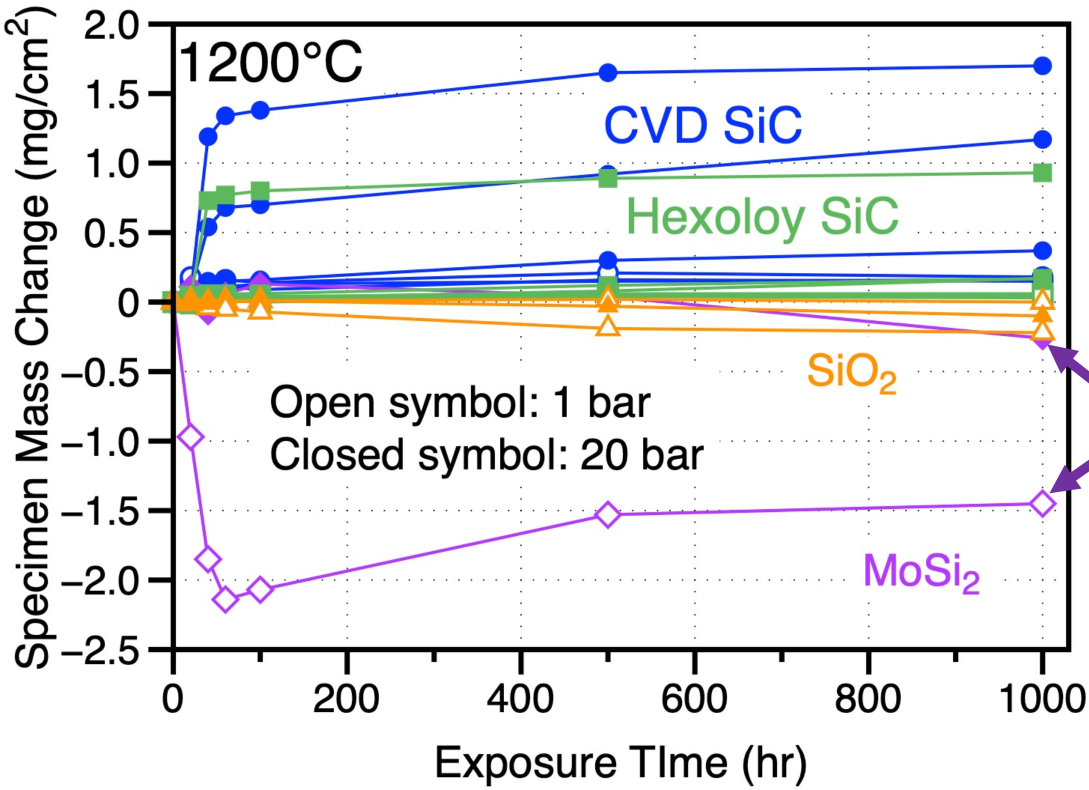
1 bar CO_2



20 bar CO_2

- 20 bar: alumina scale with Fe-rich outer layer (no Fe layer in air)
  - k_p ~$3x10^{-11}$ g^2/cm^4s ~10X higher than in air
- 1 bar: very thick oxide with Fe and Cr incorporation

Silica-formers seem to be an option at 1200°C



SiC: higher mass gains at 20 bar for some specimens

Mo-based cermet: Possible for silicide-type coating

Light microscopy shows thin reaction products on CVD SiC

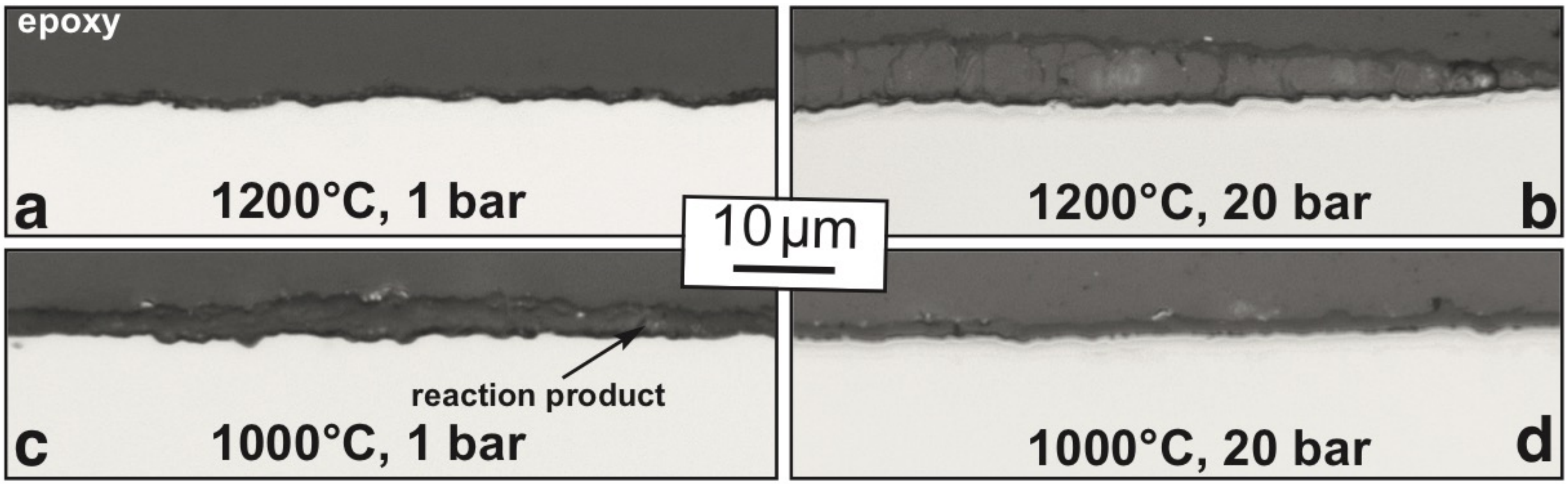
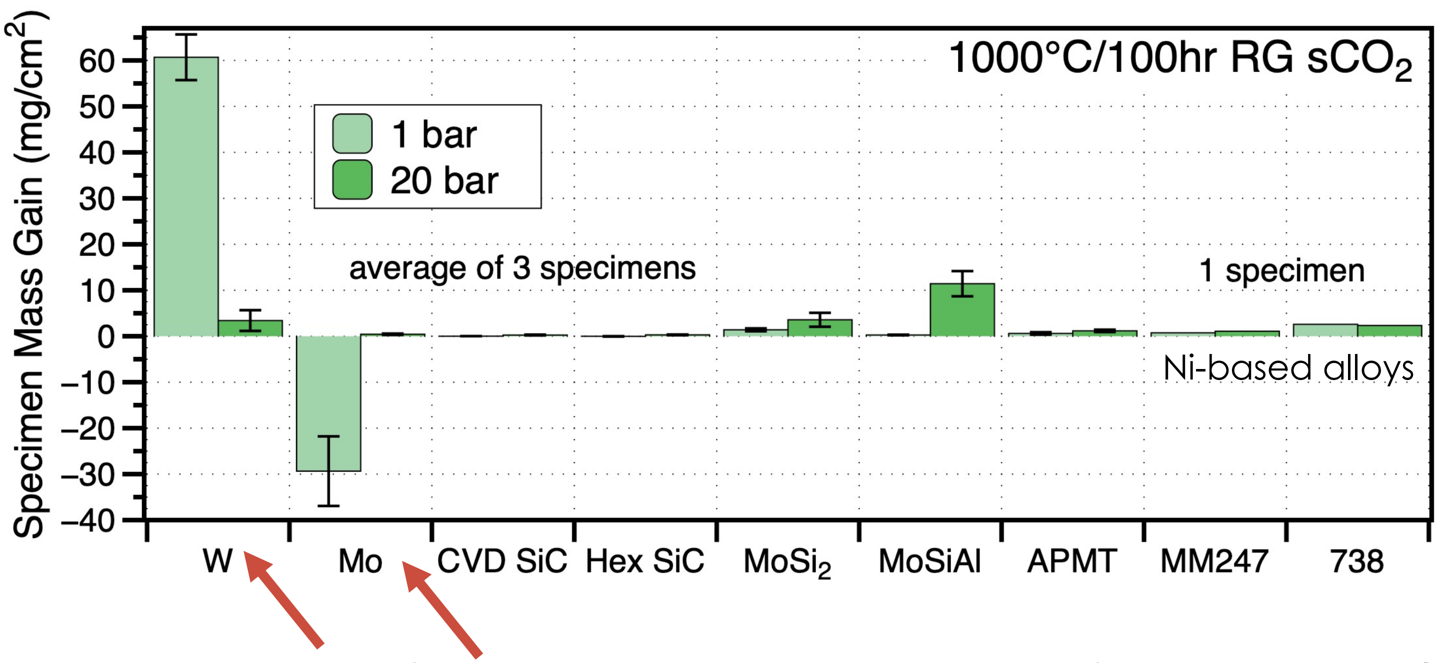


Figure 5. Light microscopy of CVD SiC specimens exposed at (a,b) 1200°C and (c,d) 1000°C in (a,c) 1 and (b,d) 20 bar RG CO_2.

1000°C: 100h results show large mass changes for Mo/W

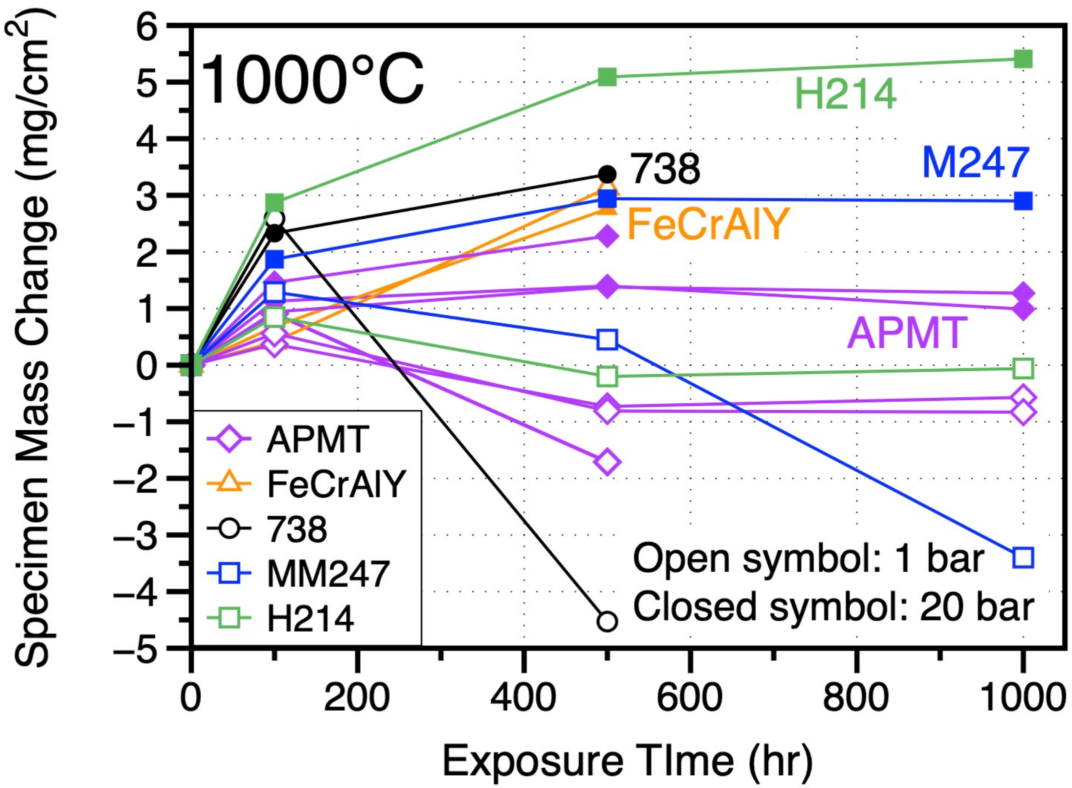


1000°C: highest W/Mo mass change in 1 bar CO_2 (opposite to 1200°C)

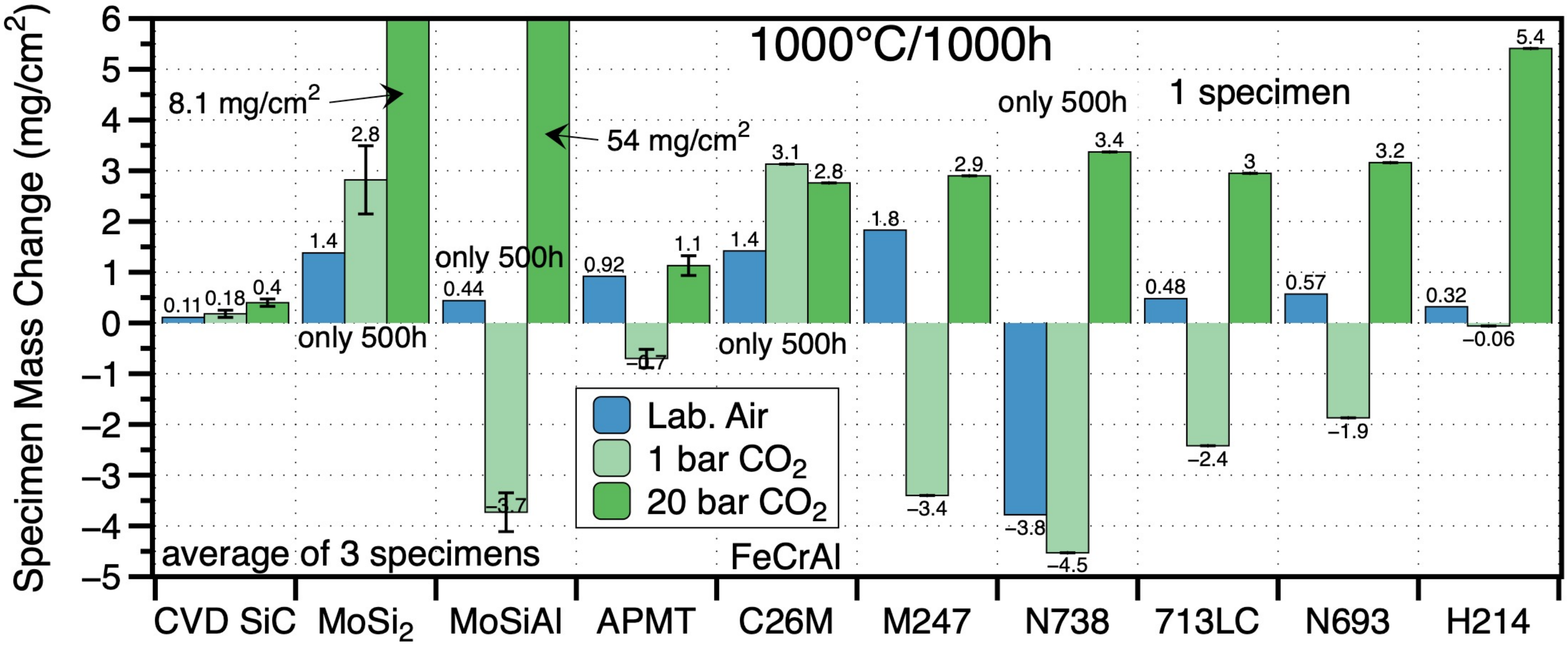
W - 1 bar (reduced evaporation?)

- 20 bar (more evaporation?)

Metallic specimens showed high mass changes

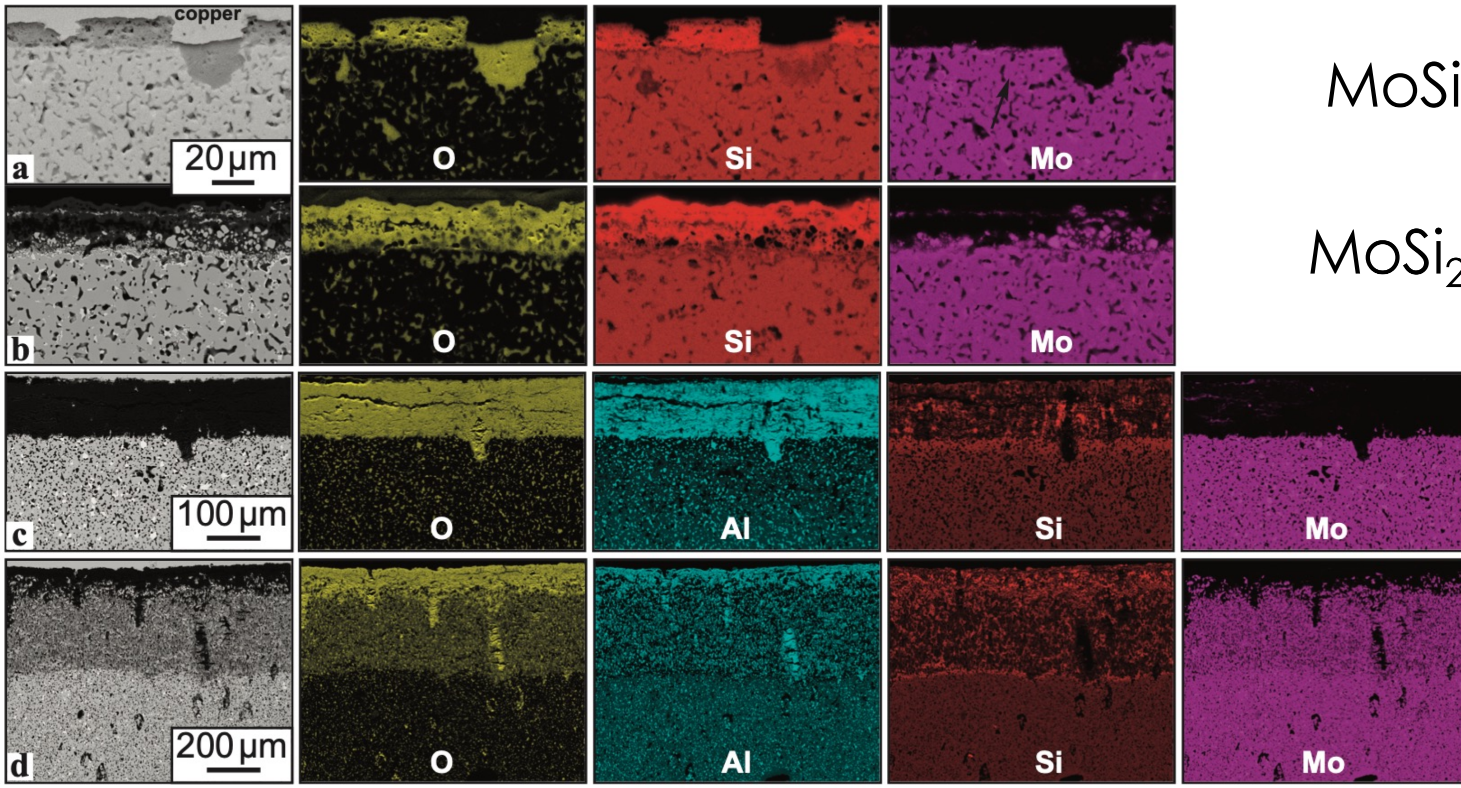


1000°C/1000 h: comparison to laboratory air
20bar: high mass gain for most alloys & $MoSi_2$



Typically, lower mass gain in laboratory air

$MoSi_2/Mo(Si,Al)_2$ 500h/1000°C: no protective SiO_2 layer



$MoSi_2$: 1 bar

$MoSi_2$: 20 bar

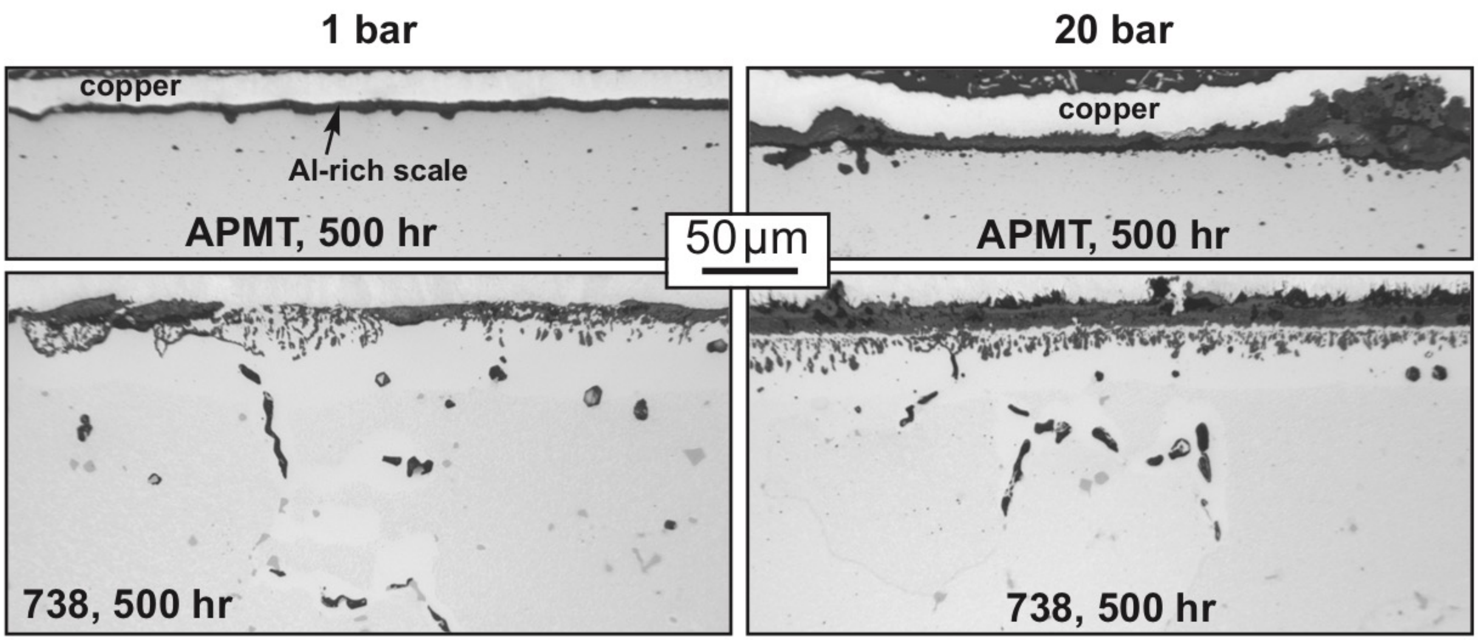
$Mo(Si,Al)_2$
1 bar

$Mo(Si,Al)_2$
20 bar

- Contrast to thin oxide formed on CVD SiC

1000°C/500 h: thicker scales forming at 20 bar

APMT: 69Fe-22Cr-**4.9Al**-2.8Mo
738: 61Ni-17Cr-8.6Co-**3.7Al-3.4Ti**-2.6W-**1.8Ta**-1.7Mo



nodules

Deep penetrations

Internal oxidation more uniform

- Increased scale thickness and internal oxidation with higher pressure

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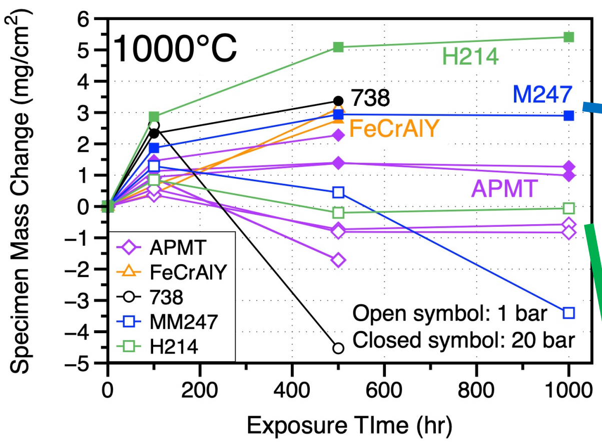
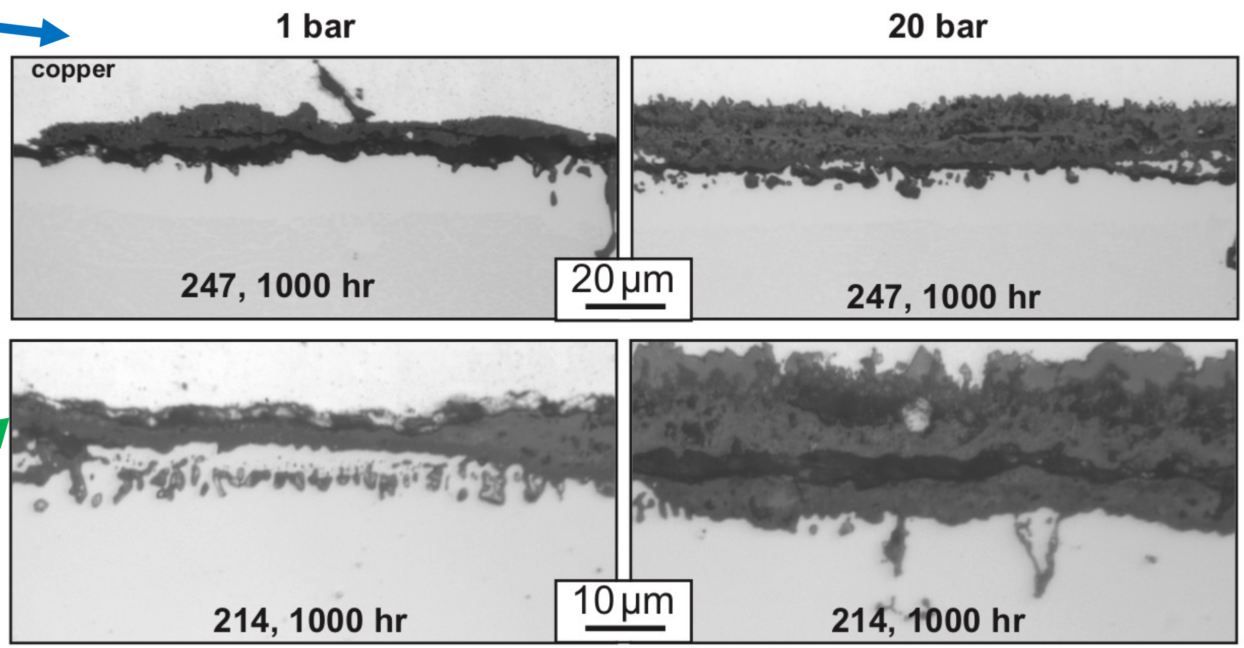
1000°C/1000 h: not forming thin alumina scale

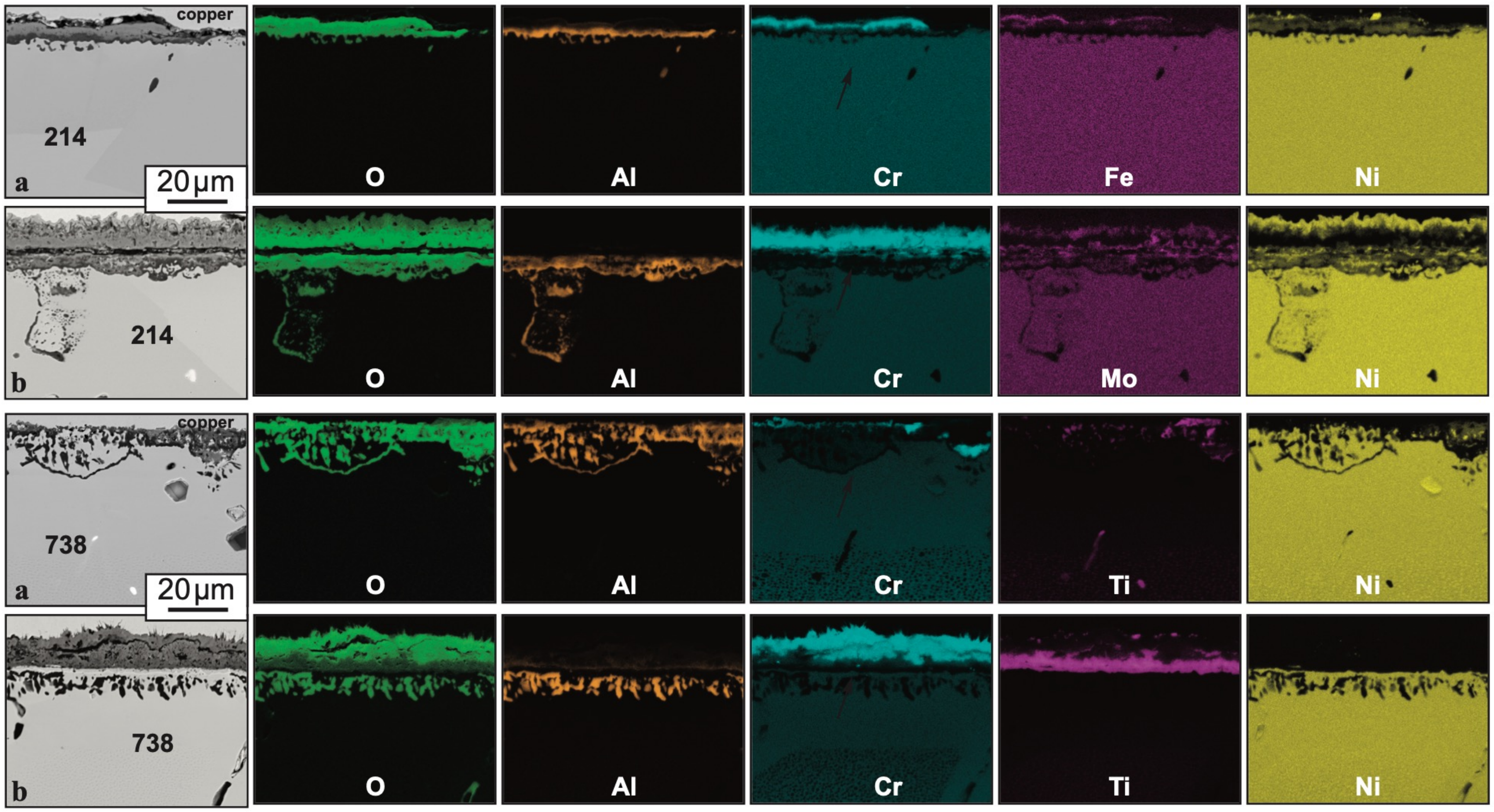


247: 60Ni-8.5Cr-**5.7Al**-9.8Co-9.9W-0.7Mo-3.1Ta-**1.0Ti**-1.4Hf
214: 76Ni-16Cr-**4.3Al**-3.5Fe-0.02Zr-0.004Y



- Thicker reaction products observed, especially at higher pressure

EDS examples: Ni-based alloys: P effect observed



214: 1 bar

1,000 h, 1000°C

214: 20 bar

738: 1 bar

500 h, 1000°C

738: 20 bar

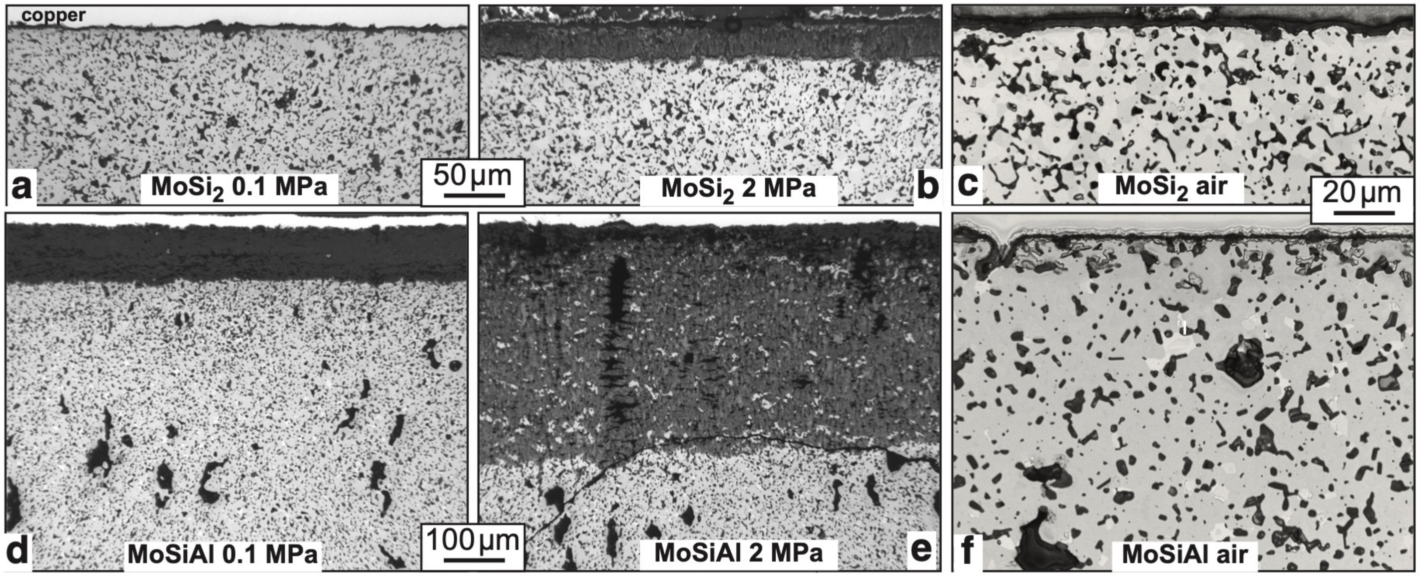
- 214 in 0.1MPa CO_2 was able to form alumina scale

Summary: assessment of sCO_2 compatibility

- High temperature sCO_2 (700°-800°C) appears achievable
  - Low C solubility in Ni-based alloys may be key to compatibility
- Challenges for conventional steels at 450°-650°C
  - Current focus of DOE FECM project (Thursday presentation)
- Higher temperatures (900°-1200°C) are challenging in CO_2
  - Cermets will require coatings with Mo/W matrix
    - Sandhage (Cu coating with CO/CO_2 control)
    - Catastrophic attack concerning if coating fails
  - Alumina-forming FeCrAl alloys heavily attacked at 1200°C
    - More protective behavior at 900°-1100°C
  - SiC promising at ≤1200°C to 1000 h
    - However, $MoSi_2$ and MoSiAl did not show protective behavior

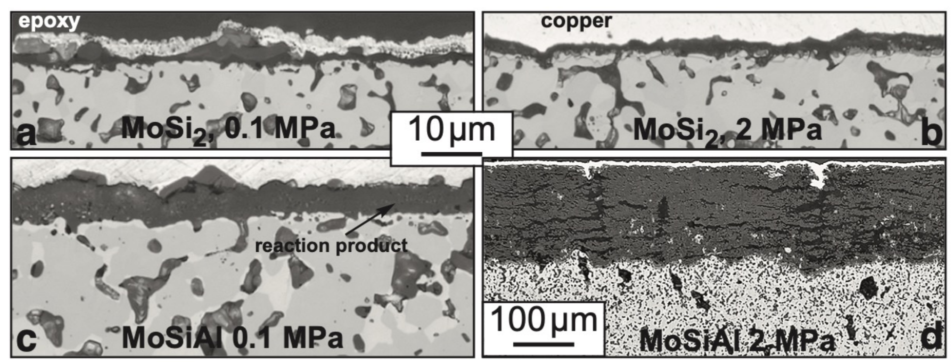
Questions?

Accelerated attack, especially in 2 MPa CO_2



500 h, 1000°C

500 h, 1100°C



- MoSiAl/2MPa spall at 1100°C hid the high attack
  - Al to inhibit pesting

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Pressure effect: Higher mass losses for Mo and W with P
But, reduced attack of FeCrAl with higher P