High-temperature oxidation of Ni-based alloys in CO_2 containing combustion impurities

Richard P. Oleksak[1,2], Joseph H. Tylczak[1], Gordon R. Holcomb[1], Ömer N. Doğan[1]

[1]National Energy Technology Laboratory, 1450 Queen Ave SW, Albany, OR 97321, USA
[2]Leidos Research Support Team

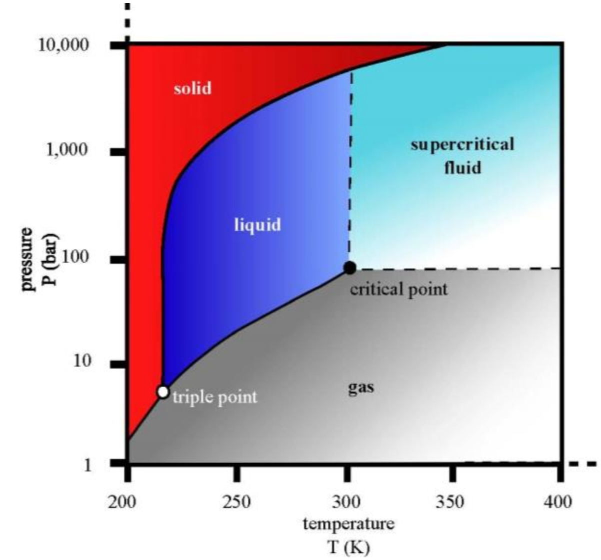
Material Science & Technology Annual Meeting, Portland, OR, Sept. 29 – Oct. 3, 2019

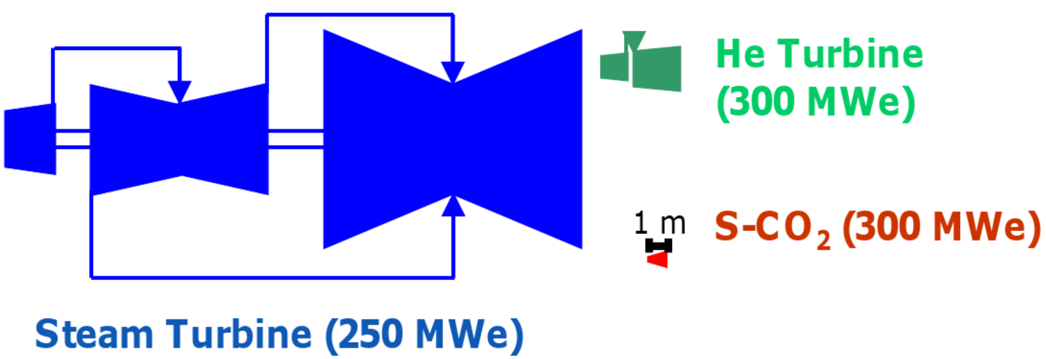
Acknowledgements

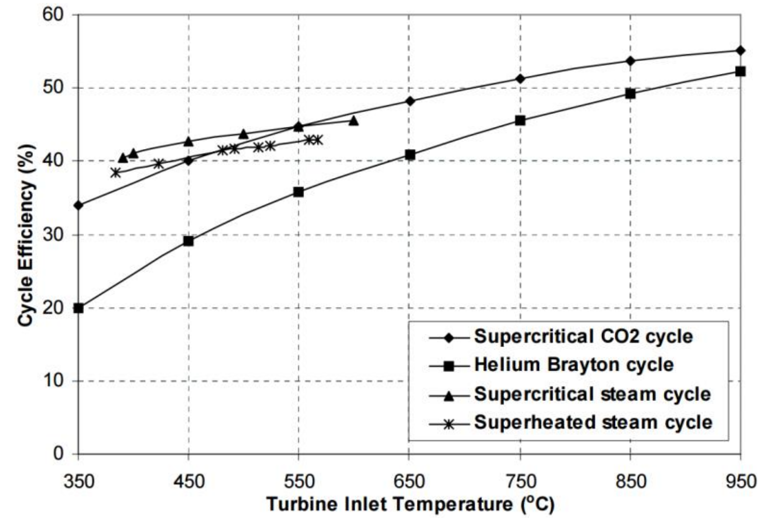
This work was performed in support of the U.S. Department of Energy's Fossil Energy Crosscutting Technology Research Program. The Research was executed through the NETL Research and Innovation Center's Advanced Alloy Development Field Work Proposal. Research performed by Leidos Research Support Team staff was conducted under the RSS contract 89243318CFE000003.

Why supercritical CO_2 power cycles?

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





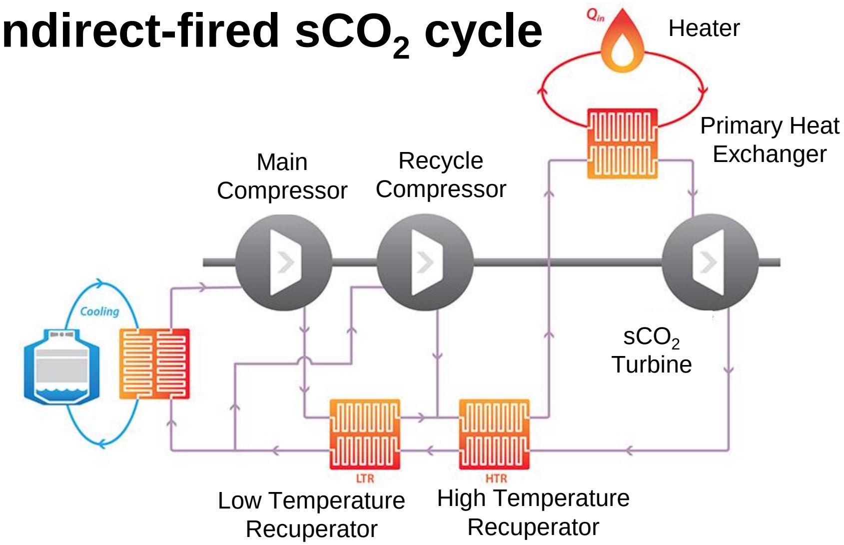


S. A. Wright, "OVERVIEW OF SUPERCRITICAL CO2 POWER CYCLE DEVELOPMENT AT SANDIA NATIONAL LABORATORIES," in *2011 University Turbine Systems Research Workshop*, Columbus, Ohio, 2011.

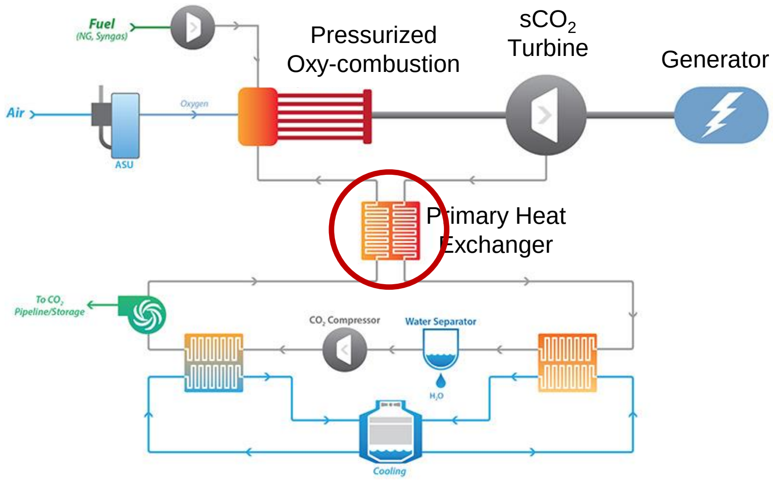
M. J. Driscoll, "Optimized, Competitive Supercritical-CO2 Cycle GFR for Gen IV Service," MIT-GFR-045, 2008.

Materials considerations

Indirect-fired sCO_2 cycle



Direct-fired 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 based on fuel (e.g., SO_2)
	Turbine	1150	20-30	800	3-8	
	HX	800	3-8	100	3-8	

Candidate alloys

Several commercially available Ni-based alloys were tested:

wt%	Fe	Ni	Cr	Co	Mo	Mn	W	Nb	Si	Ti	Al	C
Ni-based (solution strengthened)												
600	7.6	75.0	**16.0**	0.1	0.2	0.2	<0.010	0.1	0.2	0.3	0.1	-
617	0.4	55.1	**21.9**	11.5	9.6	0.04	<0.010	0.03	0.02	0.5	0.9	-
230	0.4	59.8	**22.2**	0.3	1.3	0.5	14.4	0.04	0.4	0.01	0.4	-
625	4.4	60	**22.3**	0.03	8.3	0.4	-	3.5	0.2	0.2	0.1	0.1
Ni-based (precipitation strengthened)												
718	18.1	53.8	**18.0**	0.2	3.0	0.2	-	5.3	0.1	1.0	1.6	0.1
282	0.2	58.2	**19.3**	12.1	8.4	0.1	-	0.02	0.2	2.1	1.3	-
263	0.4	50.7	**20.3**	19.7	5.8	0.4	-	0.08	0.02	2.2	0.4	0.1
740H	<0.010	50.4	**24.5**	20.2	0.3	0.2	<0.010	1.5	0.1	1.4	1.2	-

Increasing Cr content

High-temperature oxidation exposures

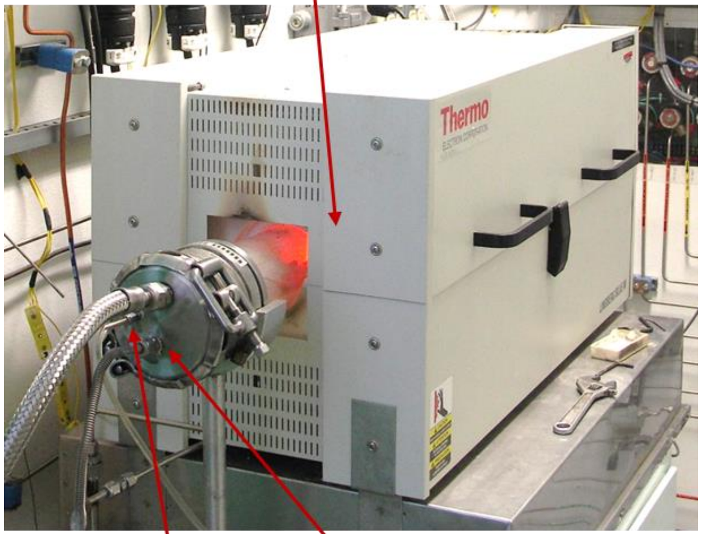
Gas 1 (vol%): 95% CO_2, 4% H_2O, 1% O_2

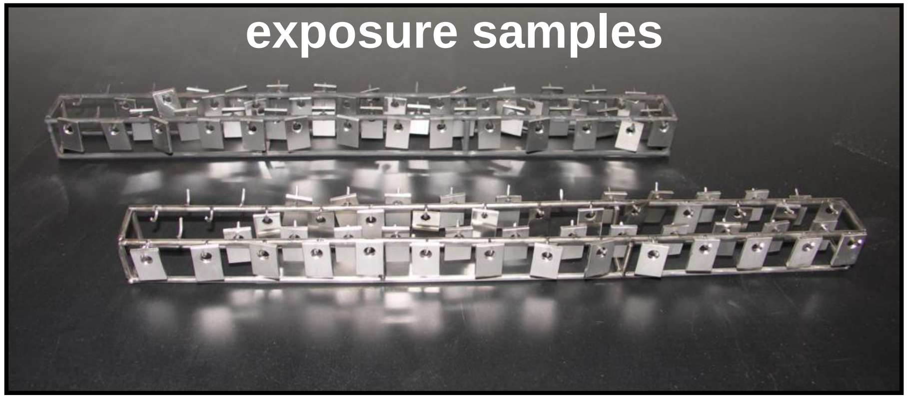
Gas 2 (vol%): 95% CO_2, 4% H_2O, 1% O_2, 0.1% SO_2

Pressure: 1 atm

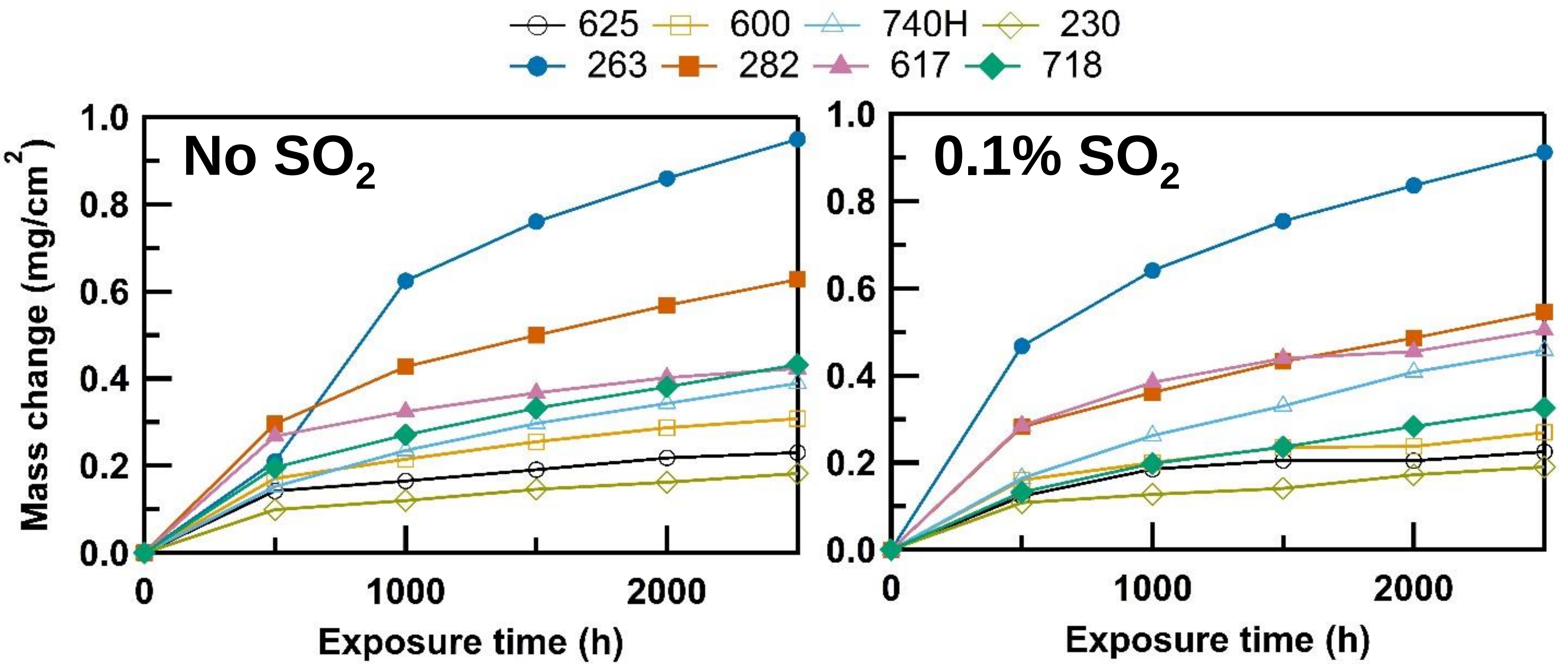
Temperature: 600-750 °C

Duration: Up to 2500 h (500 h increments)





Mass change (750 °C)



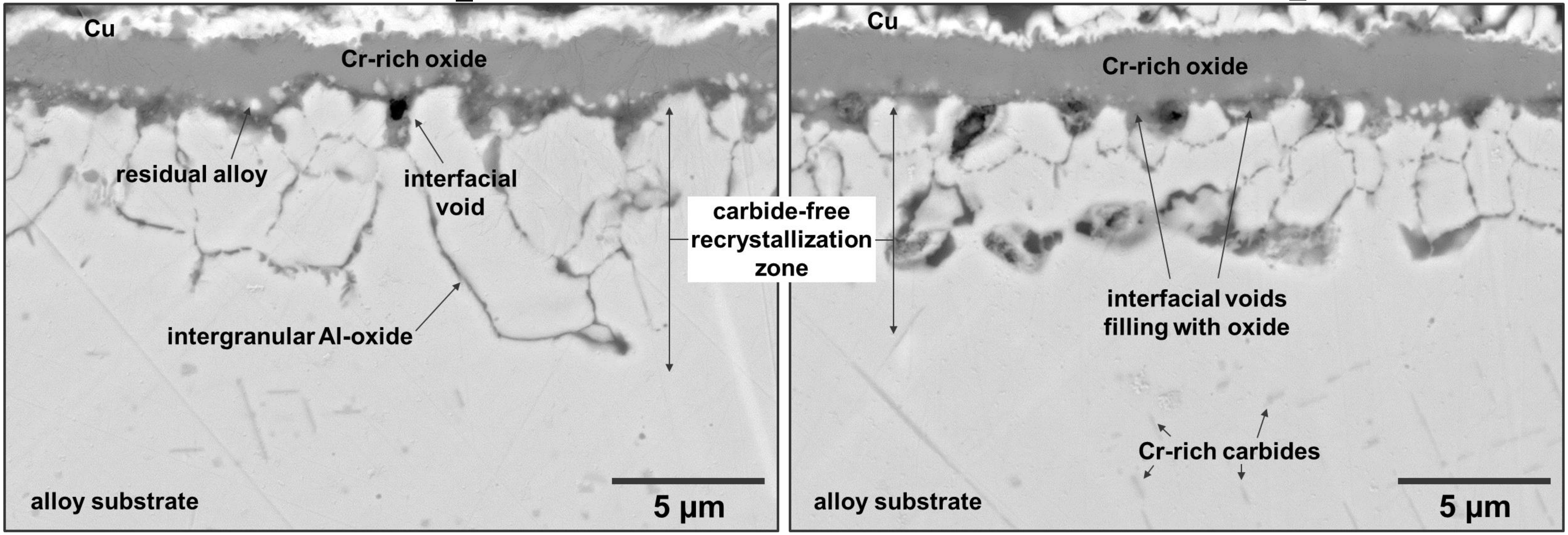
- Low mass gains for all Ni alloys—notably higher for Alloy 263.
- XRD identified corrosion products as Cr_2O_3 with minor spinel oxide and TiO_2.
- Little or no effect of SO_2.

Alloy 740H (750 °C)

NATIONAL ENERGY TECHNOLOGY LABORATORY

Cross-sectional SEM

No SO_2 | **0.1% SO_2**



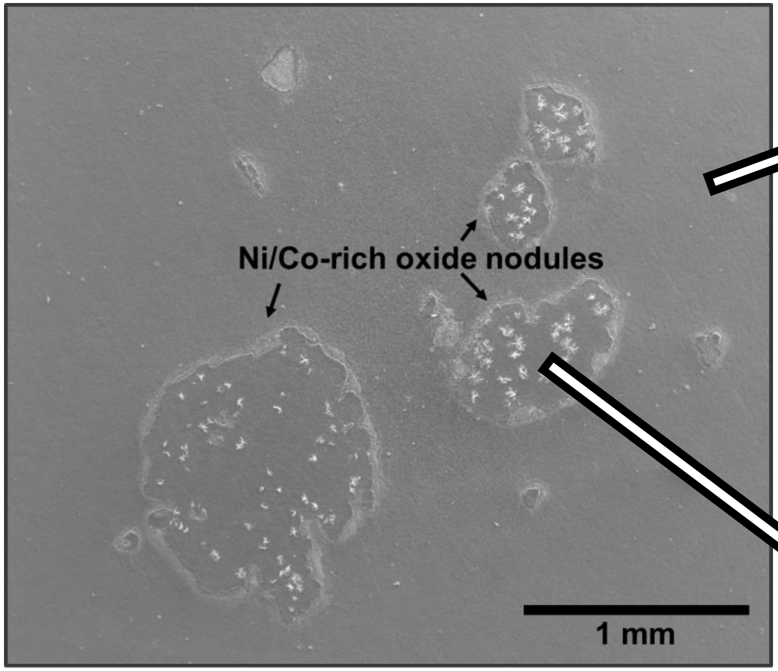
- Chromia scale and internal oxidation of Al.
- Sub-surface voiding and recrystallization.*
- Similar observations for most Ni alloys.
- No effect of SO_2, consistent with mass gains.

* Oleksak et al., Structural evolution of a Ni alloy surface during high-temperature oxidation, *Oxid. Met.* (2017)
Oleksak et al., The role of metal vacancies during high-temperature oxidation of alloys, *npj Mater. Degr.* (2018)

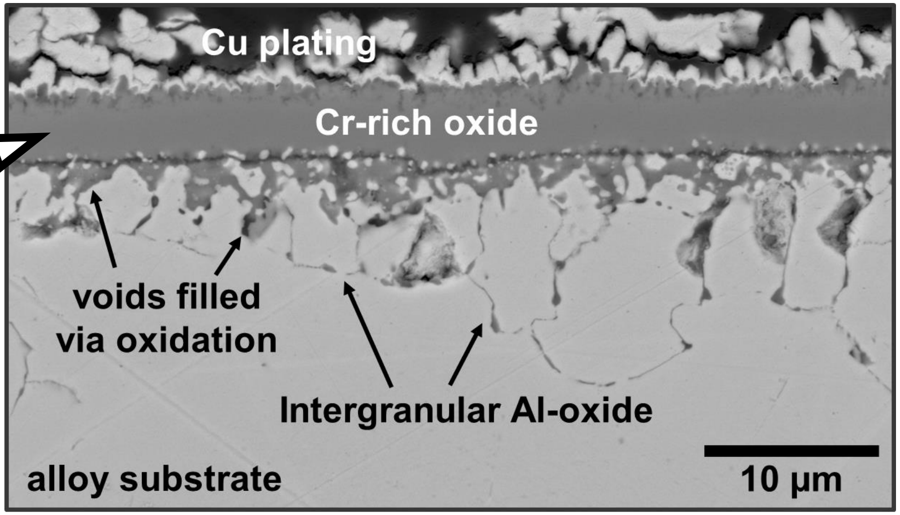
Alloy 263 (750 °C, no SO_2)

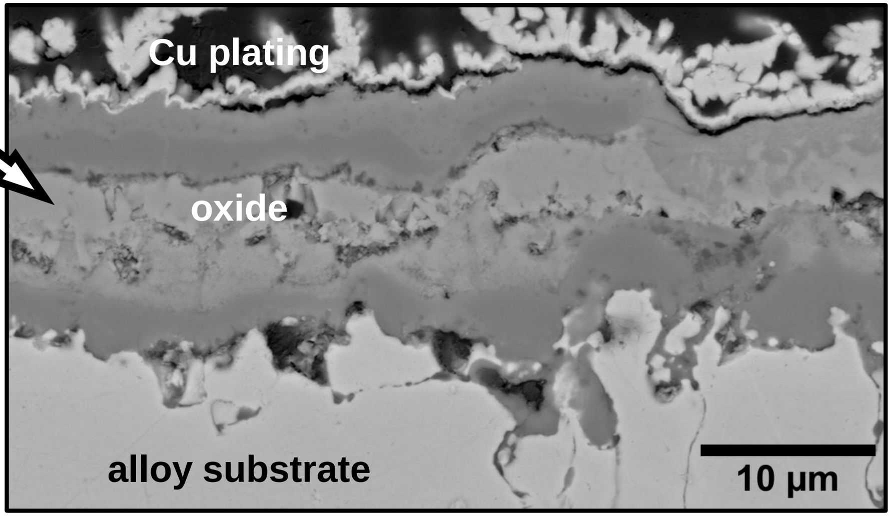
NATIONAL ENERGY TECHNOLOGY LABORATORY

Surface SEM



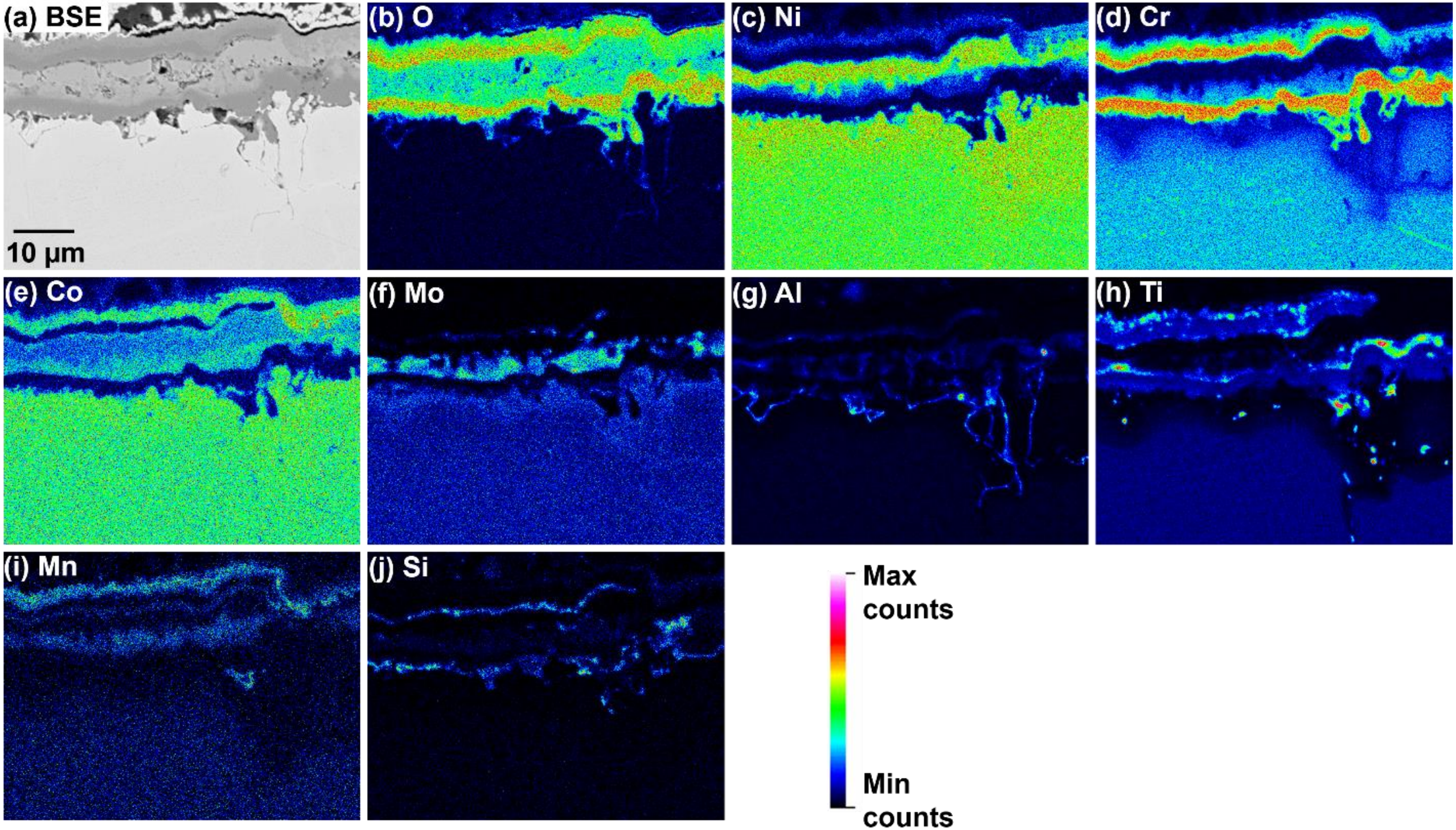
Cross-sectional SEM





- Thicker chromia layer and occasional nodules responsible for increased mass gain.
- TiO_2 also detected by XRD.

Alloy 263 (750 °C, no SO_2) EPMA mapping

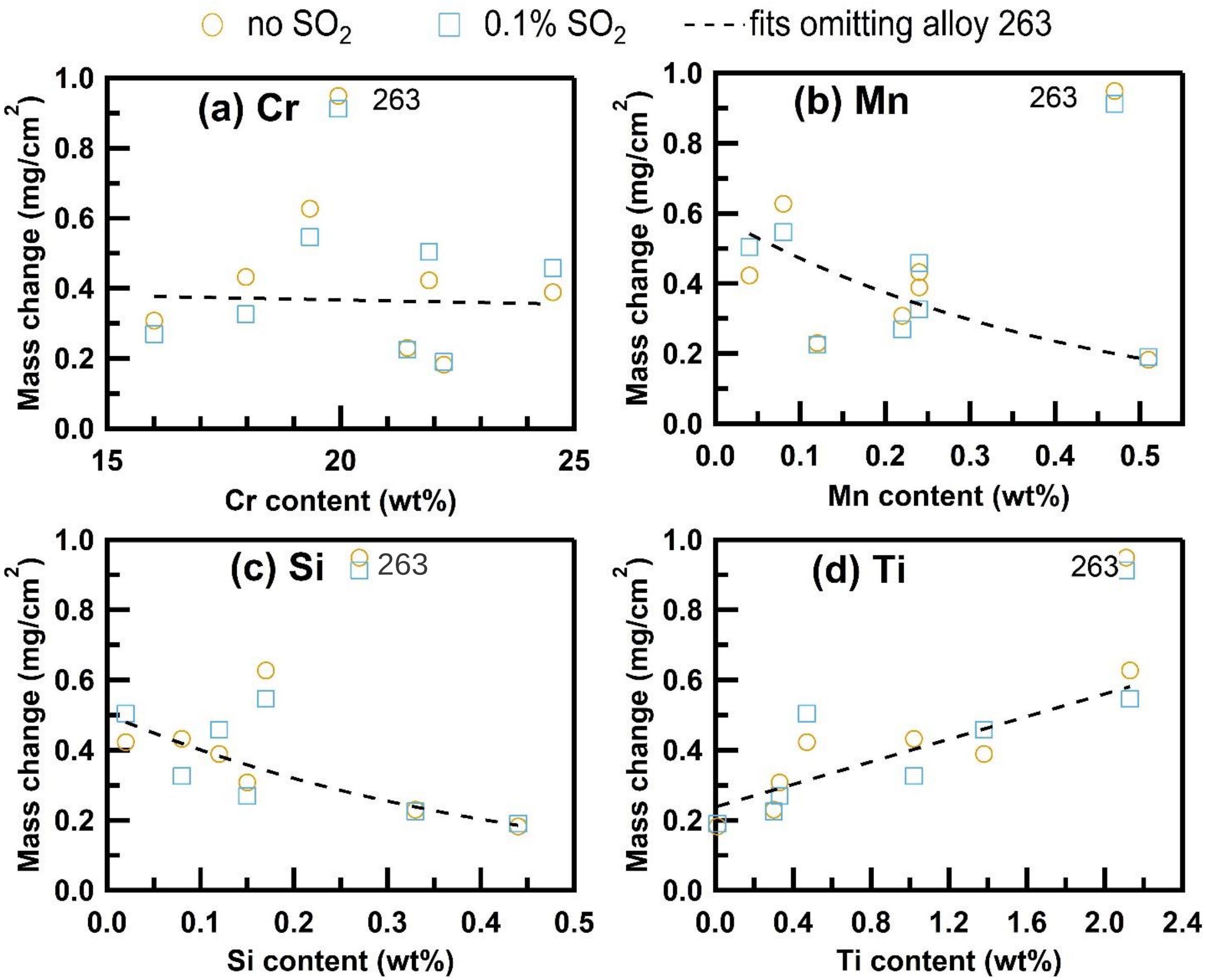


Oxide nodules rich in Ni/Co/Mo observed occasionally for alloy 263.

Effect of minor elements on chromia formation/growth (750 °C)

NATIONAL ENERGY TECHNOLOGY LABORATORY

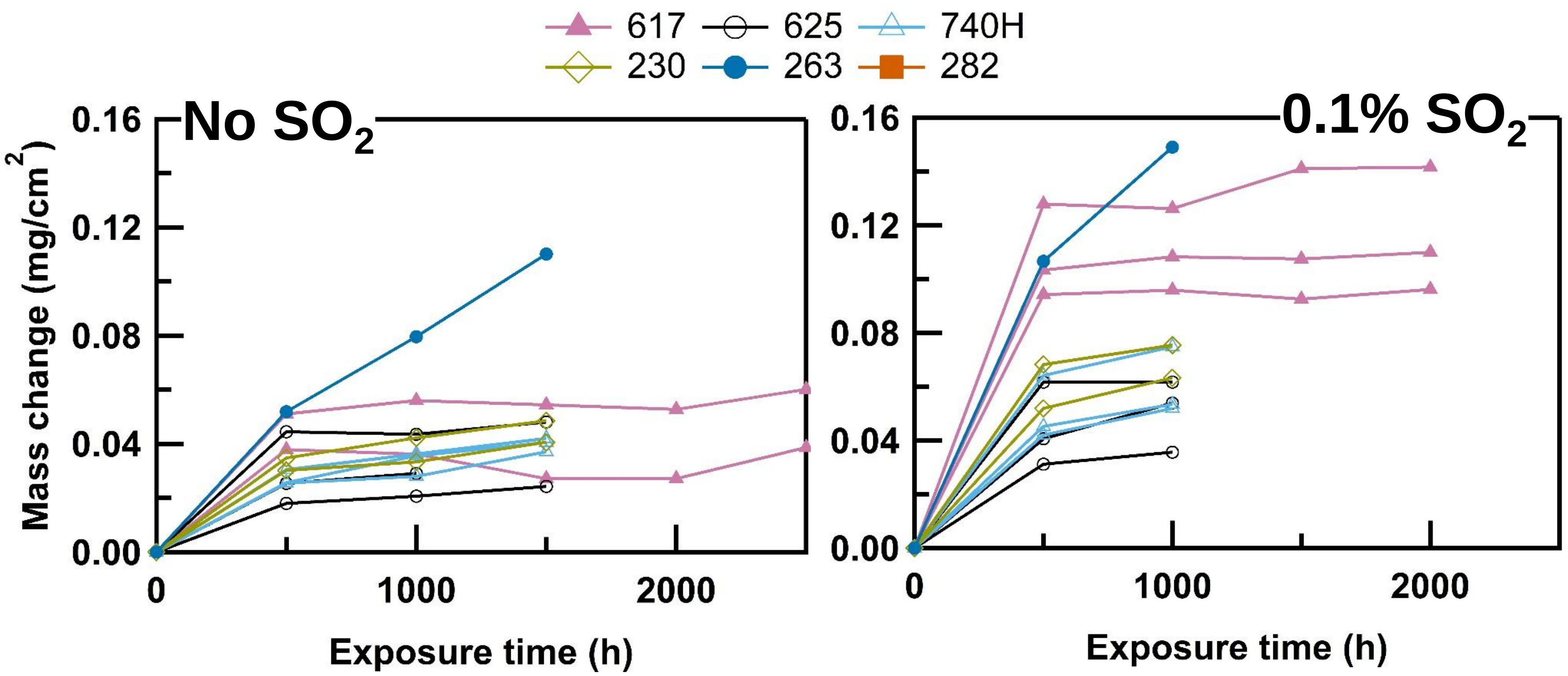
Mass change at 2500 h exposure time vs. alloy wt% Cr, Mn, Si, Ti



- No effect of Cr.
- **Decreased** mass gain with increased Si and Mn.
- **Increased** mass gain with increased Ti.
- High mass gain of alloy 263 associated with high Ti content, possibly also with high Mn content.

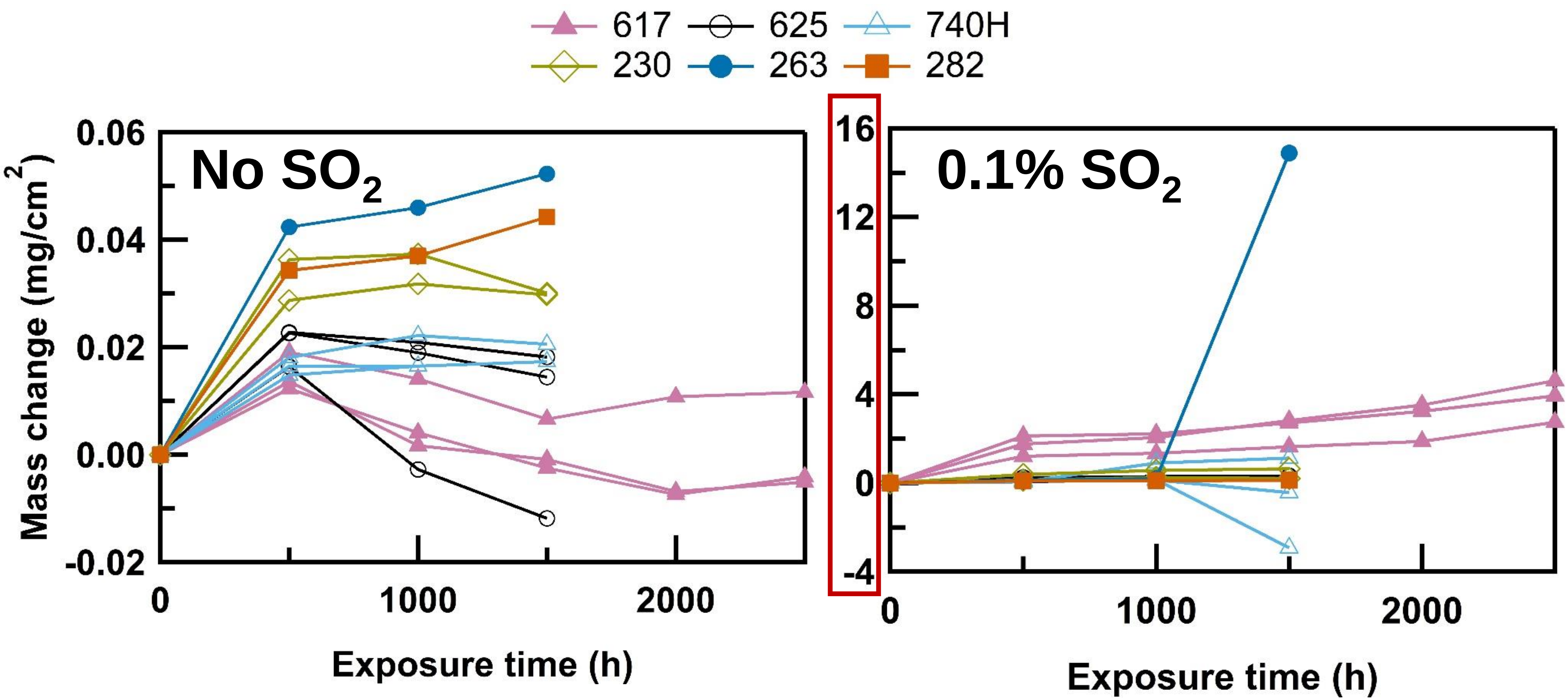
Oleksak et al., High temperature oxidation of Ni alloys in CO_2 containing impurities, *Corros. Sci.* (2019)

Mass change (650 °C)



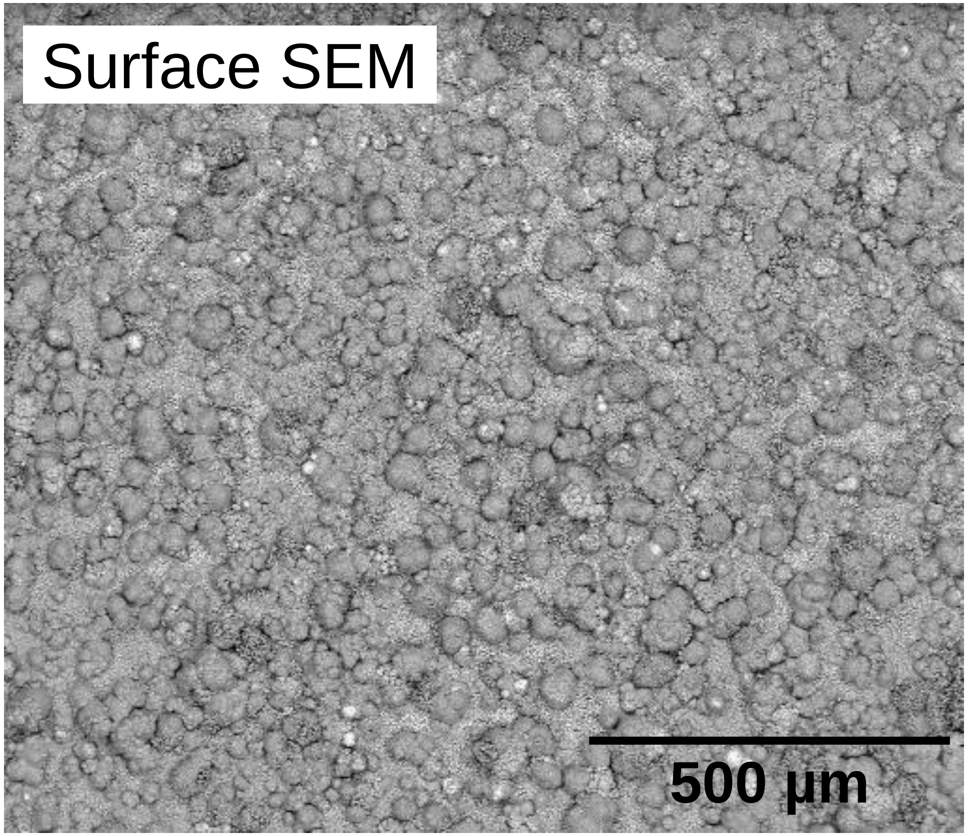
- Low mass gains and no significant effect of SO_2, similar to exposures done at 750 °C.
- XRD confirmed primary reaction product = chromia.

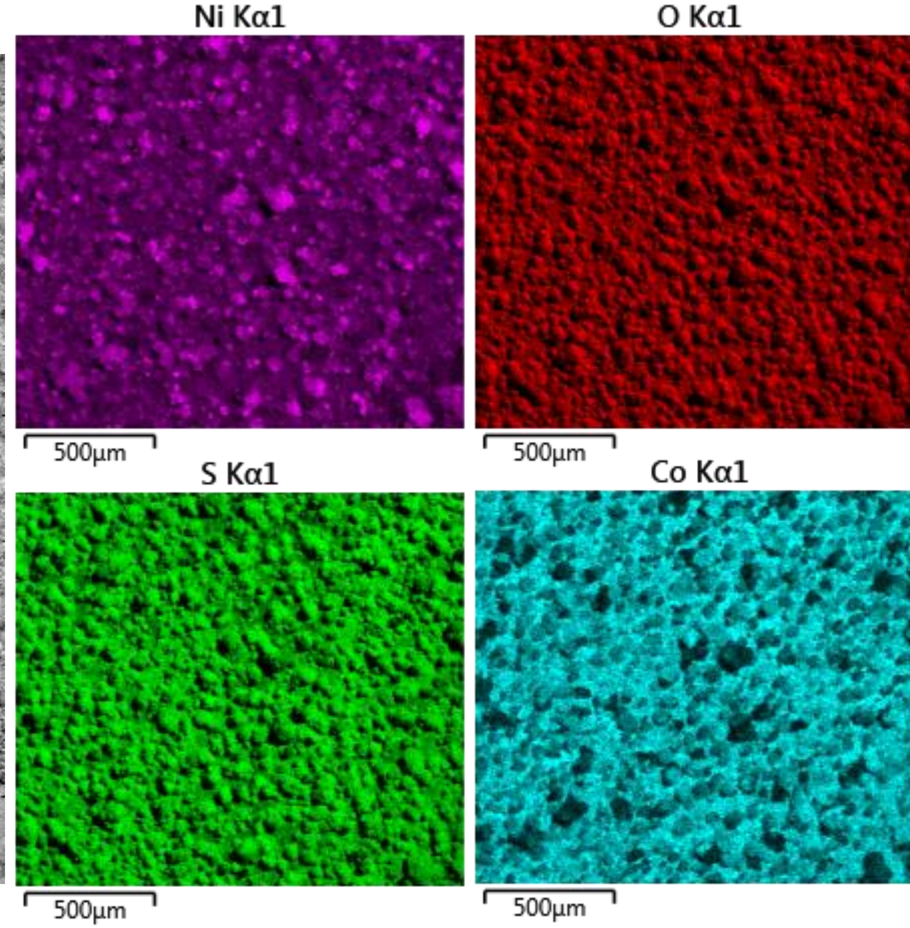
Mass change (600 °C)



- **Significantly higher corrosion rates in the presence of SO_2.**
- 2-3 orders of magnitude higher mass gains + spallation.

Alloy 617 (600 °C, 0.1% SO_2)

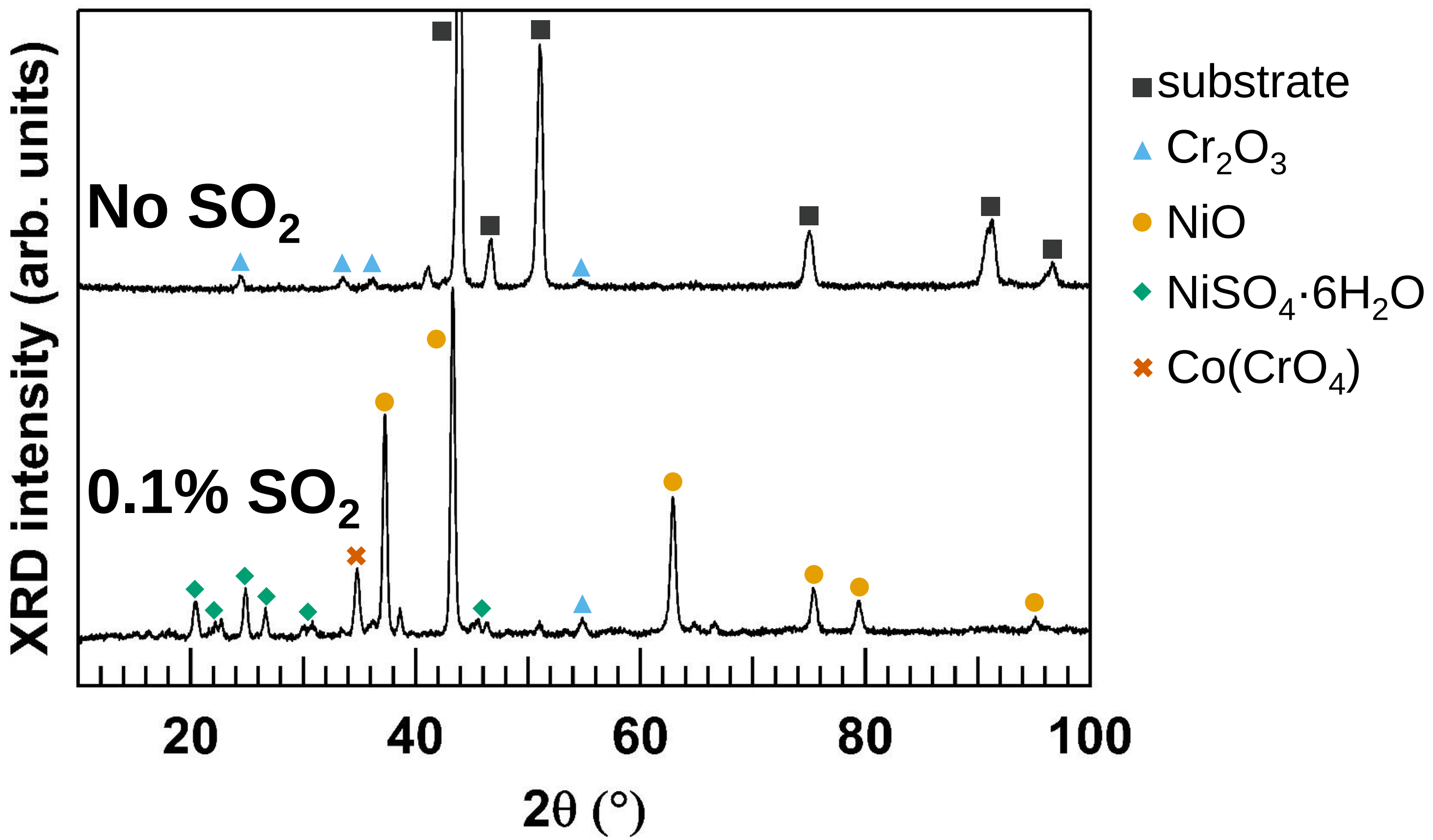




- Large surface nodules formed in presence of SO_2.
- EDS confirmed surface rich in Ni, Co, O, S.

XRD of alloy 617 (600 °C)

NATIONAL ENERGY TECHNOLOGY LABORATORY



- Only thin protective Cr_2O_3 layer formed in the absence of SO_2.
- Non-protective oxides and sulfates formed in SO_2 exposure.

Summary and Conclusions

- Several commercially available Ni-based alloys were exposed to high-temperature CO_2 containing H_2O, O_2, with and without SO_2 to simulate environments expected in direct-fired sCO_2 power cycles.

- At temperatures of 650-750 °C:
  - All alloys formed thin chromia scale leading to low corrosion rates.
  - Slightly increased corrosion for alloy 263, resulting from localized chromia failure which was correlated with increased Ti (and possible Mn) in the alloy.
  - No effect of SO_2.

- At temperature of 600 °C:
  - Thin chromia scales leading to low corrosion rates in absence of SO_2.
  - Significantly higher corrosion rates (2-3 orders of magnitude) in SO_2, characterized by growth of non-protective oxides and sulfates.

- Ni-based alloys are suitable in the absence of SO_2, however caution is needed when extrapolating corrosion performance to lower temperatures when SO_2 is present.