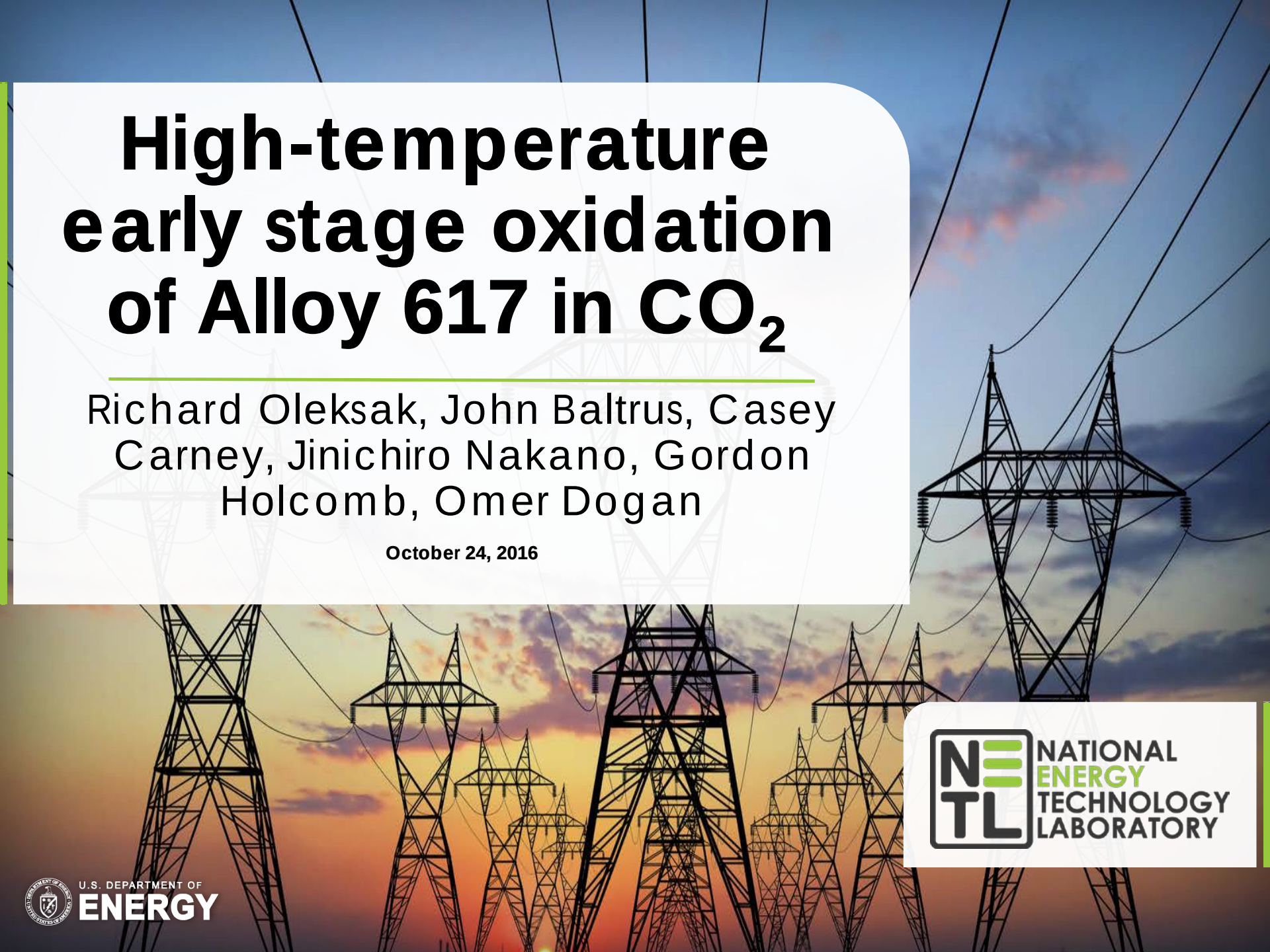
High-temperature early stage oxidation of Alloy 617 in CO_2

Richard Oleksak, John Baltrus, Casey Carney, Jinichiro Nakano, Gordon Holcomb, Omer Dogan

October 24, 2016



NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

Acknowledgements

- Anna Nakano (NETL)
- Joseph Tylczak (NETL)
- Monica Kapoor (NETL)

This project is conducted in support of DOE-FE Advanced Combustion, and Advanced Turbine, and Crosscutting Technology Research Programs. The project is executed through NETL Research and Innovation Center's Advanced Alloy Development Field Work Proposal. This research was supported in part by an appointment (Name of the ORISE fellow) to the National Energy Technology Laboratory Research Participation Program sponsored by the U.S. Department of Energy and administered by the Oak Ridge Institute for Science and Education.

Outline

Background/Experimental

- Materials for sCO_2 power cycles
- Exposure conditions
- Techniques overview

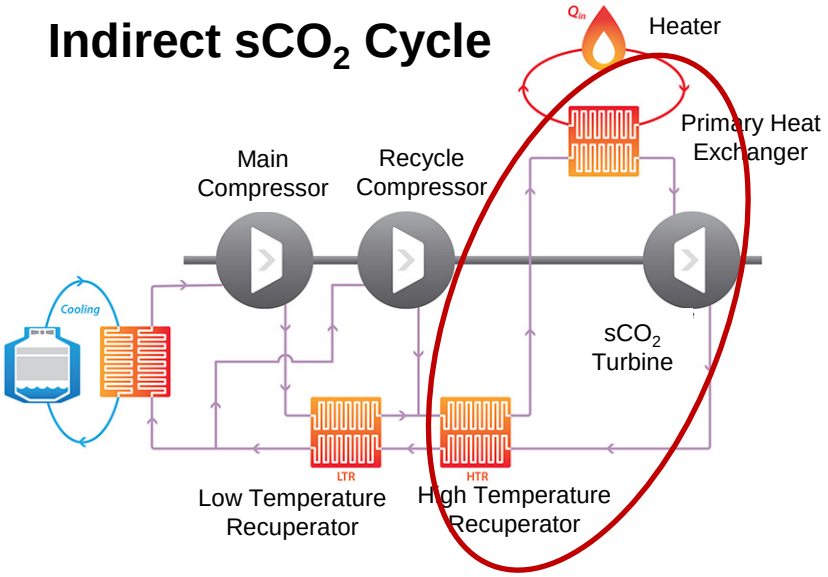
Results

- Surface imaging (white light, SEM)
- Cross-sectional TEM
- X-ray photoelectron spectroscopy (XPS)

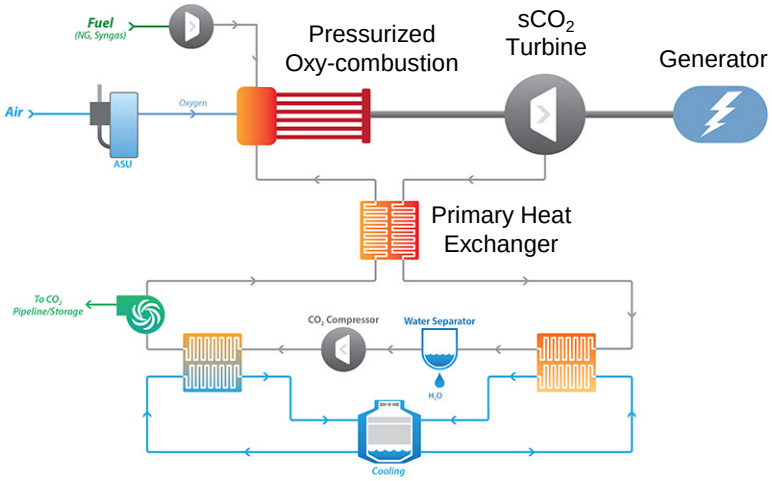
Conclusions and future work

Supercritical CO_2 power cycles

Indirect sCO_2 Cycle

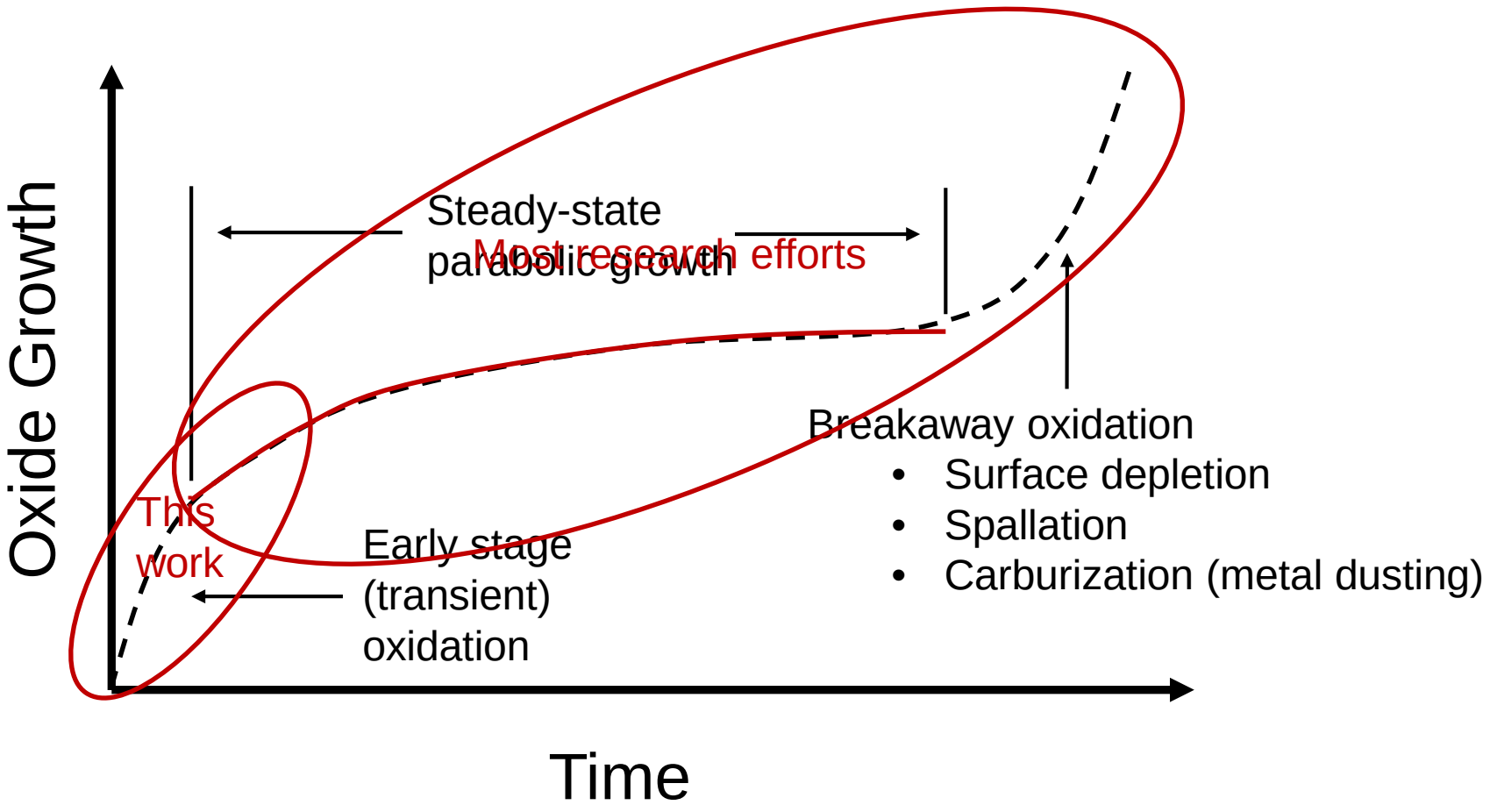


Direct sCO_2 Cycle



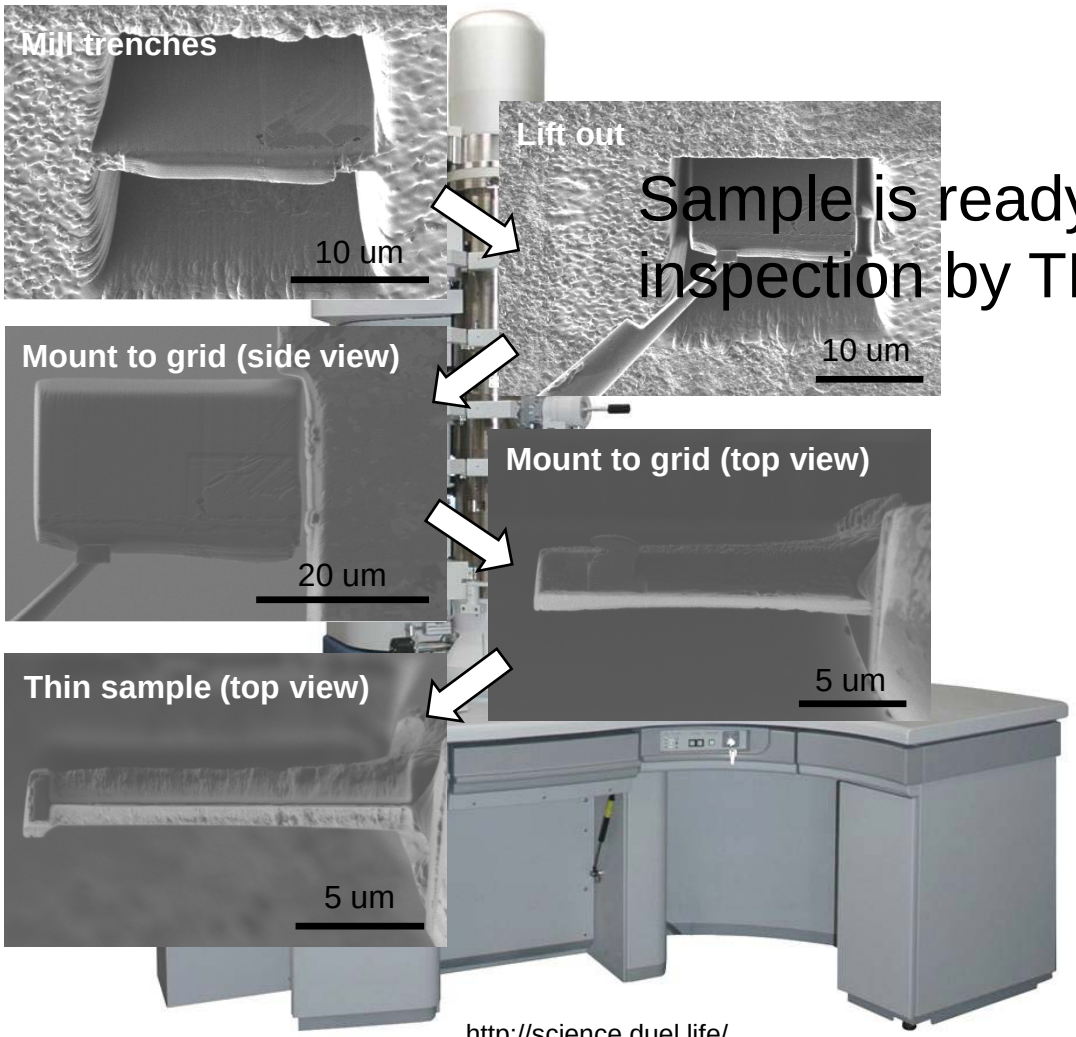
Cycle Type	Component	Inlet		Outlet		Fluid components
		T (°C)	P (MPa)	T (°C)	P (MPa)	
Indirect	Heater	450-535	1-10	650-750	1-10	High purity CO_2
	Turbine	650-750	20-30	550-650	8-10	
	HX	550-650	8-10	100-200	8-10	
Direct	Combustor	750	20-30	1150	20-30	CO_2 containing H_2O, O_2, and other impurities
	Turbine	1150	20-30	800	3-8	
	HX	800	3-8	100	3-8	

Typical stages of alloy oxidation



Background: Cross-sectional TEM

- Site-selective analysis using focused ion beam (FIB) lift-out method
- The cross-section is mounted to a support grid and thinned to <100 nm to allow electron transmission
- This allows cross-sectional analysis of an oxidized surface at atomic resolution



http://science.duel.life/

Exposure conditions

T = 700 °C, P = 1 bar

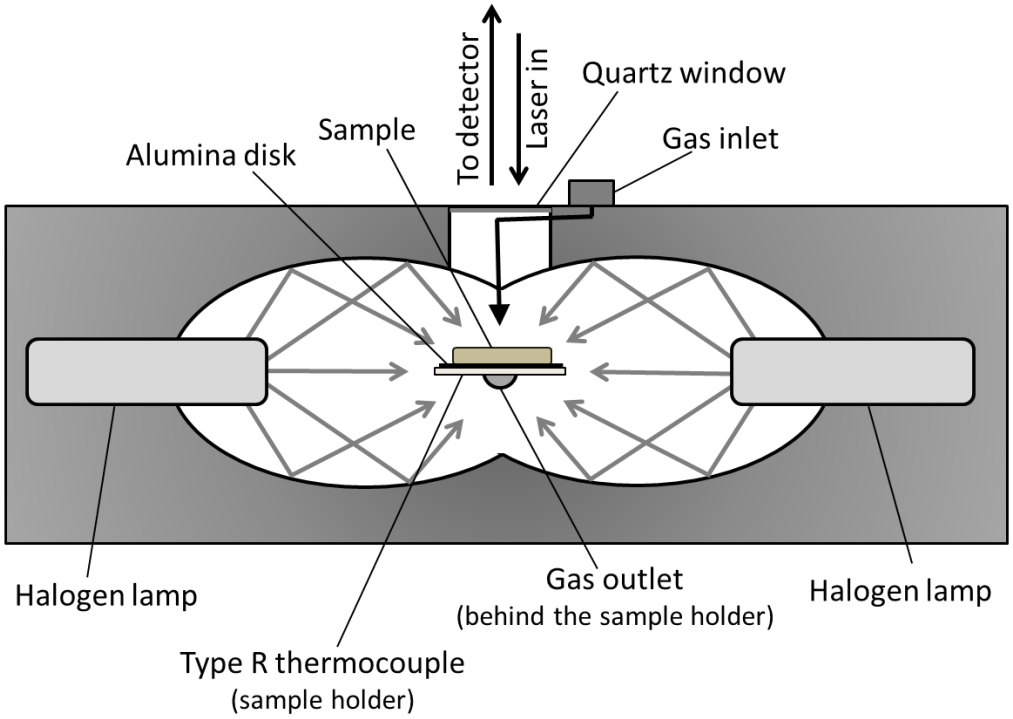
High-temperature confocal scanning laser microscope (CSLM)

- Reaction gas 1 = 99.999% CO_2
- Reaction gas 2 = 99.999% Ar containing ≤ 1 ppb O_2
- Exposure time = **5 min**

Tube furnace

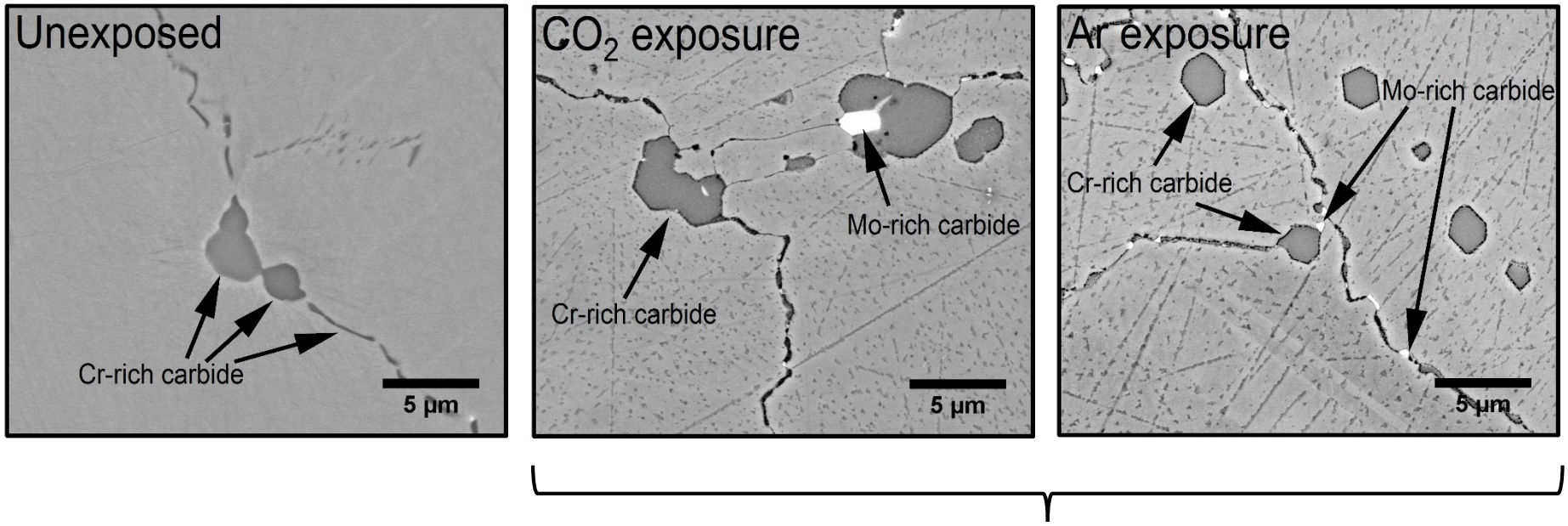
- Reaction gas = 99.999% CO_2
- Exposure time = **2 - 500 hours**

CSLM apparatus



In situ imaging of 5 min CO_2 exposure

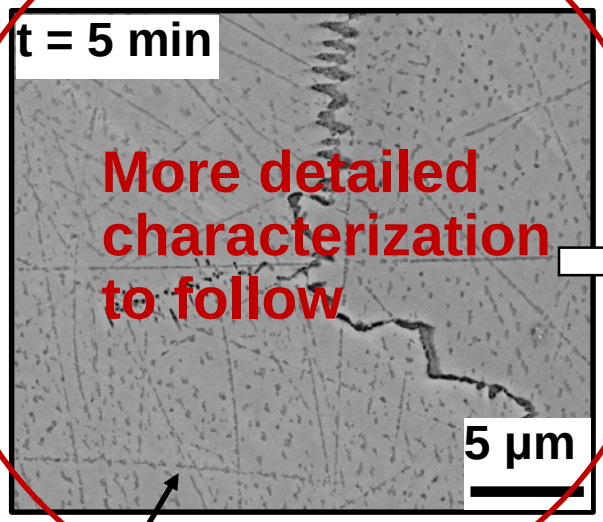
Surface imaging of 5 min CO_2 and Ar exposures

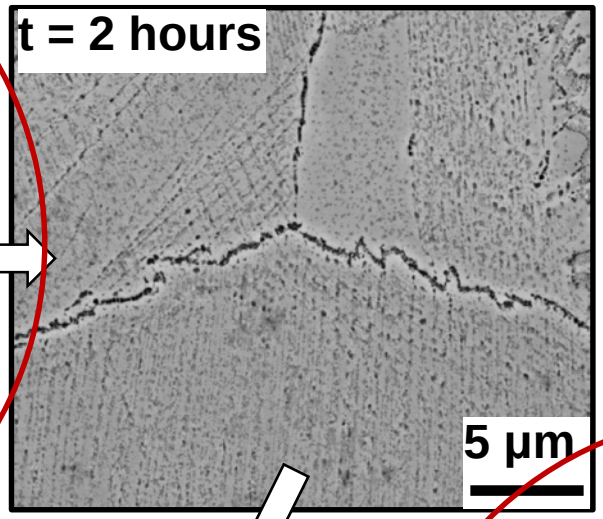


Uniform surface

Dark spots < 100 nm located preferentially along micro-scratches, grain boundaries, and carbide/matrix interfaces

Evolution of surface morphology during exposure to CO_2

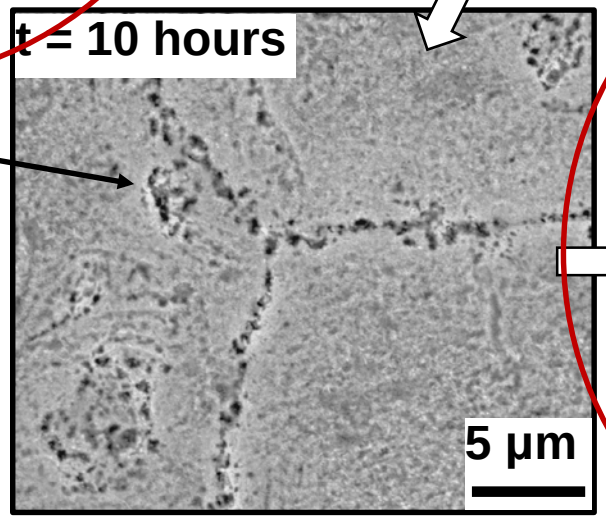


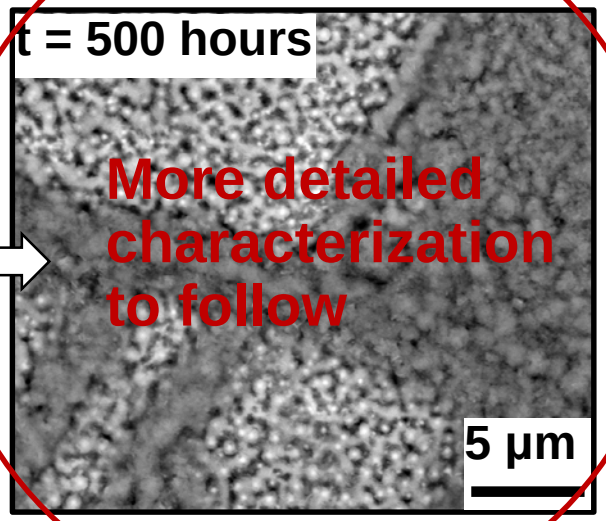


More detailed characterization to follow

Some orientations are preferentially oxidized

Dark contrast spots grow over time.

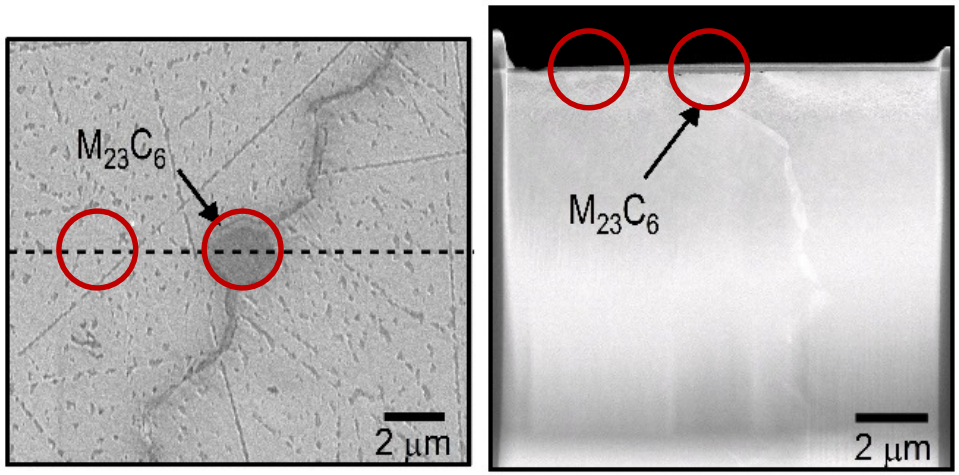


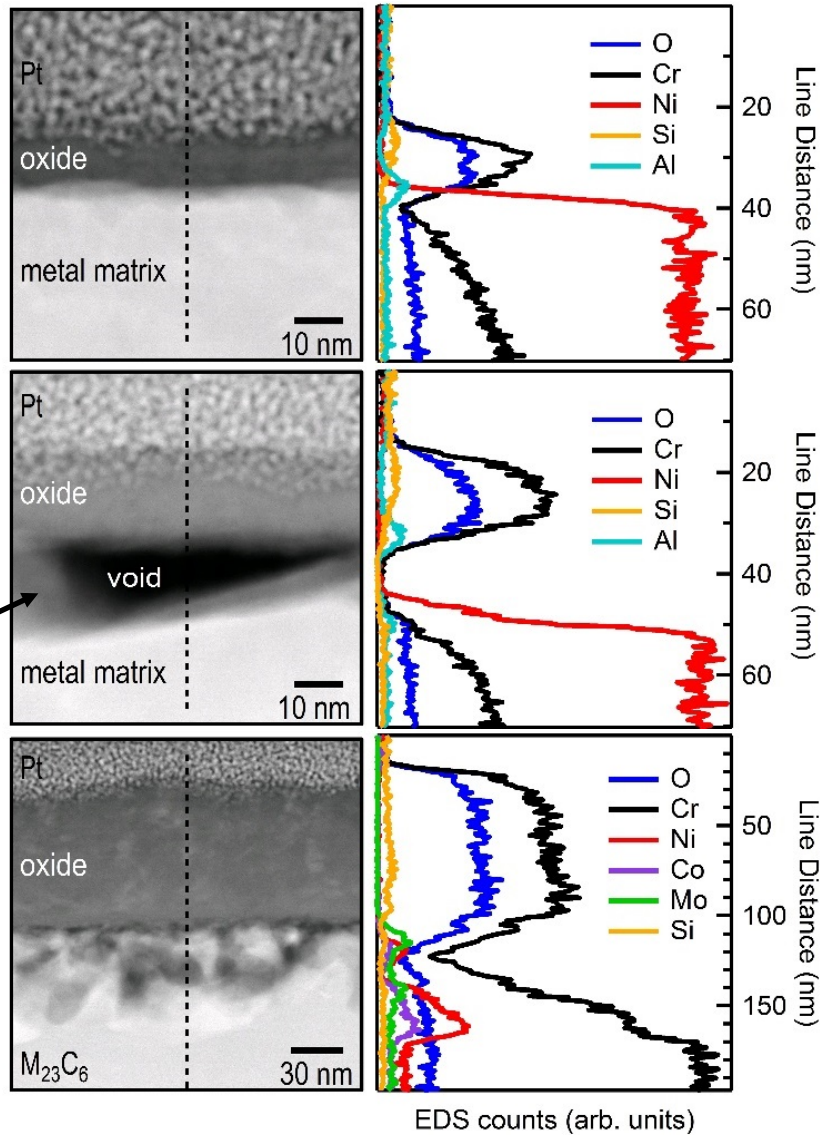


More detailed characterization to follow

Early stages governed by selective oxidation processes

Cross-sectional TEM of 5 min CO_2 exposure





In high purity CO_2 at 1 bar and 700 °C, expected $pO_2 \approx 10^{-6}$ - 10^{-5} bar. Yet, no Ni-oxides are formed.

Ni

metal

($pO_2 = 10^{-17}$ bar

vacancies formed during oxidation.

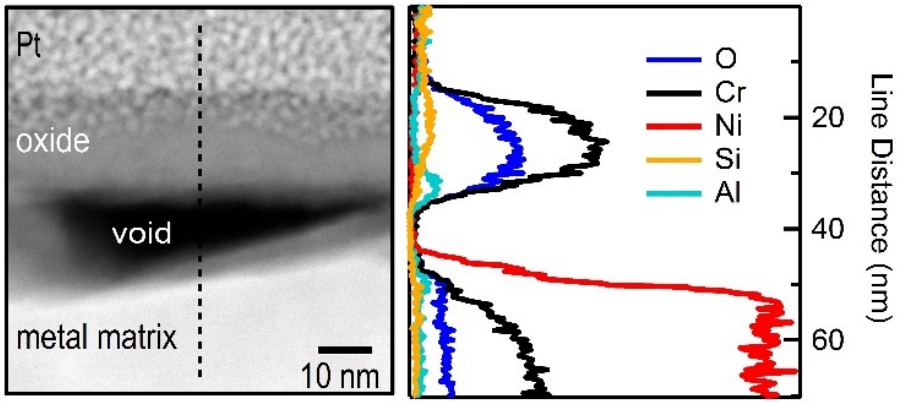
ΔG: $Al_2O_3 < SiO_2 < Cr_2O_3 < NiO$

Thermodynamic stability

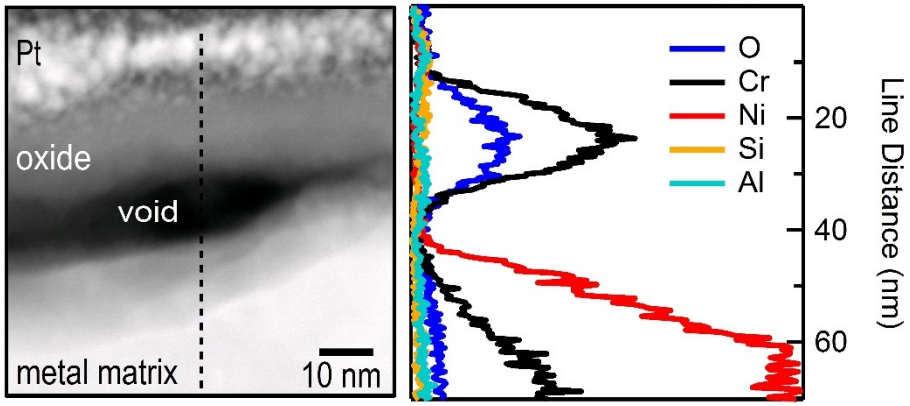
The role of oxygen impurities

Cross-sectional TEM of 5 min CO_2 and Ar exposures

CO_2 exposure (1-10 ppm O_2)



Ar exposure (≤1 pbb O_2)

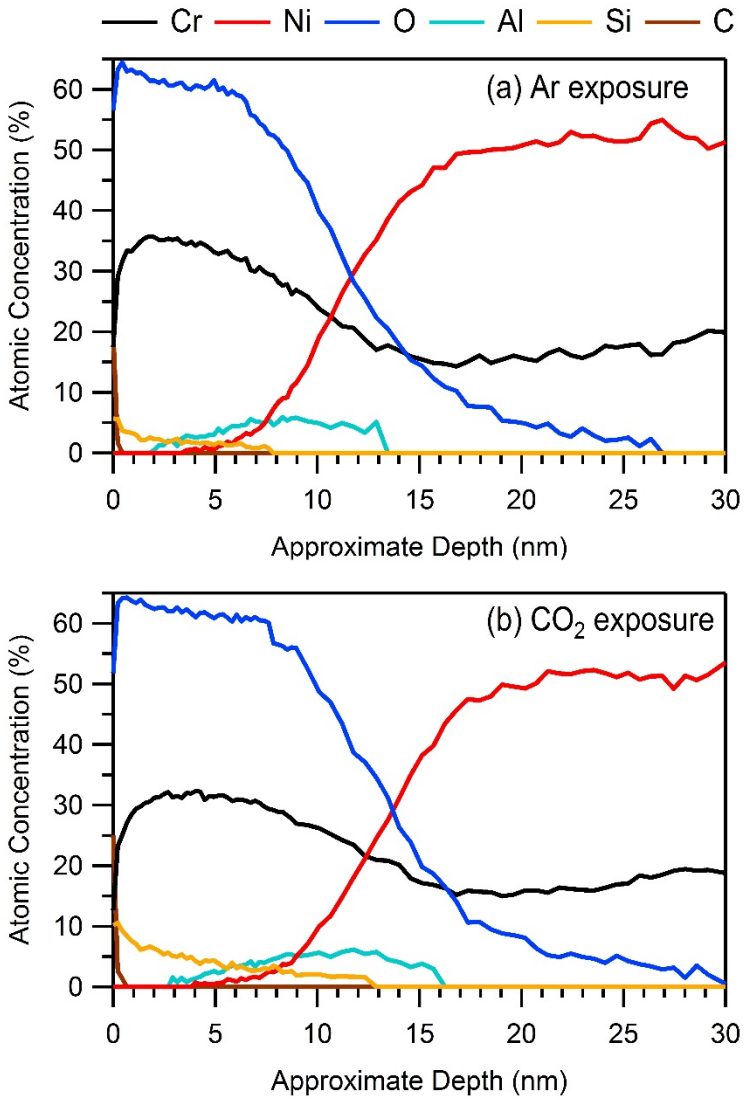


After 5 min at 700 °C, the surface oxides formed by exposure to CO_2 are nearly identical to those formed by exposure to a low pO_2 environment

Composition profiles over larger areas

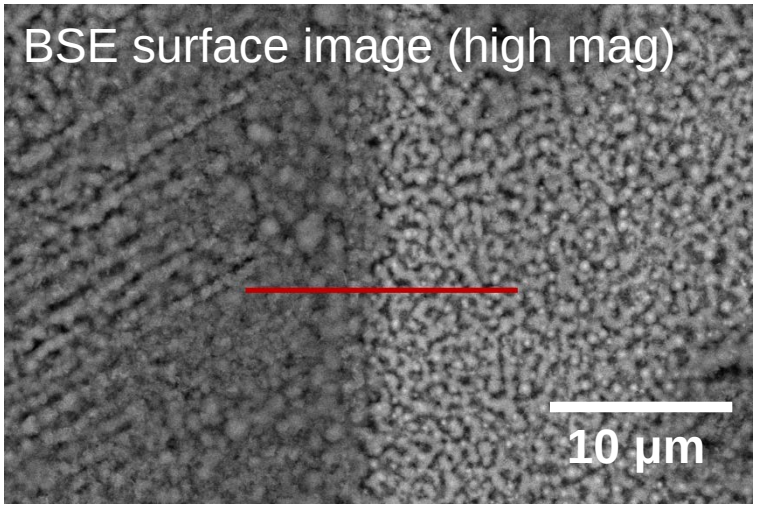
XPS depth profiling of 5 min CO_2 and Ar exposures

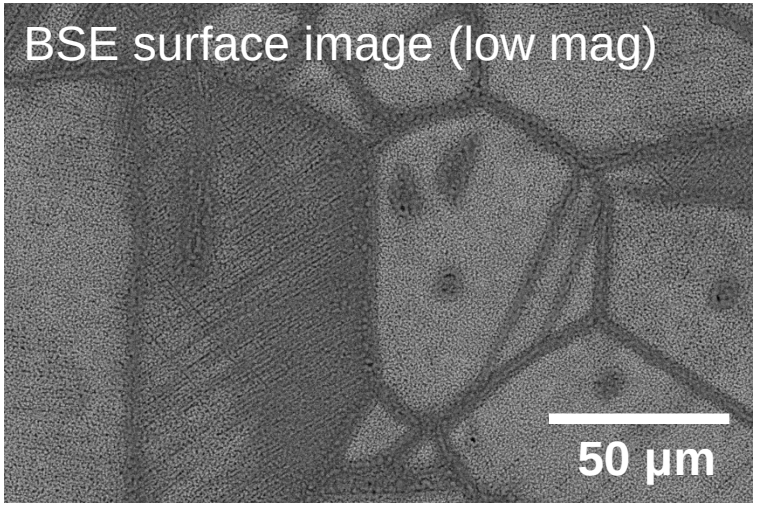
- Good agreement with cross-sectional TEM results (trends hold true over large areas)
- Ni 2p spectrum suggests little or no NiO (Ni metal only)
- Little or no carbon is present in or below the oxide layer

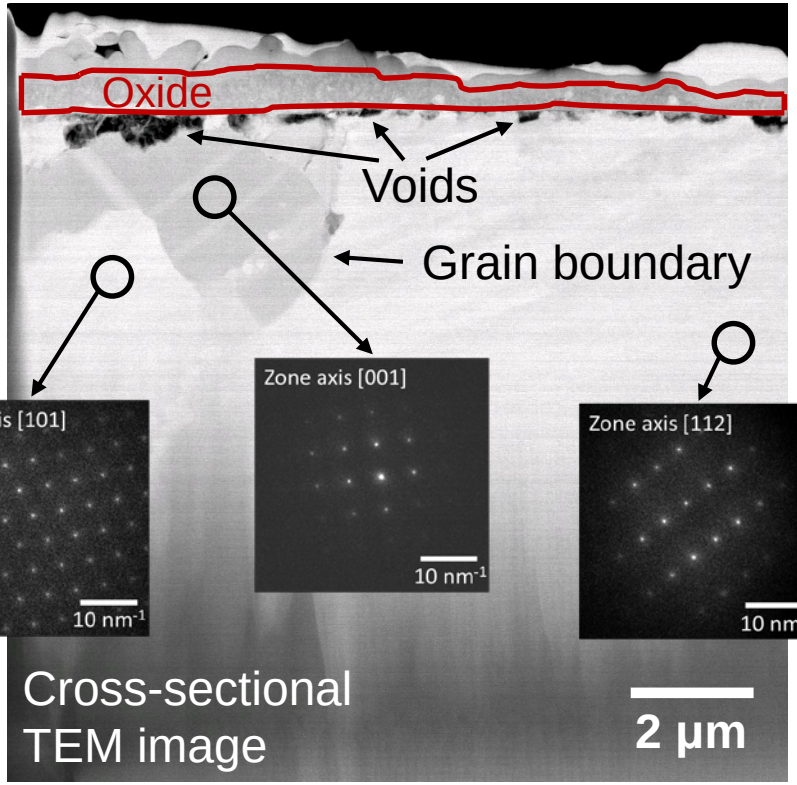


Analysis of longer term exposure

Cross-sectional TEM of 500 hour CO_2 exposure

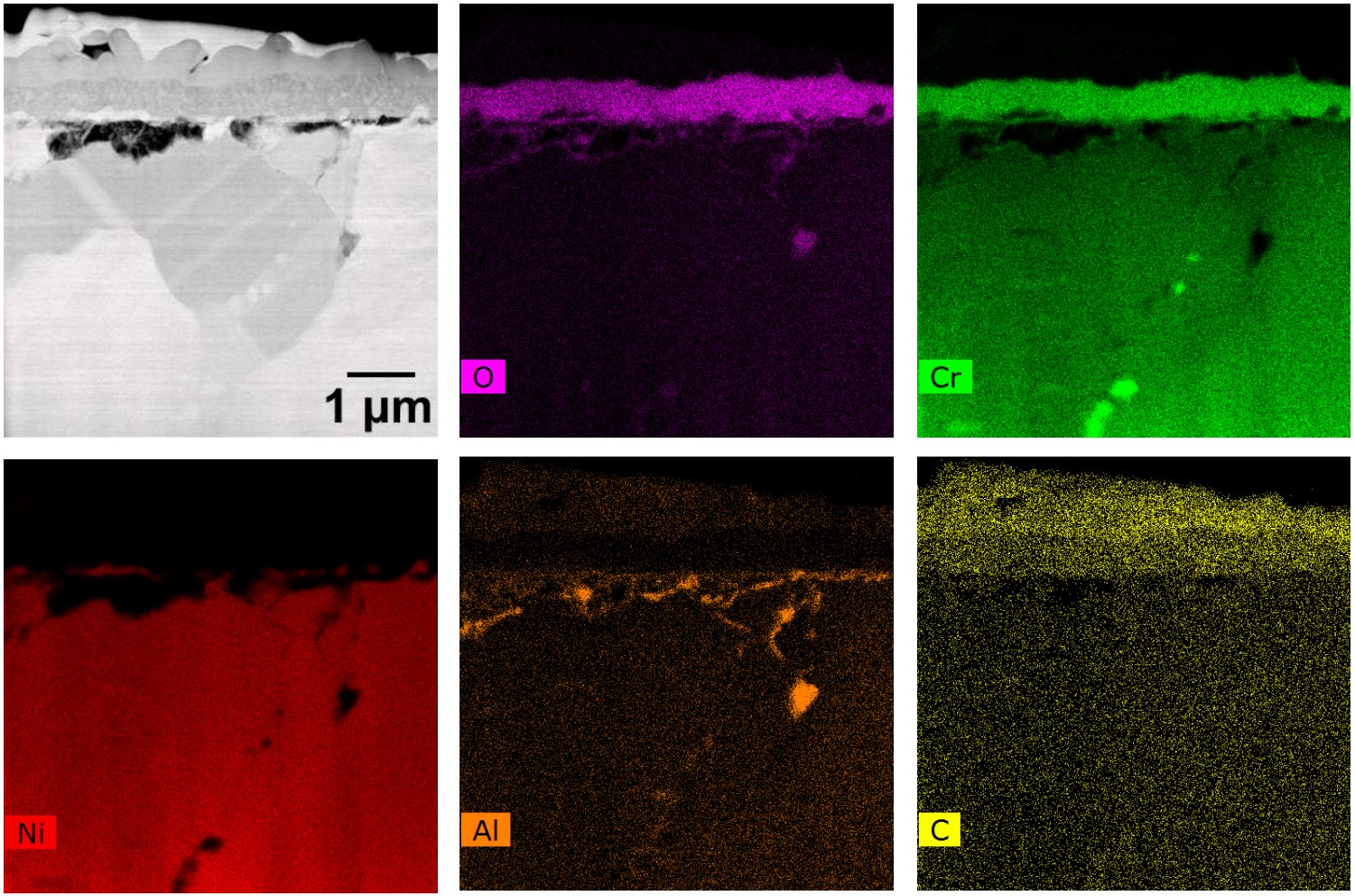






Composition of longer term exposure

Cross-sectional TEM / EDS mapping of 500 hour CO_2 exposure



Cr-rich oxide surface layer

"Internal oxidation" of Al in association with void formation

Possibly carbon in oxide layer, requires confirmation

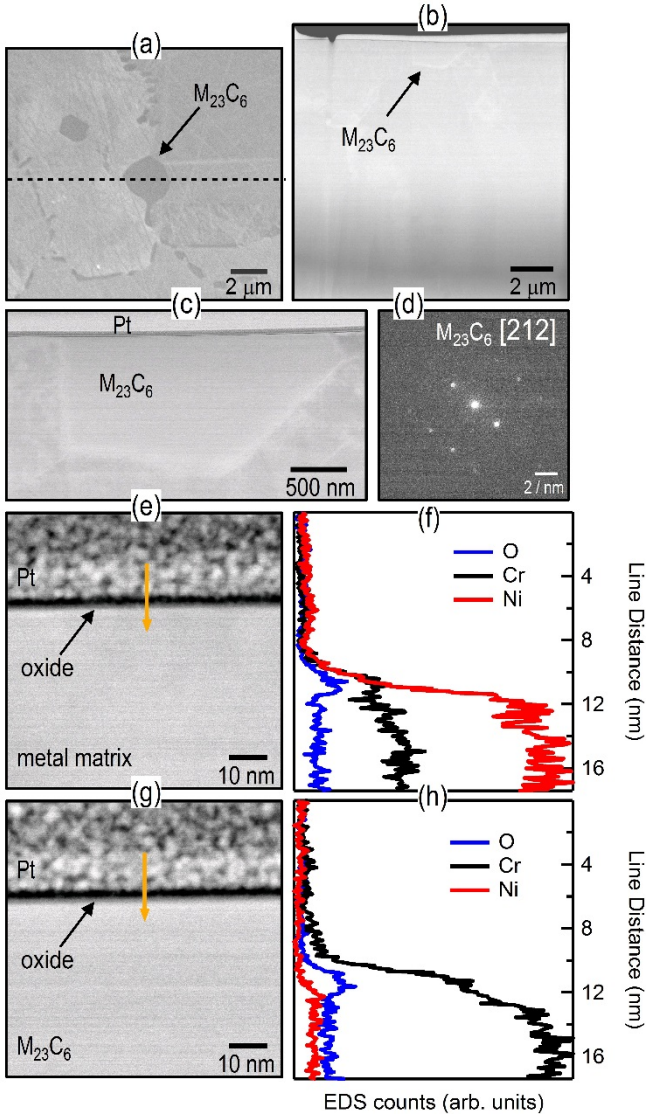
Summary/Conclusions

- Investigated oxidation behavior of Alloy 617 in 1 bar CO_2 at 700 °C for times ranging from 5 min – 500 h.
- Selective oxidation occurred (Cr-rich oxide), even for very short exposure times (5 min).
- Similarities between CO_2 and Ar exposures suggest O_2 impurities in the CO_2 gas may dominate early stages of oxidation.
- Little-to-no carburization observed thus far.
- In general, the alloy is a promising candidate for sCO_2 power cycle applications.
- Voids formed during high temperature oxidation warrant further investigation.

Thank you for listening.

Questions?

Extra slides - Alloy 617 unexposed sample



- Cr-rich carbides identified as $M_{23}C_6$
- Thin native oxide layer ≈2 nm thick prior to exposures