Early stage oxidation of Alloy 617 in CO_2 power cycle environments

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February 27, 2017

U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

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Acknowledgements

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 (RO) 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.

Why supercritical CO_2 power cycles?

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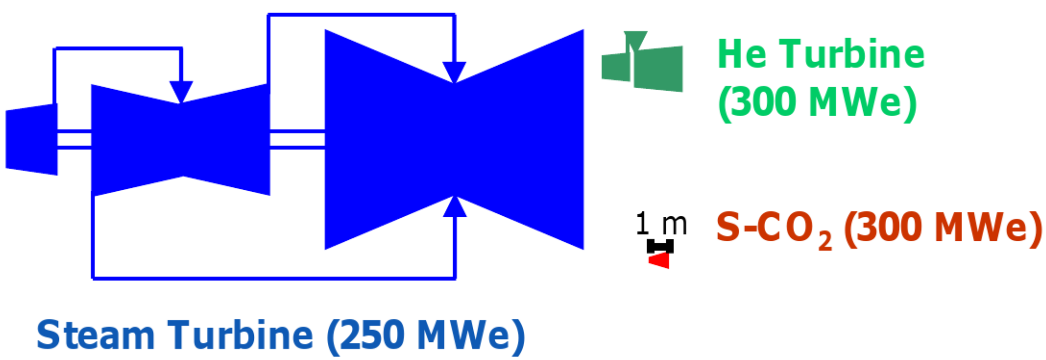
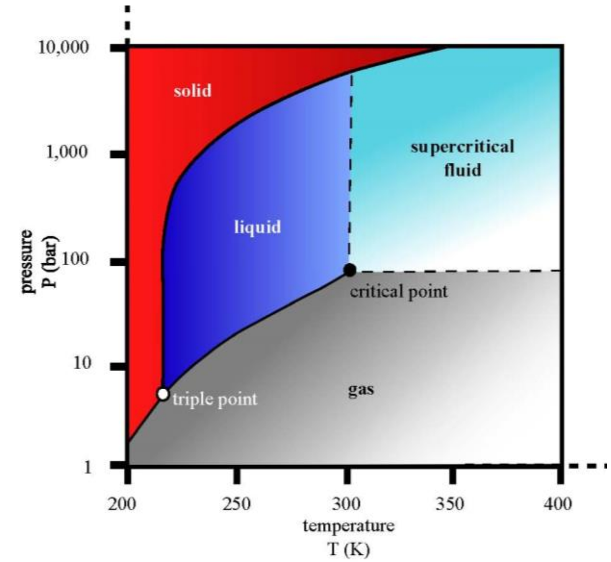
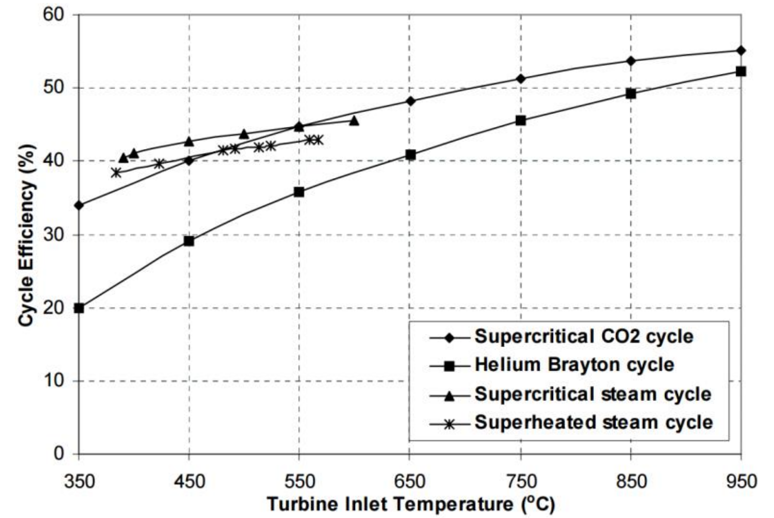
Properties of sCO_2 Cycles	Impact
No phase change (Brayton Cycle)	Higher efficiency
Recompression near liquid densities	Higher efficiency
High heat recuperation	Higher efficiency
Compact turbo machinery	Lower capital cost
Simple configurations	Lower capital cost
Dry/reduced water cooling	Lower environmental impact
Storage ready CO_2 in direct cycles	Lower environmental impact





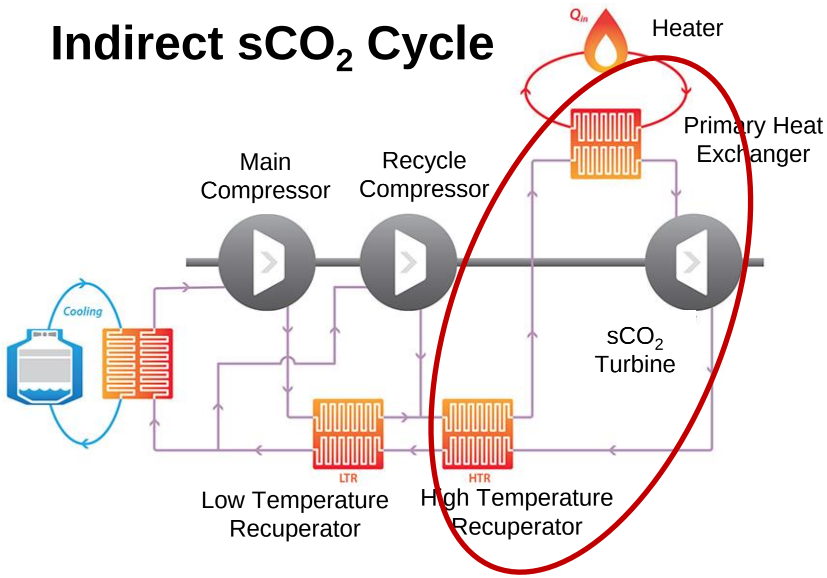


S. A. Wright, "OVERVIEW OF SUPERCRITICAL CO2 POWER CYCLE DEVELOPMENT AT SANDIA NATIONAL LABORATORIES," in *2011 University Turbine Systems Research Workshop*, Columbus, Ohio, 2011.

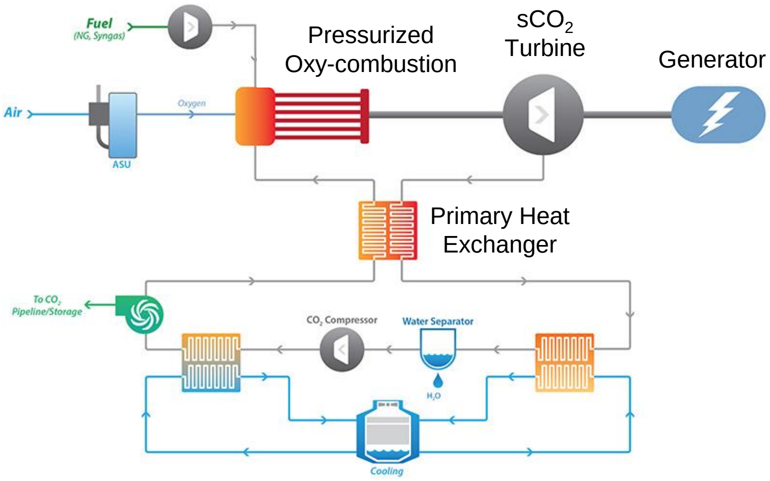
M. J. Driscoll, "Optimized, Competitive Supercritical-CO2 Cycle GFR for Gen IV Service," MIT-GFR-045, 2008.

sCO_2 power cycles – materials considerations

Indirect sCO_2 Cycle

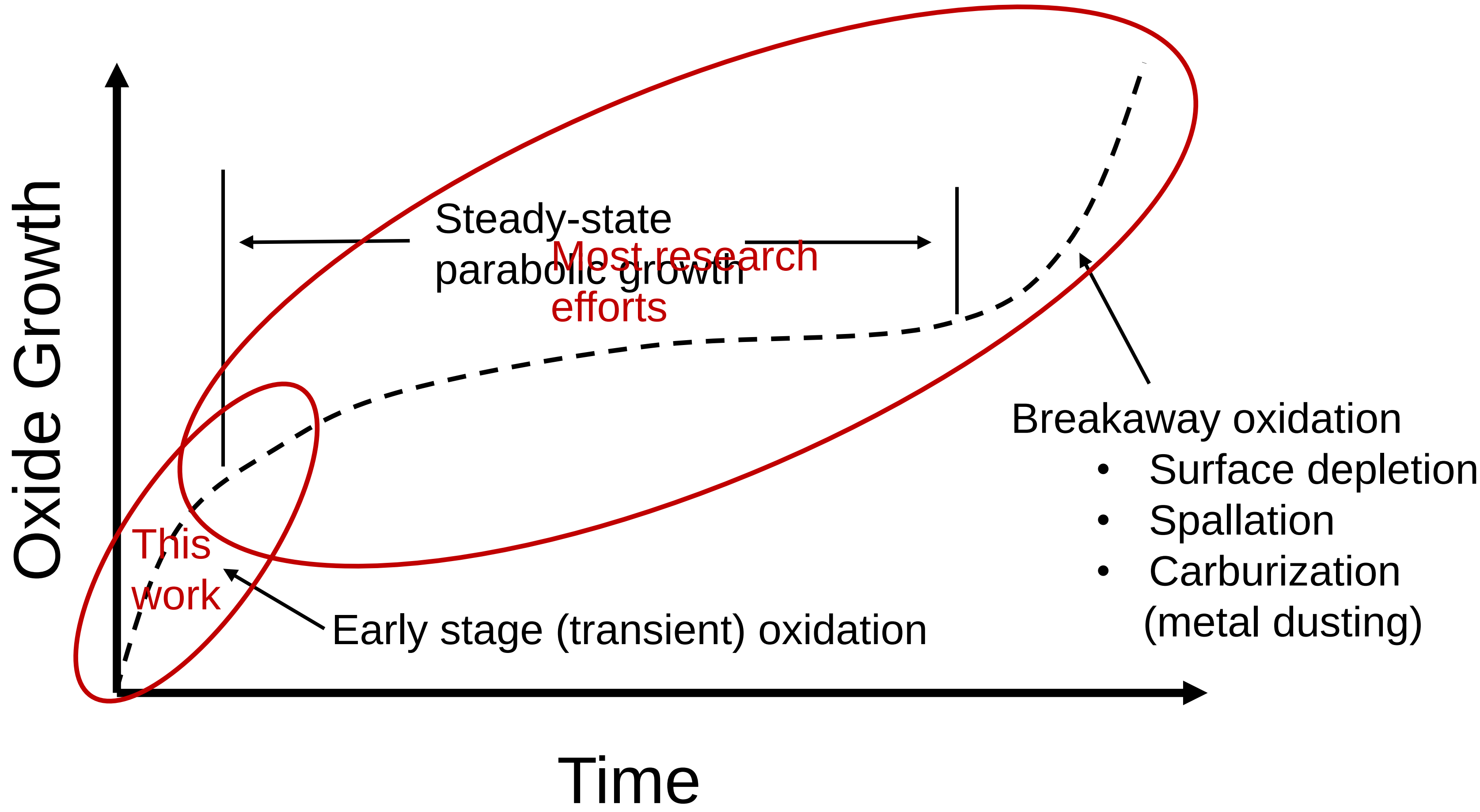


Direct sCO_2 Cycle



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 high-T alloy oxidation



Experimental

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Exposure Conditions

- Fluid = 99.999% CO_2
- T = 700 °C
- P = 0.1 MPa (atmospheric) or 20 MPa (supercritical)
- t = 5 min – 500 h

Exposure Apparatus

- High-temperature confocal scanning laser microscope
  - t = 5 min, P = 0.1 MPa
- Tube furnace
  - t = 1 – 500 h, P = 0.1 MPa
- Autoclave
  - t = 500 h, P = 20 MPa

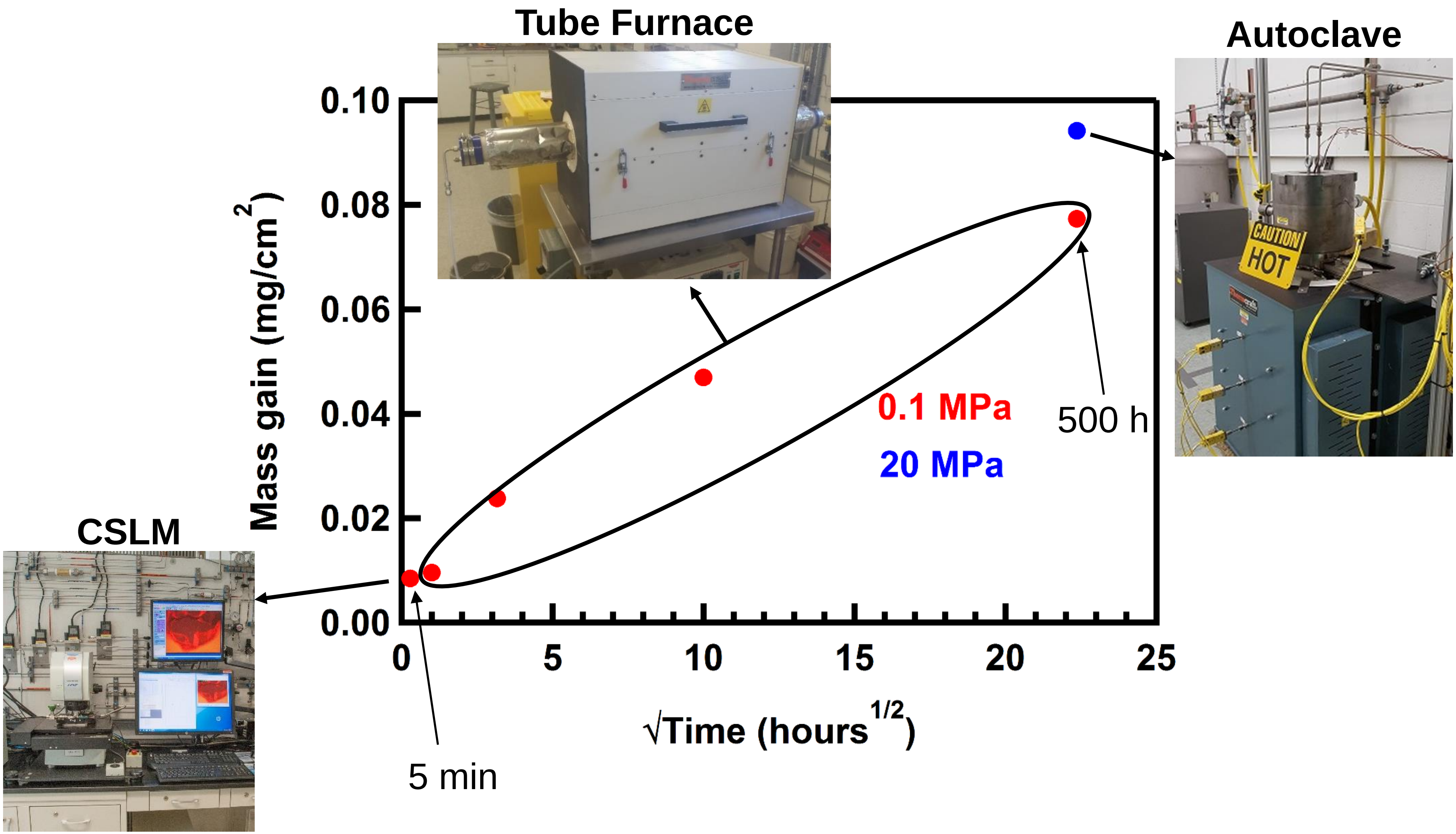
Analysis

- Cross-sectional transmission electron microscopy
- Samples generated using focused ion beam lift-out method

Alloy 617 composition

Element	wt%
Ni	**53.3**
Cr	**22.4**
Co	11.5
Mo	9.6
Al	**1.1**
Fe	1.1
Ti	0.3
C, Si, Mn, Cu	<0.1
B, P, S	<0.01

Mass change



Tube Furnace
Autoclave
CSLM
CAUTION
HOT
0.10
0.08
0.06
0.04
0.02
0.00
Mass gain (mg/cm^2)
0
5
10
15
20
25
√Time (hours$^{1/2}$)
0.1 MPa
20 MPa
500 h
5 min

Evolution of surface morphology

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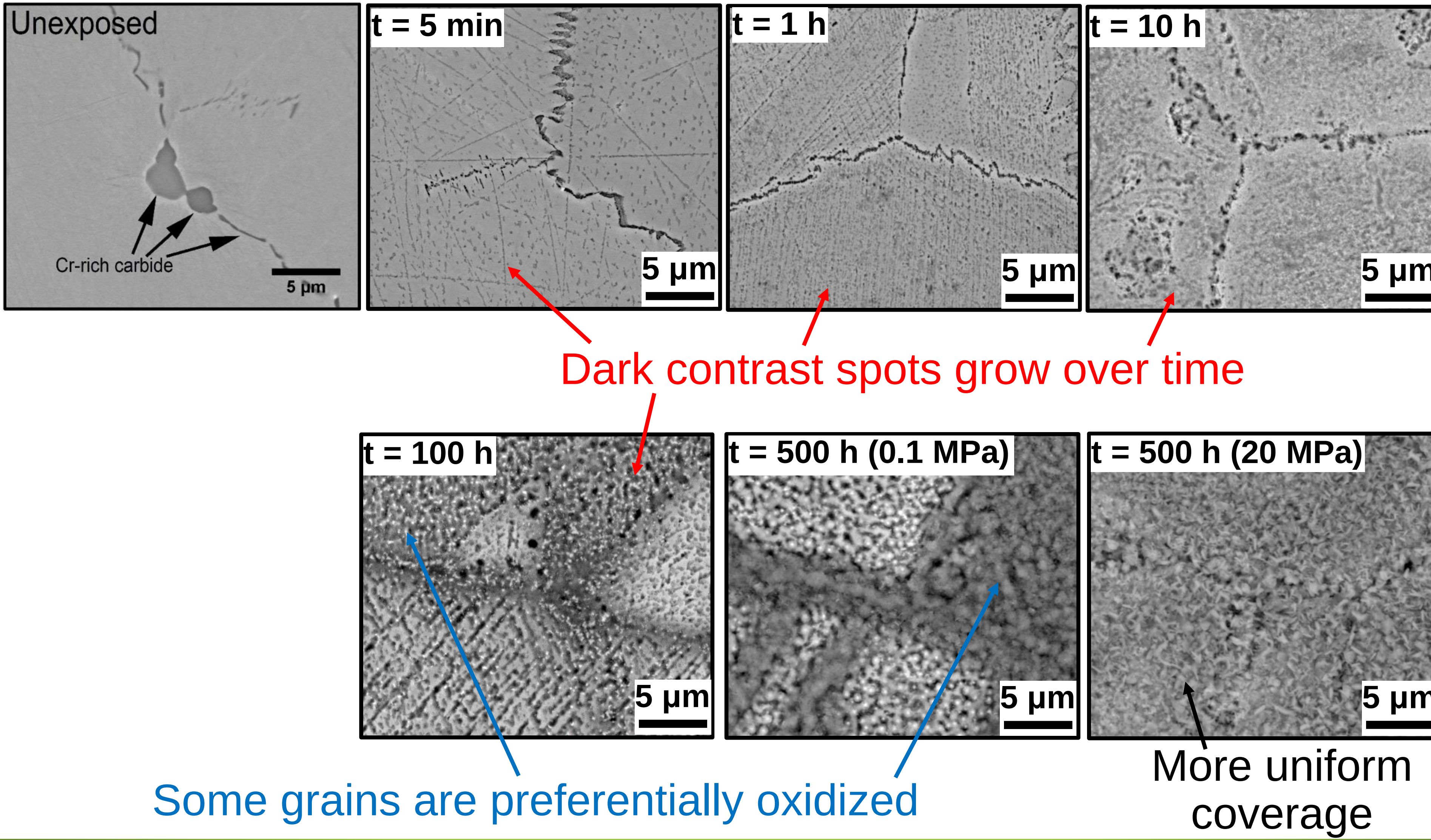

Sub-surface void formation

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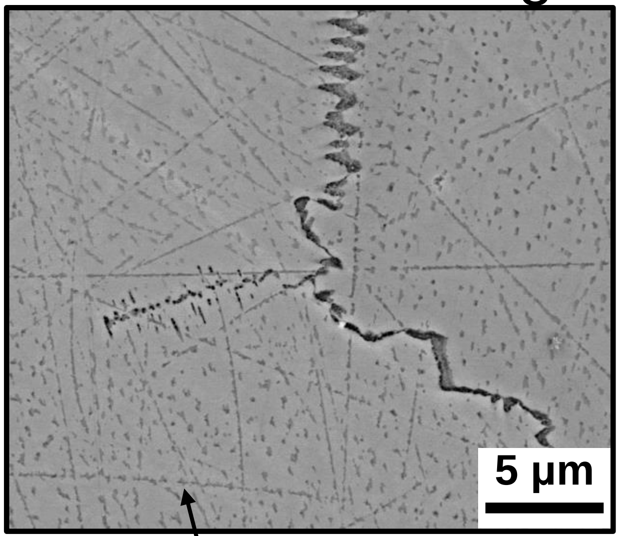
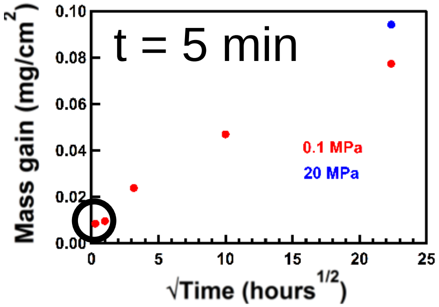
BSE surface image





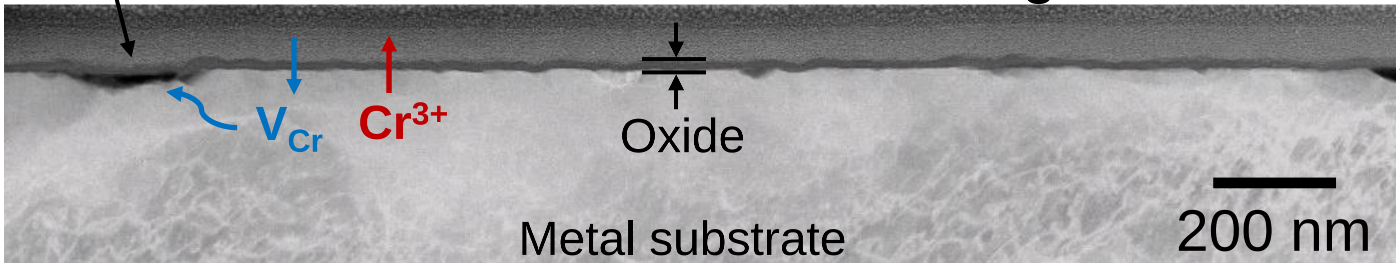
Voids are formed at the oxide/metal interface during the initial stages of oxidation, most likely due to condensation of Cr vacancies.

These voids are formed preferentially along micro-scratches and grain boundaries.

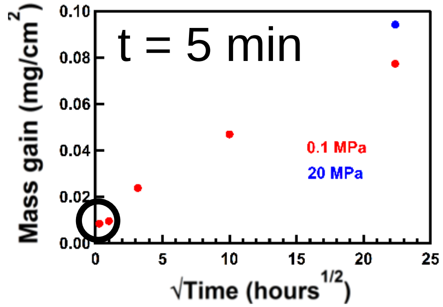
Sub-surface voids

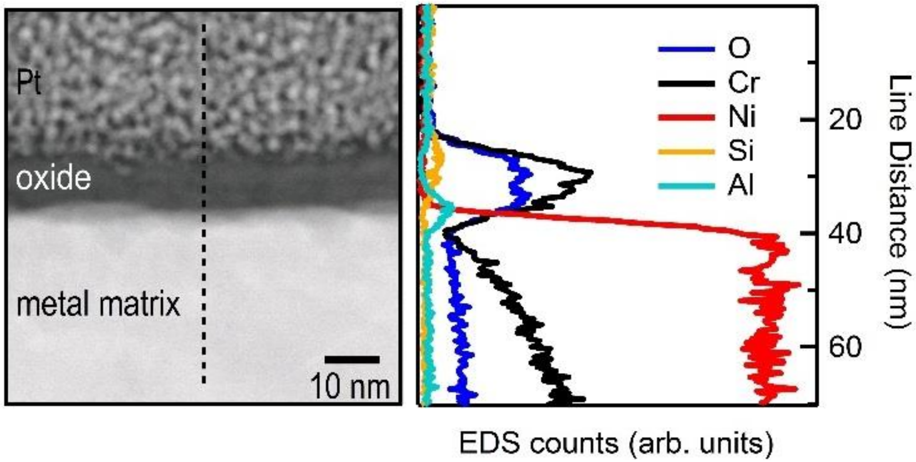
Cross-sectional TEM image

Sub-surface void

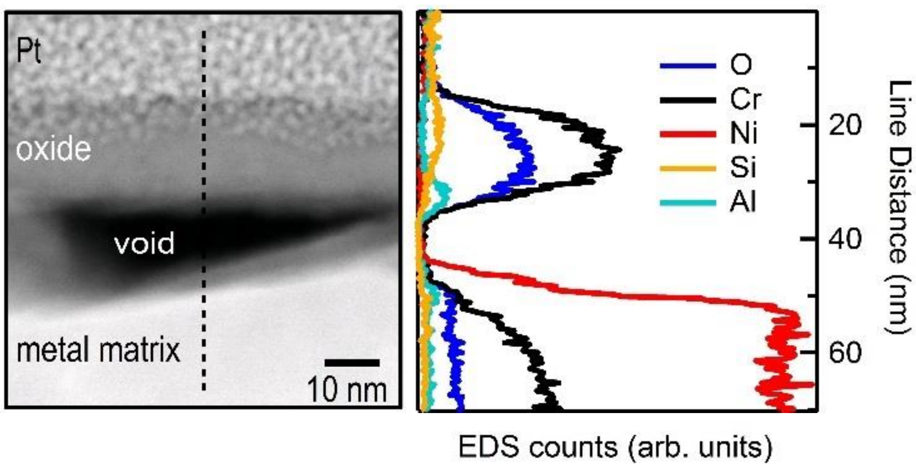


Selective oxidation of Cr





After a short (5 min) exposure the oxide is Cr-rich, containing some Si and Al.



In high purity CO_2 at 0.1 MPa and 700 °C, expected $pO_2 \approx 10^{-7}$ - 10^{-6} MPa. Yet, no Ni-oxides are formed.

Ni

↑

$pO_2 = 10^{-18}$ MPa

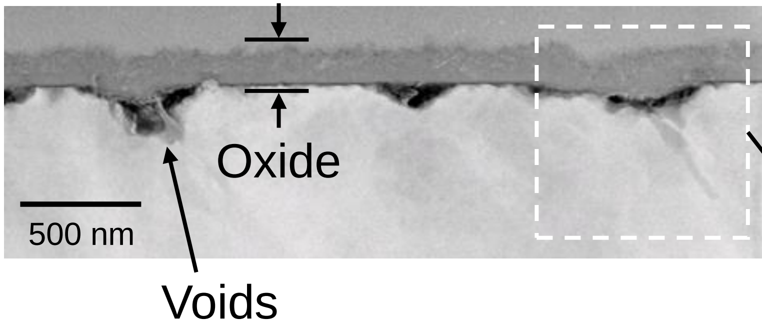
↓

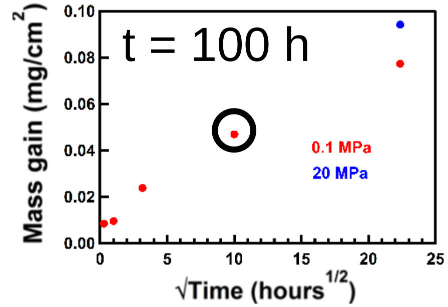
ΔG: $Al_2O_3 < SiO_2 < Cr_2O_3 < NiO$

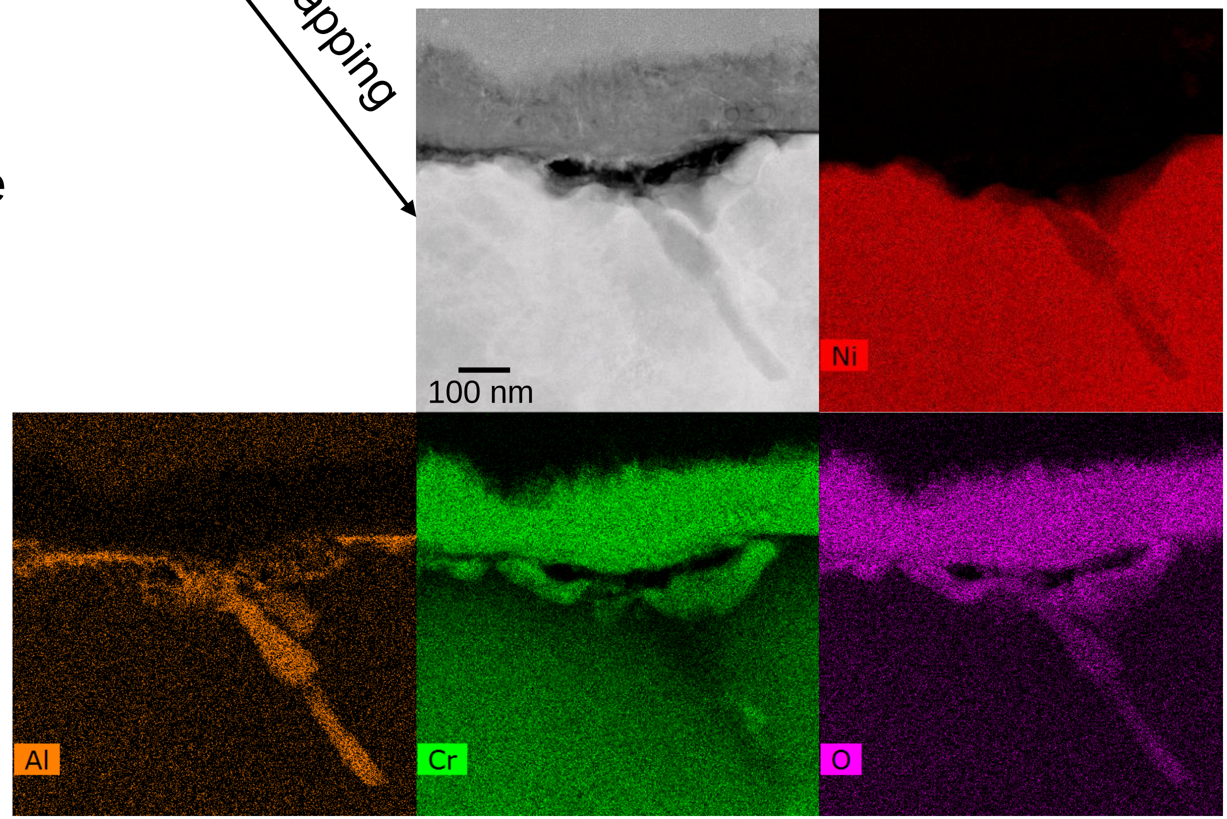
←

Thermodynamic stability

Continued oxide growth





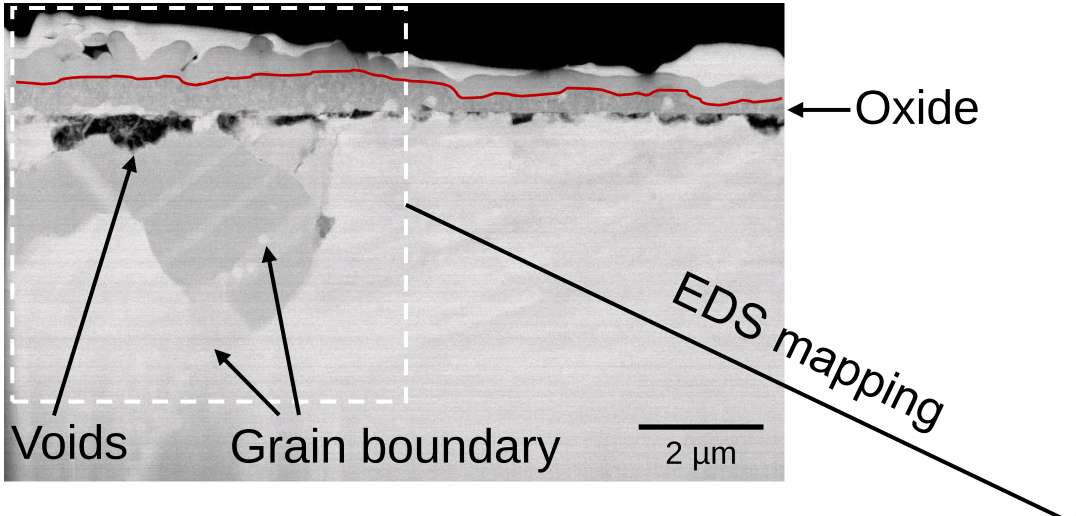


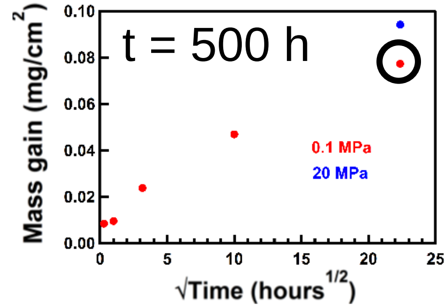
Sub-surface voids continue to grow. Al is oxidized inside and adjacent to the voids.

Cr-oxide forms above and below voids.

This suggests that both outward and inward oxide growth has occurred.

Continued oxide growth

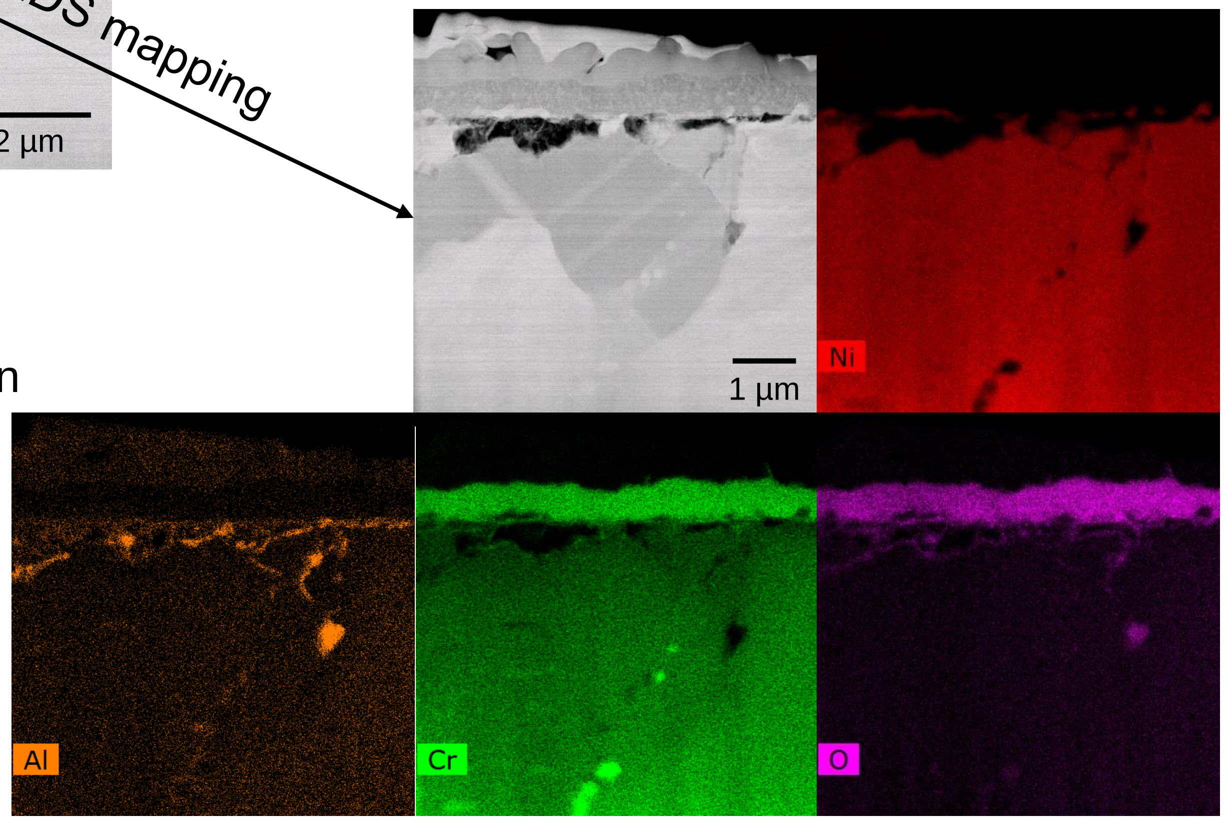




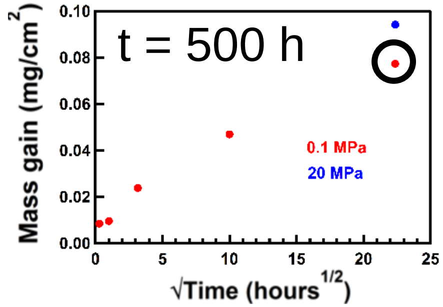
Continued void growth.

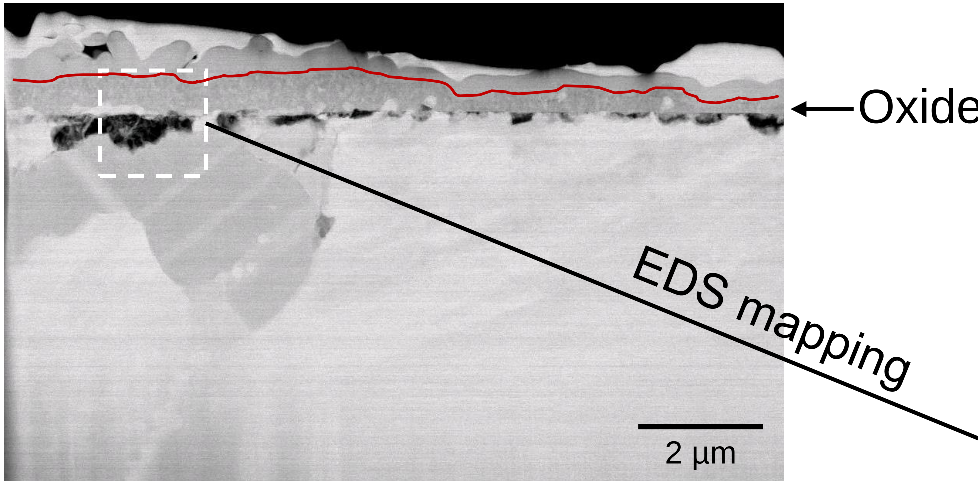
Cr-depletion and recrystallization near the alloy surface.

Short-circuit diffusion paths created by voiding and recrystallization lead to further internal oxidation of Al.

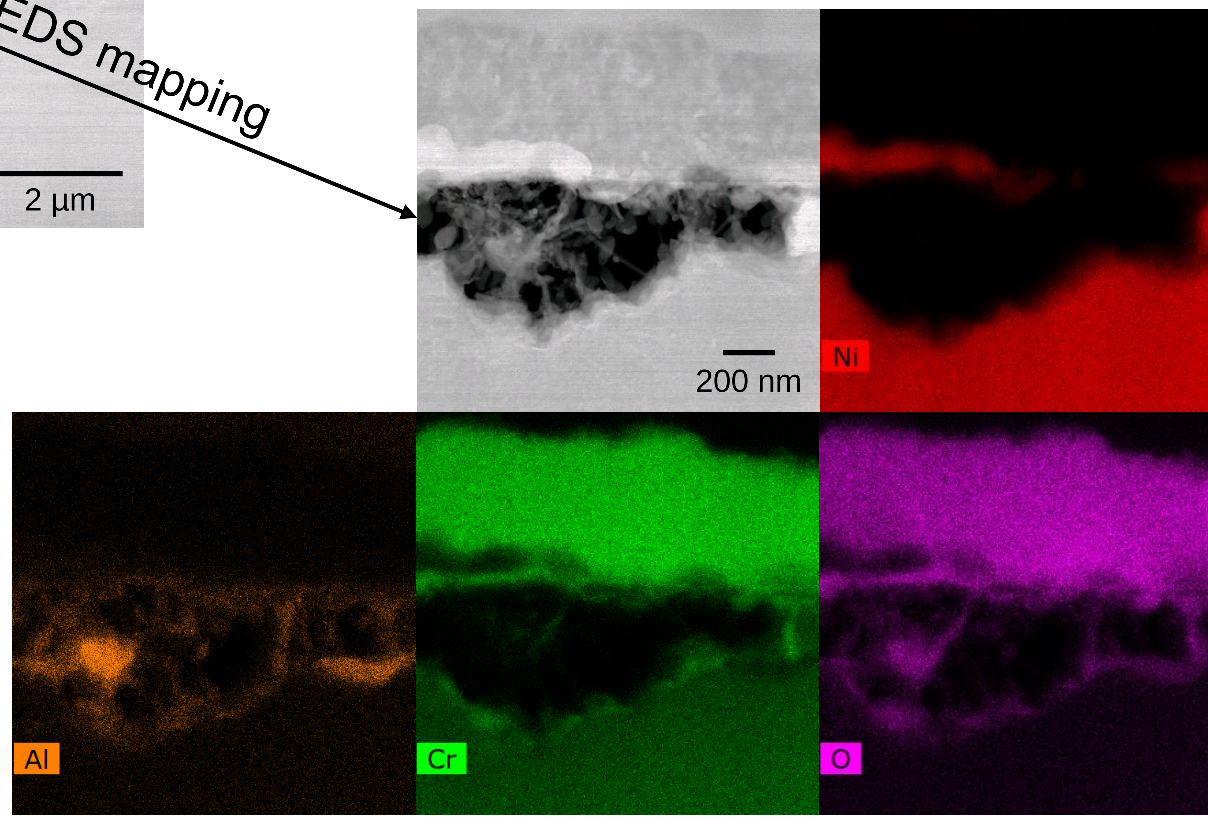


Role of voids during oxidation





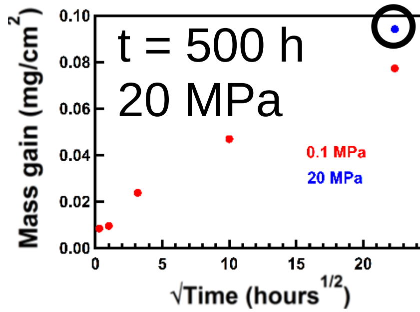
EDS mapping

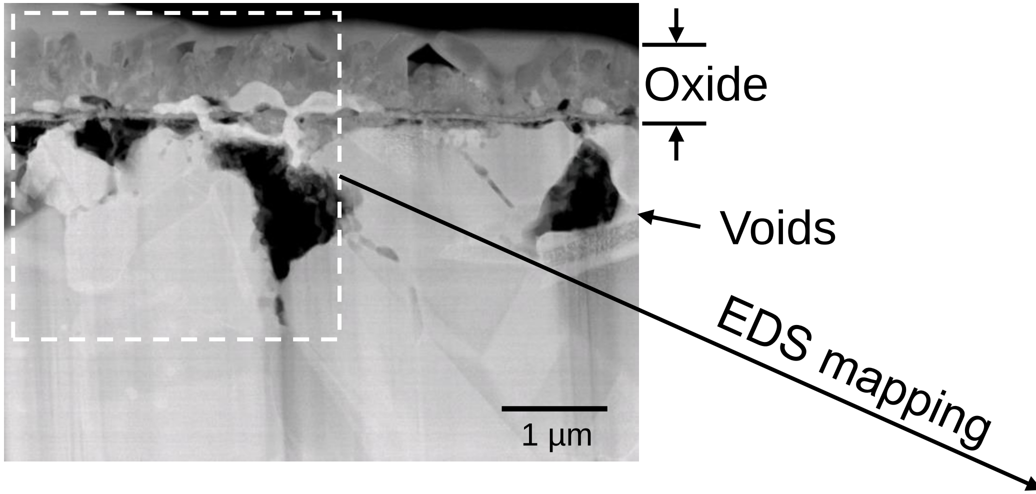


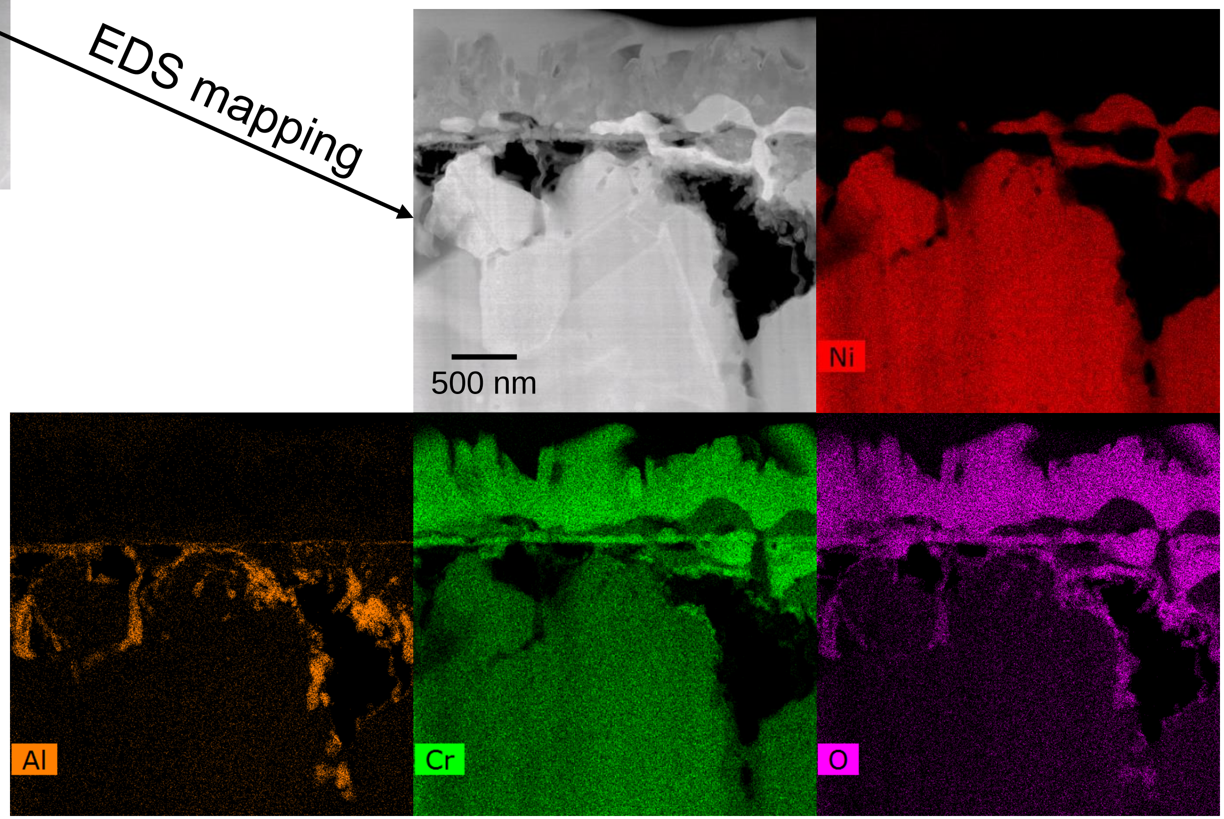
As voids form near the oxide/alloy interface, metal that is depleted of Cr becomes trapped and is incorporated into the scale.

Over time, the voids are filled with Al-oxide.

The effects of pressure





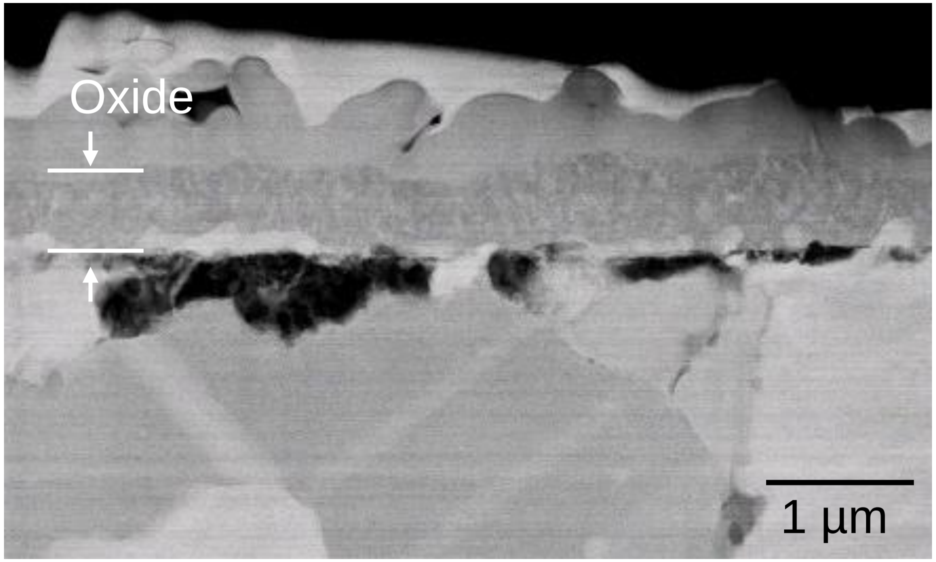


As with the 0.1 MPa exposure, we observe:

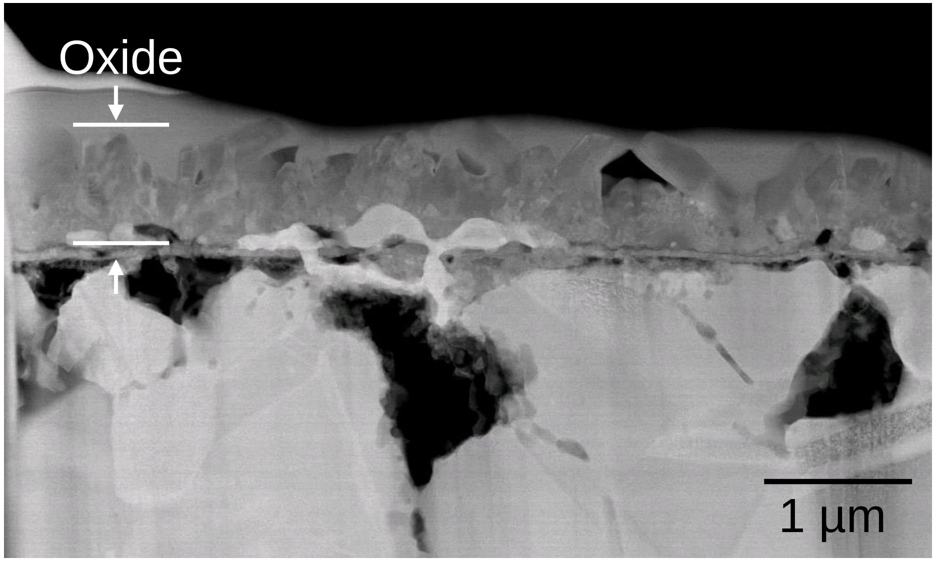
- Sub-surface voids
- Recrystallization
- Trapping of Cr-depleted metal
- Oxidation of Al inside and adjacent to voids

Atmospheric vs. Supercritical exposure

0.1 MPa, 500 h



20 MPa, 500 h



20 MPa exposure is controlled by similar processes as 0.1 MPa, but proceeds to a larger extent.

- 20-30% thicker oxide layer.
- More extensive sub-surface effects including voiding and recrystallization.
- Increased inward oxide growth (note Cr-depleted metal and voids that are incorporated into the oxide layer).

Summary and Conclusions

- Ni-Cr-Al alloy (617) was oxidized in CO_2 at 700 °C for 5 min – 500 hours.

- Good oxidation resistance was observed.
    - Protective Cr_2O_3-type surface forms in < 5 min.
    - < 0.1 mg/cm^2 mass gain after 500 h (both 0.1 MPa and 20 MPa).

- Similar oxidation processes were observed in 20 MPa (supercritical) and 0.1 MPa (atmospheric) exposures, however these processes were more extensive in 20 MPa exposure.

- Significant sub-surface voiding associated with surface oxidation.
    - Scale thickens by both outward (leading to void formation) and inward (leading to void filling with oxide) growth mechanisms.
    - Cr-depleted metal is trapped in the scale during voiding.
    - The low concentration, highly stable oxide-former (i.e., Al) is oxidized inside and adjacent to these voids—implications for scale adhesion and long-term stability.

Thank you for listening.

Questions?