Corrosion Kinetics & Speciation of Alloy 625 and Haynes 244 in molten eutectic Na-Mg chloride salt

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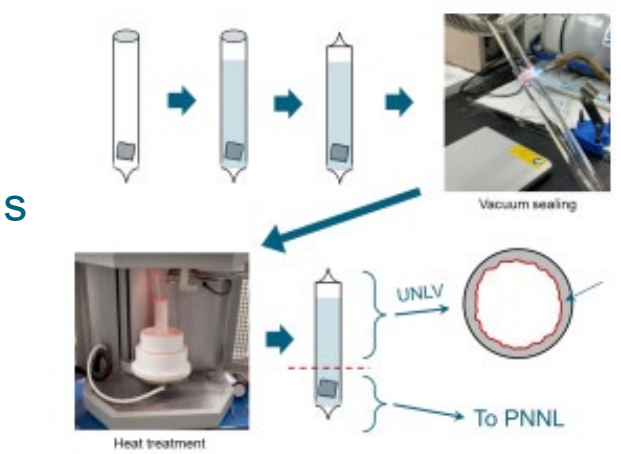
Introduction & Methods

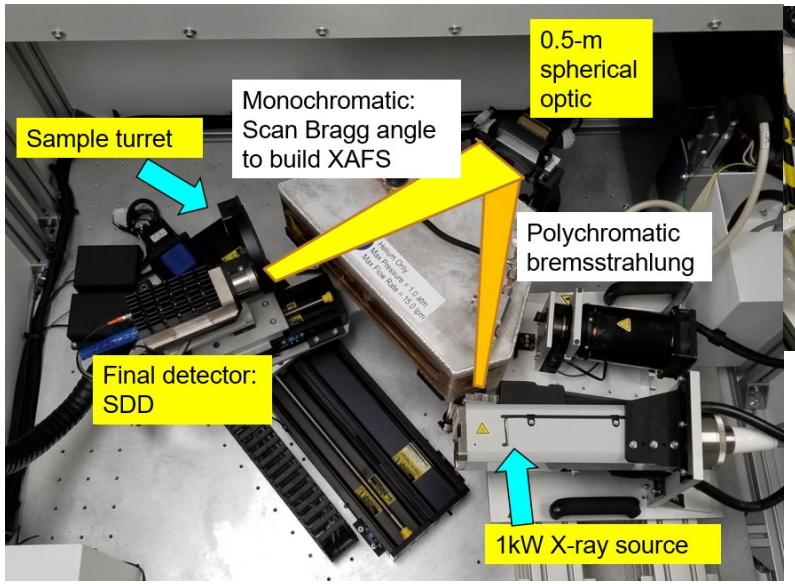
- Alloy corrosion mechanism under in operando Molten Salt Reactor (MSR) conditions (MSR) can be explained through the self diffusion of chromium and the subsequent formation of chromium chlorides at the alloy salt interface.
- While the thermodynamics of alloy corrosion is driven by redox potentials and salt impurities (moist, hydroxide, fission products such as Te), the corrosion kinetics can possibly be derived by information on chromium diffusivity and chromium species formation.
- Our overall objectives are to determine chromium diffusivity and activation energy, as well as corrosion product formation aka: chromium speciation.
- We performed static corrosion tests, using ampoules (Alloy 625, Haynes 244), filled with purified eutectic NaCl-$MgCl_2$ salt from TerraPower, sealed in silica overpack, and placed in a furnace at typical MSR temperatures (550 °C & 650 ºC or 700 °C & 850 °C) for various times.
- Alloy foils were corroded for chromium speciation.
- After heat treatment the corrosion layers will be analyzed by SEM-EDS and corroded alloy foils by XAS.

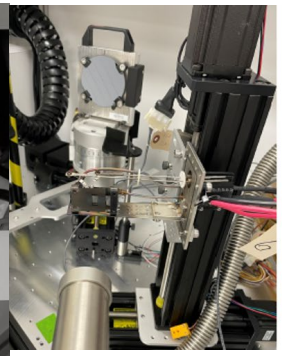


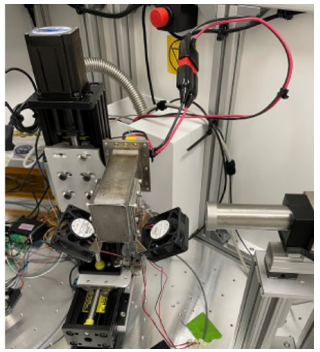
3 – SS316, vac. seal, 650C, 100d
4 – I-625, vac. seal, 650C, 30d
5 – I-625, 0.5 atm Ar seal, 650C, 30d
7 – I-625, 0.5 atm Ar seal, 650C, 100d

Proof of Concept: EasyXAFS 300 for speciation of corrosion products by EXAFS and XANES

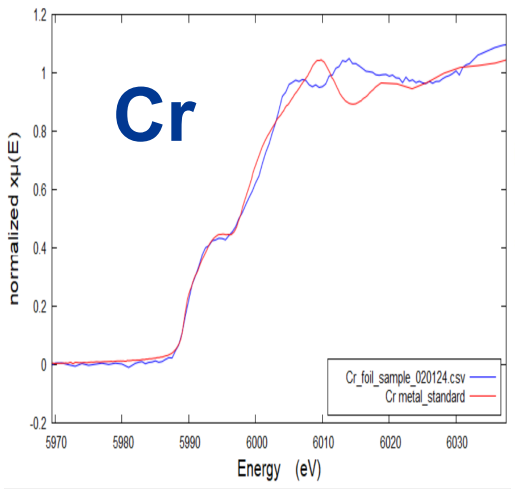
- Stainless steel foil SS316, thickness 10-20 μm (MTI Corporation).
- XAS measurements of SS316 foil compared with pure standards and metal foils of 10 μm Cr, Fe, and Ni.

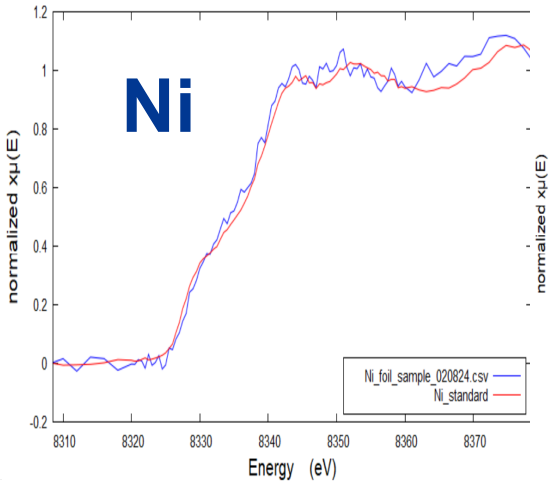


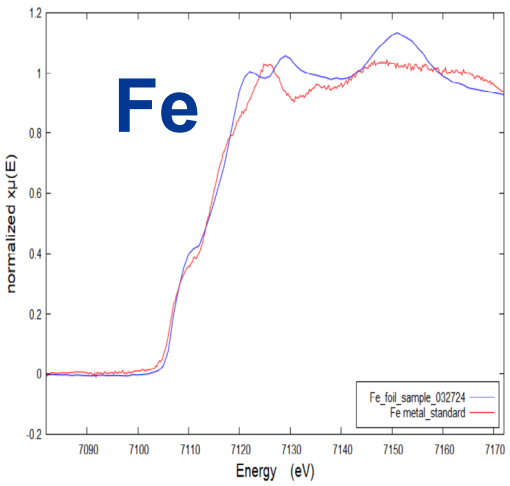




Foils vs. Standards

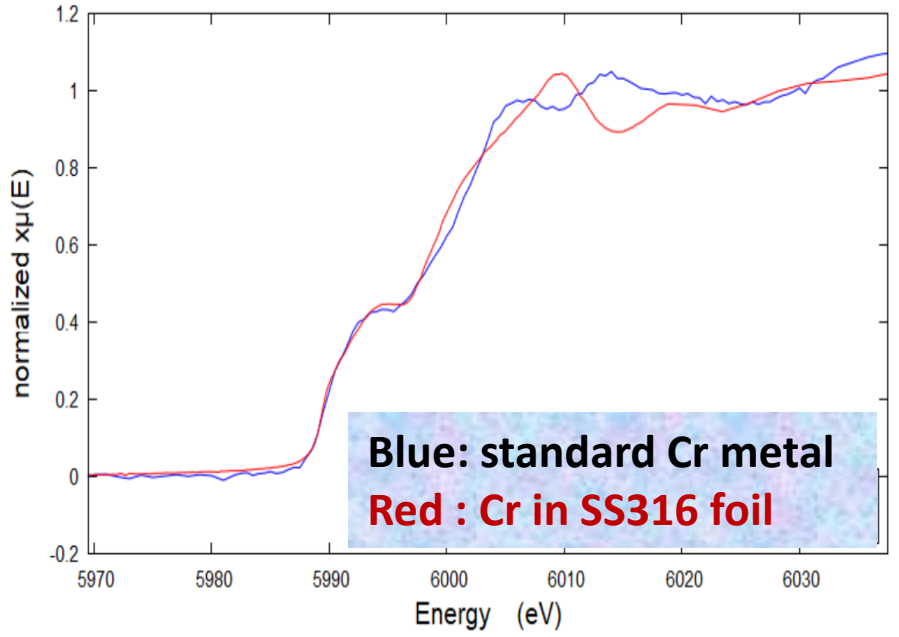






EasyXAFS300 for Cr-speciation: proof of concept

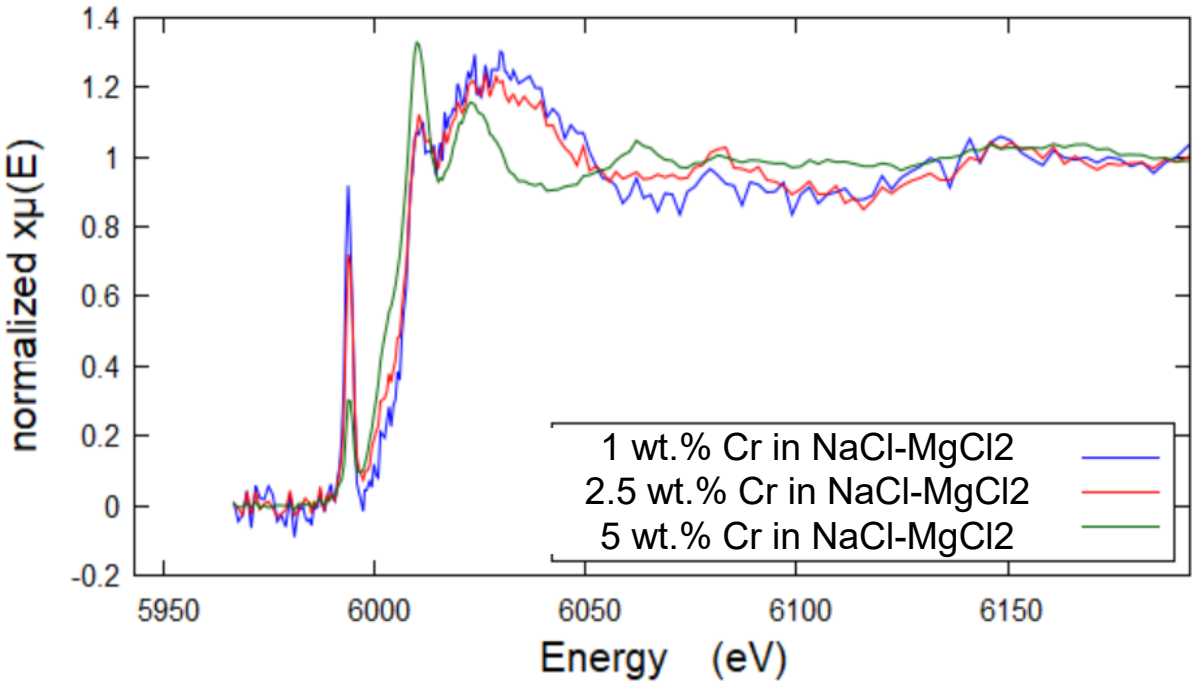
Cr K-edge XAFS measurements in solid metal



XAFS indicates different local environment of Cr in SS316 than in pure metals

- Structural changes are observable

Cr K-edge XAFS measurements in eutectic $NaCl-MgCl_2$

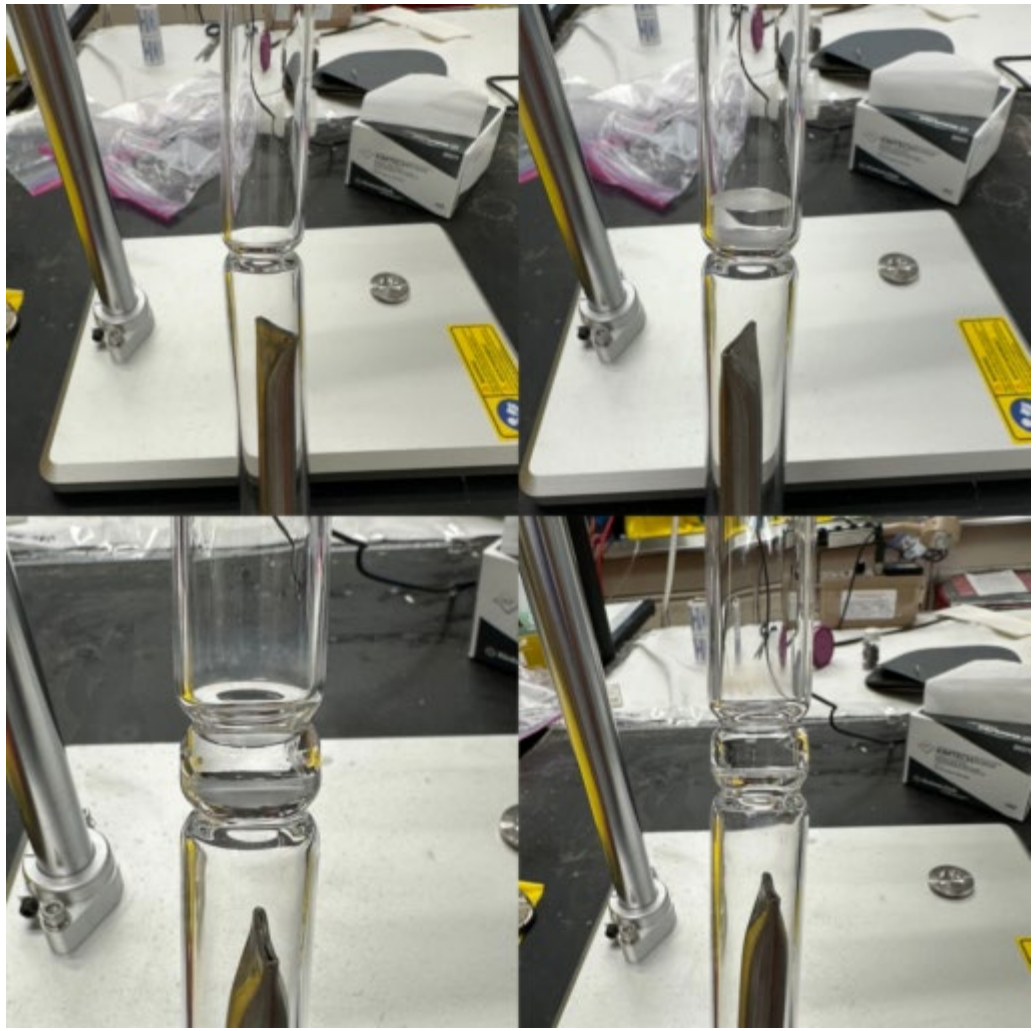


XANES: determination of Cr oxidation state is possible

- 1 and 2.5 wt% Cr samples: mostly Cr(VI)
- 5 wt% Cr sample: about equal mixture of Cr(III) and Cr(VI)

Fabrication of diffusion specimens

- Diffusion specimens of SS316 and Alloy 625 have been fabricated to determine chromium diffusivity and speciation of corrosion products.
- Alloy foils with NaCl-$MgCl_2$ salt are sealed in SS316 and Alloy 625 ampoules, which are then sealed in silica tubes, to further undergo heat treatment at 550 °C and 650 °C.

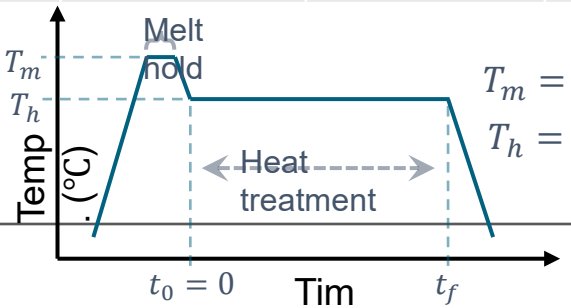


Heat treatment of SS316 & Alloy 625 specimens

10 Ampoules sealed inside Ar Glovebox

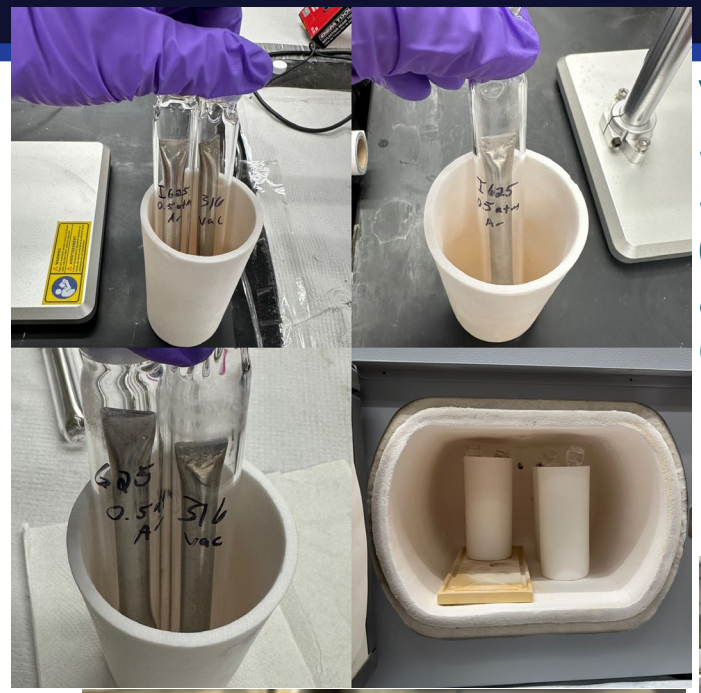
- Foils inserted near bottom of ampoules.
- 6 × Alloy 625 → Two temperatures (550 °C, 650 °C); Three heat treatment times.
- 4 × SS 316 → Two temperatures (550 °C, 650 °C); Two heat treatment times.

	1 mo.	2 mo.	4 mo.	6 mo.*
550 °C	Inconel 625 Inconel 617 SS316	Inconel 625 Inconel 617	Inconel 625 Inconel 617 SS316	Inconel 625 Inconel 617
650 °C	Inconel 625 Inconel 617 SS316	Inconel 625 Inconel 617	Inconel 625 Inconel 617 SS316	Inconel 625 Inconel 617



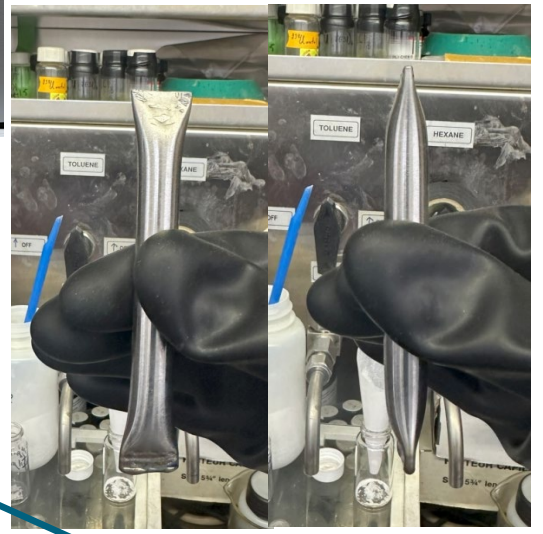
$T_m = 825$ °C
$T_h = 650$ °C

* 2024 → 2025



Vacuum-Sealed Ampoules in Silica Tubes. (a) I-625 & SS316 4-mo. crucible; (b) I-625 2-mo. crucible; (c) I-625 & SS316 1-mo. crucible; (d) Crucibles in furnace

Sealed Alloy 625 Ampoules



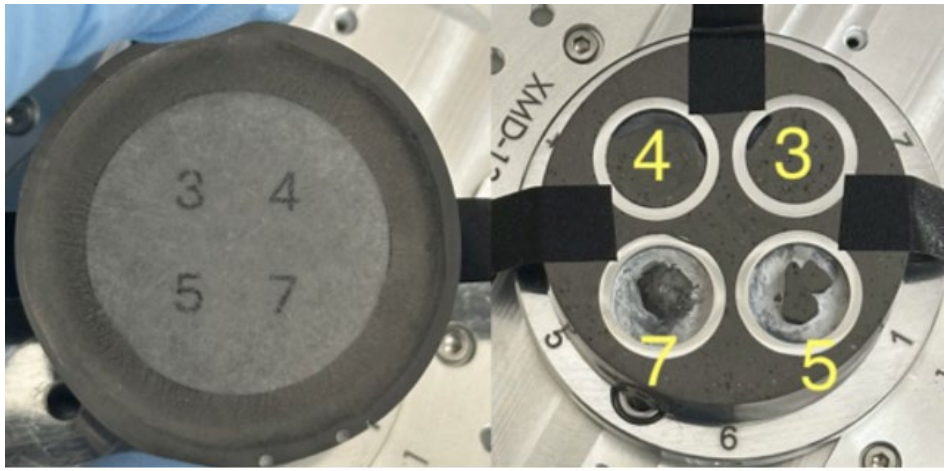
SS 316

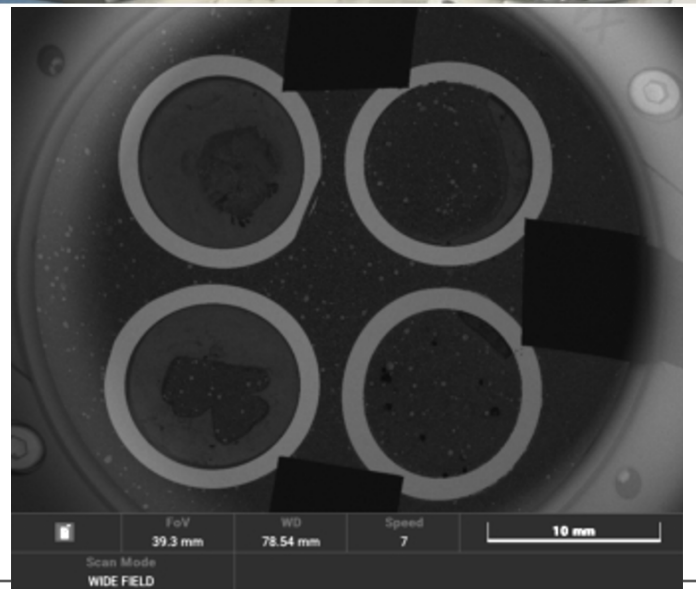
Inconel 625

Cross-sectional corrosion specimens for analysis

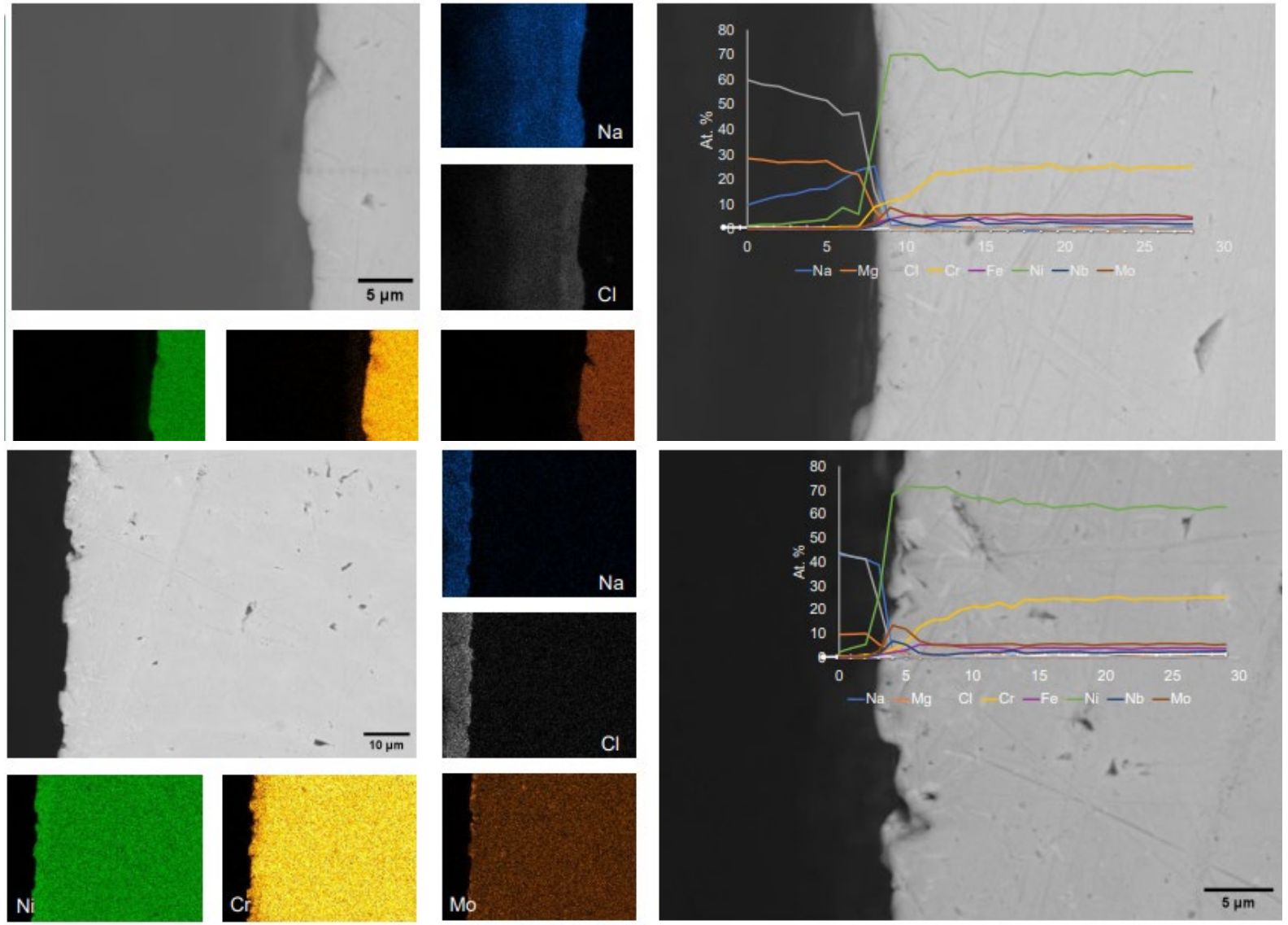
SEM Analysis of Alloy 625 and SS316 after 30 days and 100 days at 650°C in Na-Mg-Chloride

- Cross-sectional samples were embedded, ground and polished to mirror finish (< 1µm).
- Samples 5 and 7 were backfilled with 380 Torr Argon before sealing the ampoules.
- Low-resolution backscatter-electron image of four samples is shown as overview.





Mapping & quantitative line-profiles of Alloy 625

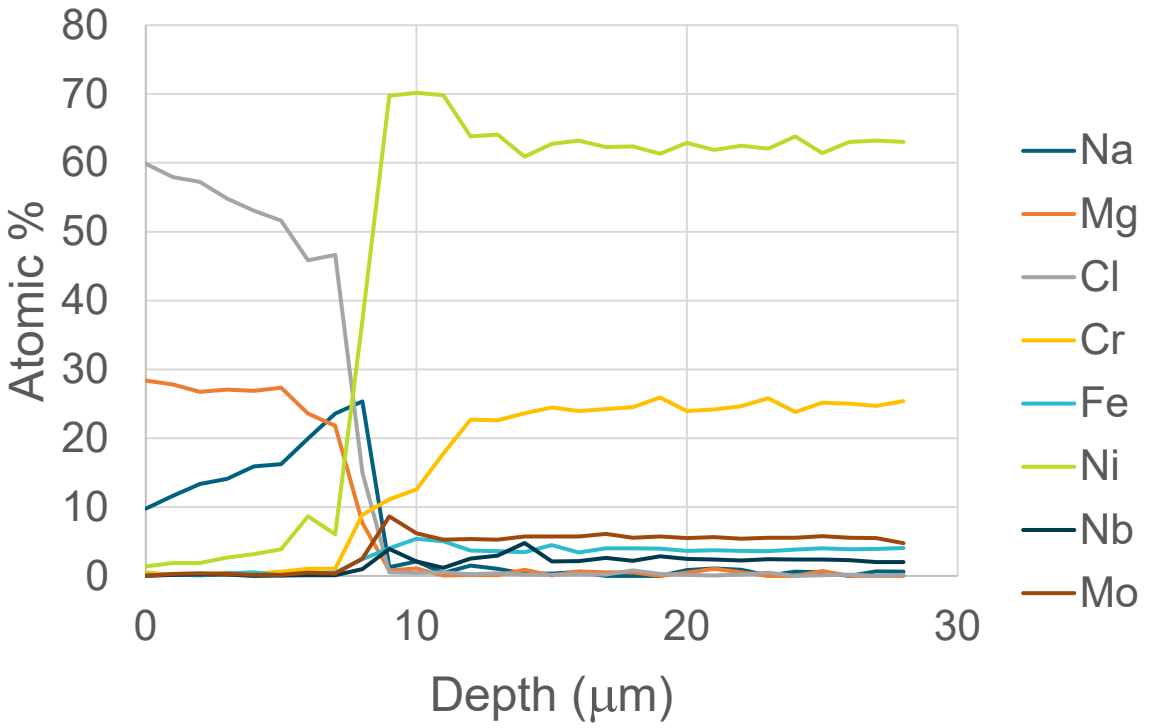


SEM Backscattered-electron image and EDS elemental color map.

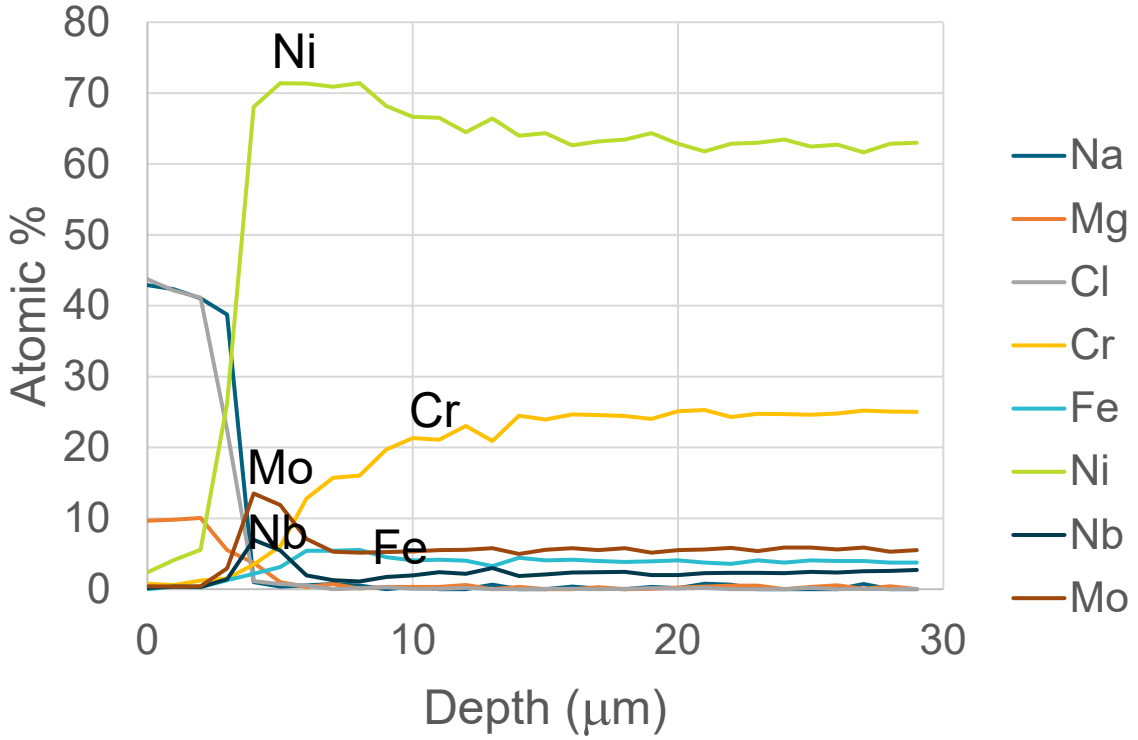
SEM Backscattered-electron image and EDS Quantitative Linescan.

- After 30 days at 650 ºC in eutectic NaCl-$MgCl_2$
- After 100 days at 650 ºC in eutectic NaCl-$MgCl_2$

Alloy 625 - EDS-based line profiles

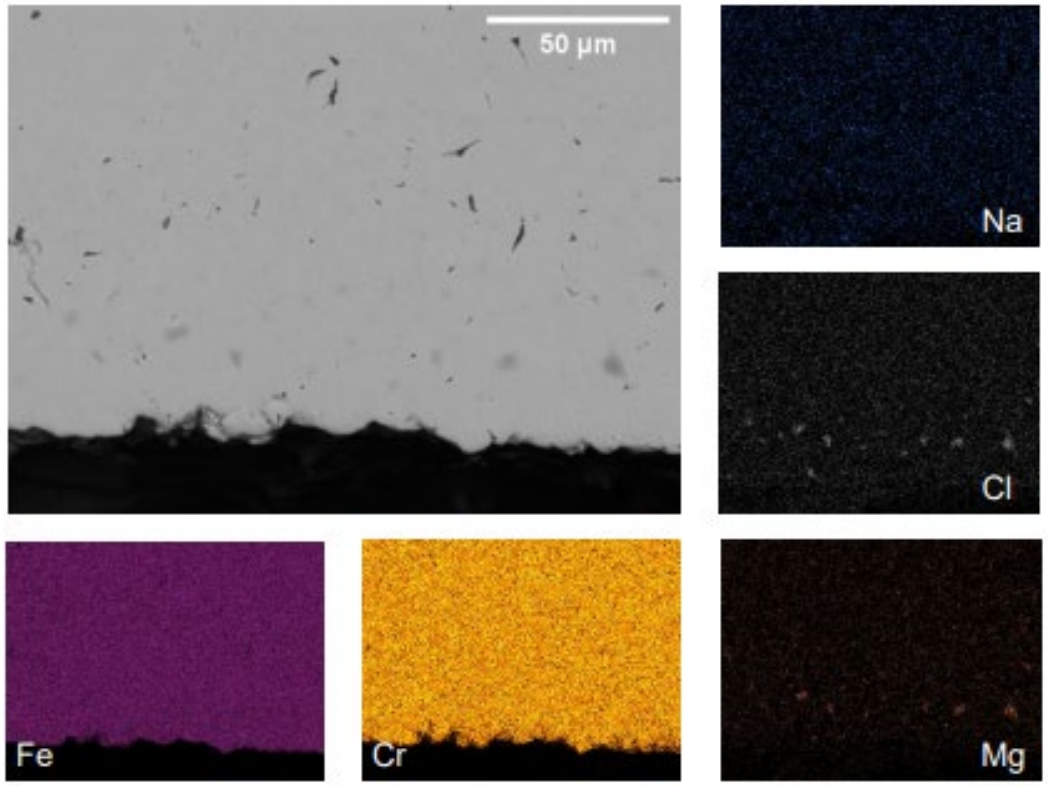


EDS Quantitative Line scan of salt-metal interface of Inconel 625, heat treated for 30 days at 650 °C.

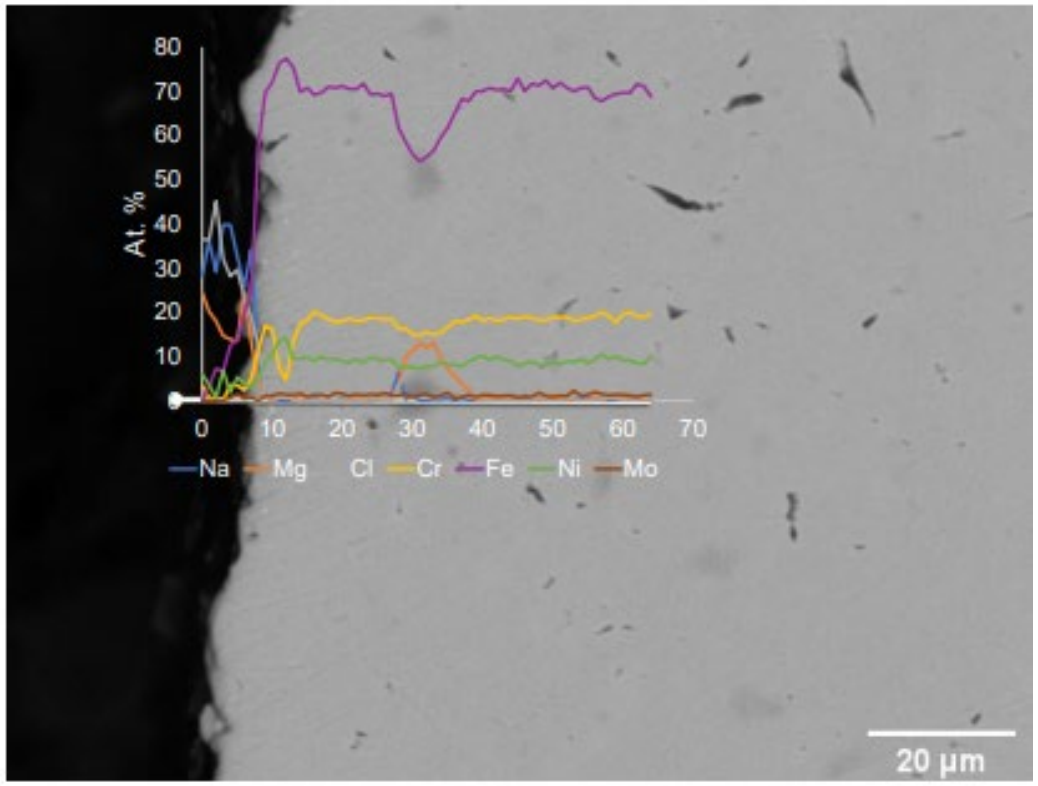


EDS Quantitative Lines can of salt-metal interface of Inconel 625, heat treated for 100 days at 650 °C.

EDS-based line-profiles of SS316



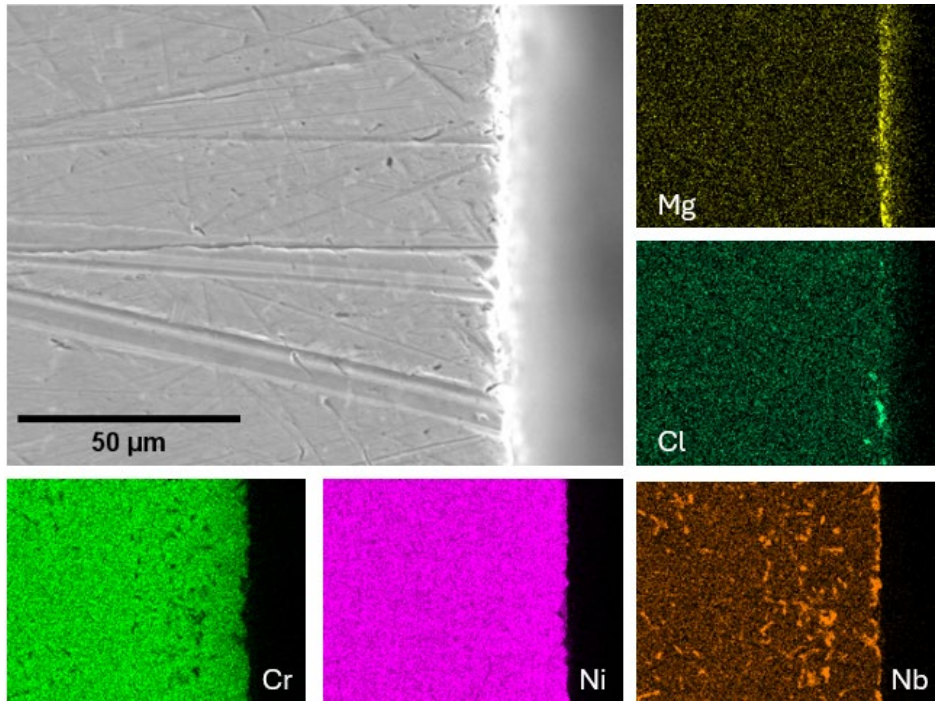
SEM Backscattered-electron image and EDS elemental color map.



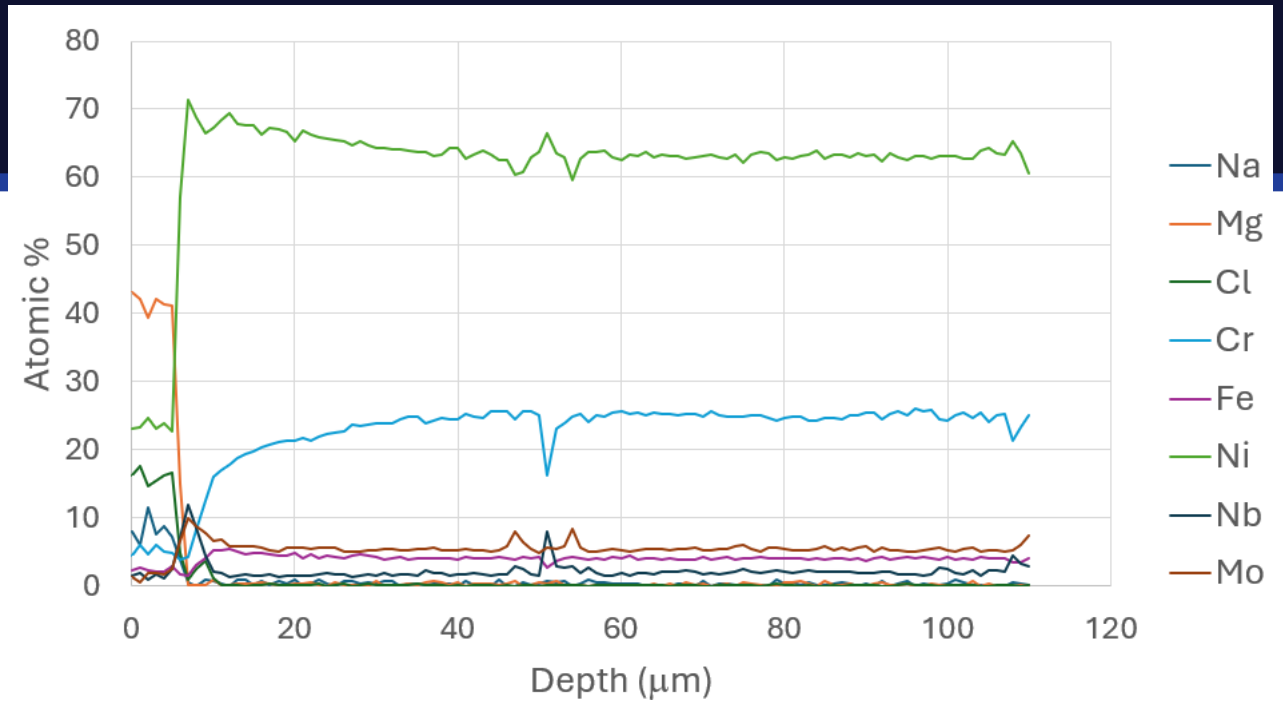
SEM Backscattered-electron image and EDS Quantitative Linescan.
(*NOTE – Linescan image rotated 90º CW from color map image.*)

Stainless steel SS316 after 30 days at 650ºC in eutectic $NaCl\text{-}MgCl_2$

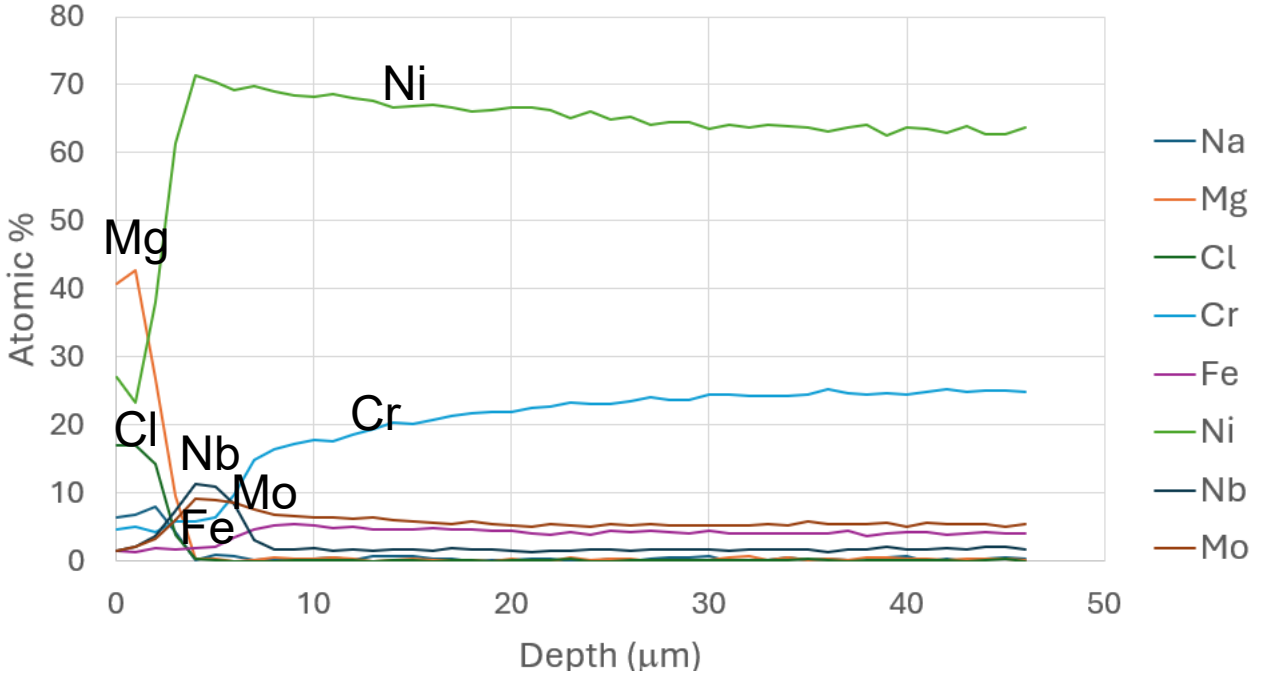
Alloy 625 Corrosion at 850 °C



Elemental Map of Alloy 625 exposed to Na-Mg-Cl at 850 °C for 10 days



Elemental EDS-based line-scans of Alloy 625 exposed to Na-Mg-Cl at 850 °C for 10 days



Chromium diffusivity of Alloy 625

Line Scan #	Chromium Diffusion Coefficient
Line scan 1	1.8 10^{-17} m^2/s
Line scan 2	2.7 10^{-17} m^2/s
Line scan 3	4.4 10^{-17} m^2/s
Average	**3.0 (±1.3) 10^{-17} m^2/s**

T (°C)	T (K)	1/T (1/K)	D (m^2/s)
650	923	0.01083	2.8×10^{-18}
850	1123	0.00089	3.0×10^{-17}

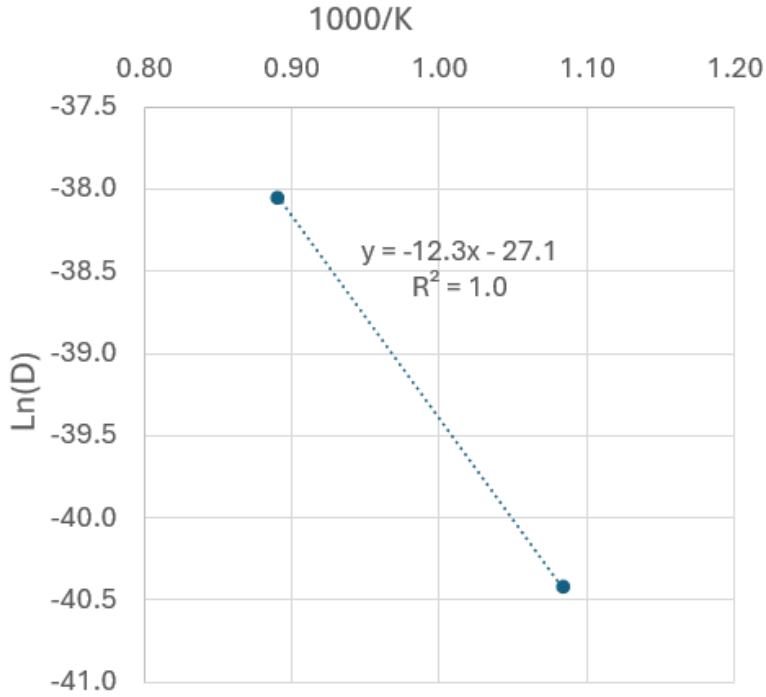
Activation Energy for chromium self diffusion in Alloy 625

Arrhenius Equation

$$D = D_0 e^{-\frac{E_a}{kT}}$$

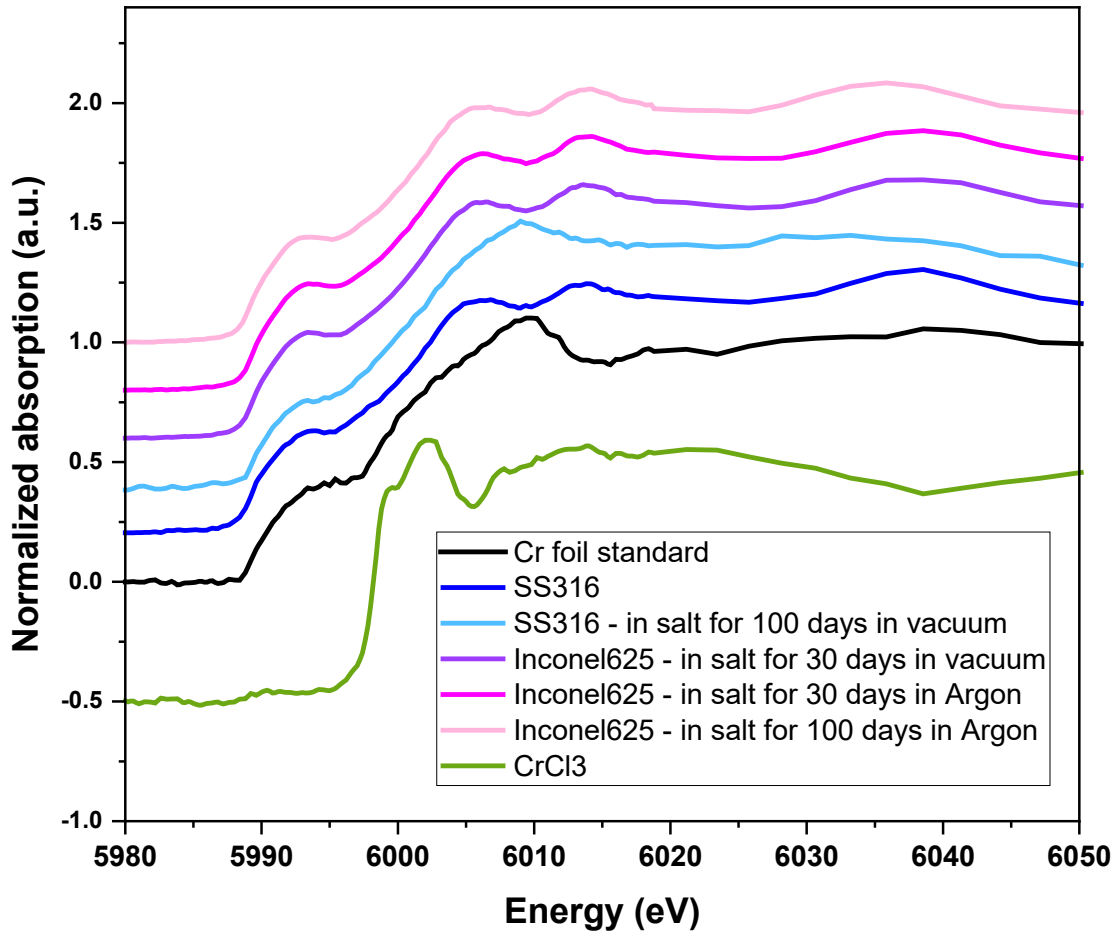
$$\ln D = -\frac{E_a}{k}\frac{1}{T} + \ln D_0$$

E_a = Activation Energy



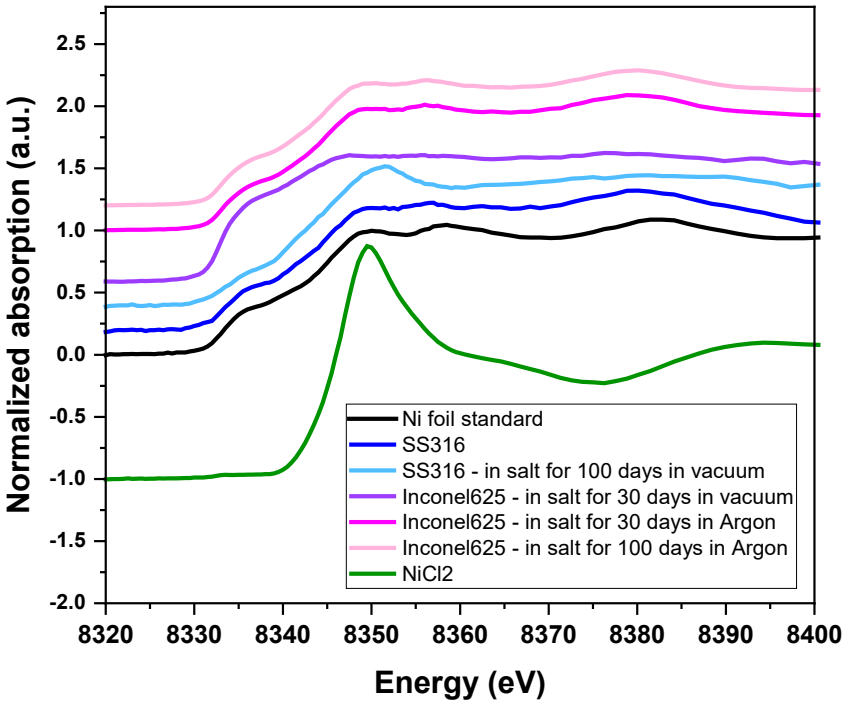
E_a	1.7×10^{-19} J	1.1 eV	102 kJ/mol

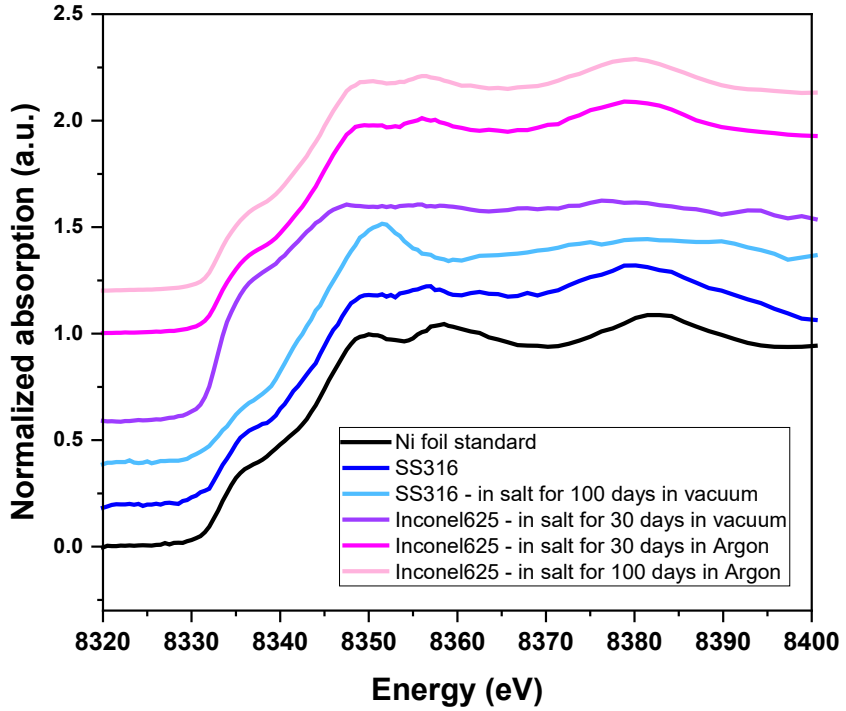
Cr K-Edge XANES of corroded SS316 and Alloy 625 Foils



- X-ray absorption spectroscopy with Cr K-edge XANES on corroded foil specimens of SS316 and Alloy 625 was unsuccessful so far in determining corrosion product speciation.

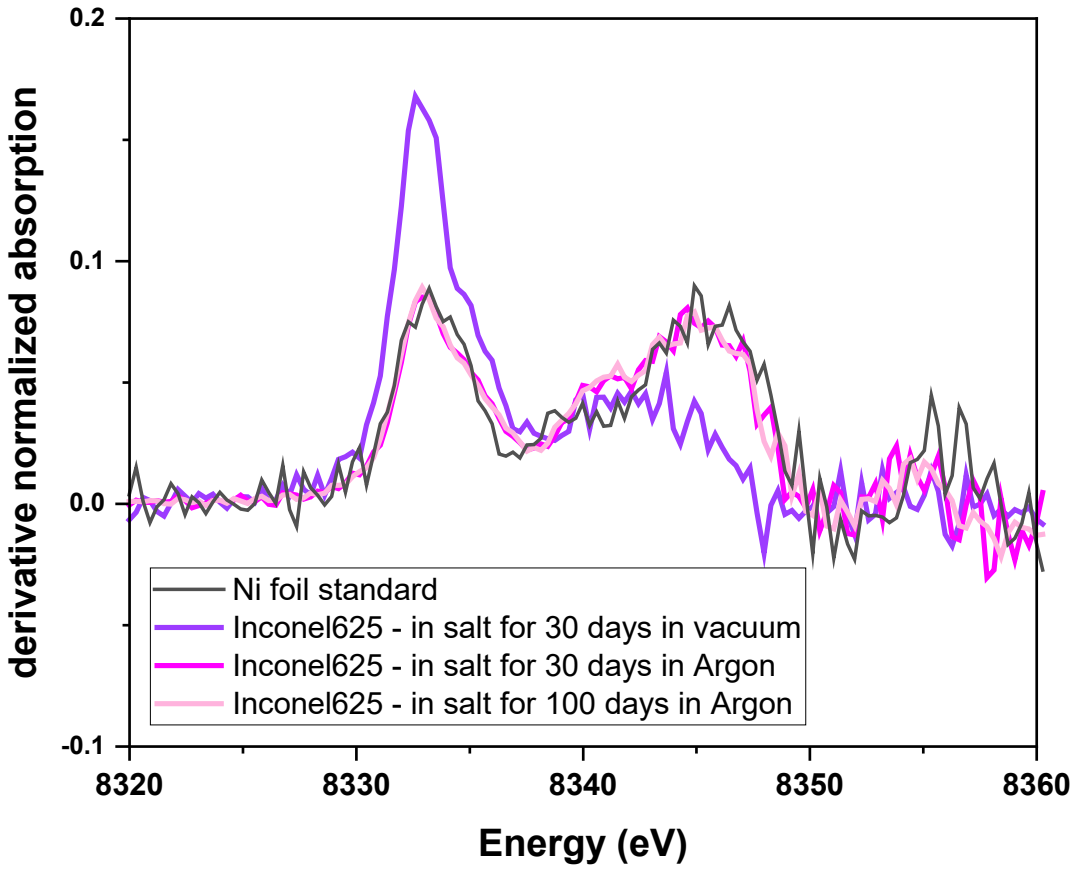
Ni K- Edge XANES of corroded SS316 and Alloy 625 Foils





- Ni K-edge XANES shows an indication of $NiCl_2$ formation on a SS316 foil specimen after 100 days at 650 °C in molten chloride salt.

Ni K- Edge XANES of corroded Alloy 625 Foils



- The first derivative of the normalized absorption spectra did not confirm the presence of oxidized nickel species.
- The absorption spectrum of Alloy 625, however, shows different intensity distribution, especially at 8,333 eV, and a peak shift at 8,352 eV.

Conclusions for Alloy 625

Corrosion of Alloy 625 in eutectic Na-Mg-Chloride at 650 °C and for 30 days and 100 days and 850 °C for 10 days.

- Under in-operando conditions, chromium as alloying constituent is active and chromium chloride formation at the alloy salt interface results in a 15-20 μm thick corrosion affected zone.
- After corroding Alloy 625 for 30 and 100 days at 650 °C the corrosion affected zones are nearly identical in width, but the total yield of chromium depletion increased with duration.
- Elemental line profiling indicates a 2-4 μm thick surface layer enriched in nickel, molybdenum, and niobium.
- With ongoing chromium depletion, corrosion could intensify because of dealloying and weakening grain boundary strength.

Conclusions for Alloy 625

Corrosion of Alloy 625 in eutectic Na-Mg-Chloride at 650 °C and for 30 days and 100 days and 850 °C for 10 days.

- The self-diffusion coefficient for chromium was determined to 3.0 (±1.3) 10^{-17} m^2/s and the activation energy to 102 kJ/mol. However, standard deviation were high and corrosion tests at additional temperatures are needed.
- Cr K-edge XANES on corroded foil specimens of alloy 625 was unsuccessful in determining corrosion product speciation.
- Ni K-edge XANES, however, shows an indication of $NiCl_2$ formation on a SS316 foil specimen after 100 days at 650 °C in molten chloride salt.

Future Work

- Corrosion tests using Haynes 244 ampoules. For now, only Haynes 244 sheet material was tested.
- Corrosion in binary NaCl-UCl_3 salt is initiated.

Temperature	1 month	2 months	9 months
750 °C	Haynes 244	Haynes 244	Haynes 244
850 °C	Haynes 244	Haynes 244	Haynes 244

Acknowledgement

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