The critical role of alloy chemistry and microstructure on the corrosion behavior and mechanical properties of structural alloys in molten halide salts

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AMMT ADVANCED MATERIALS AND MANUFACTURING TECHNOLOGIES

U.S. DEPARTMENT of ENERGY | Office of Nuclear Energy

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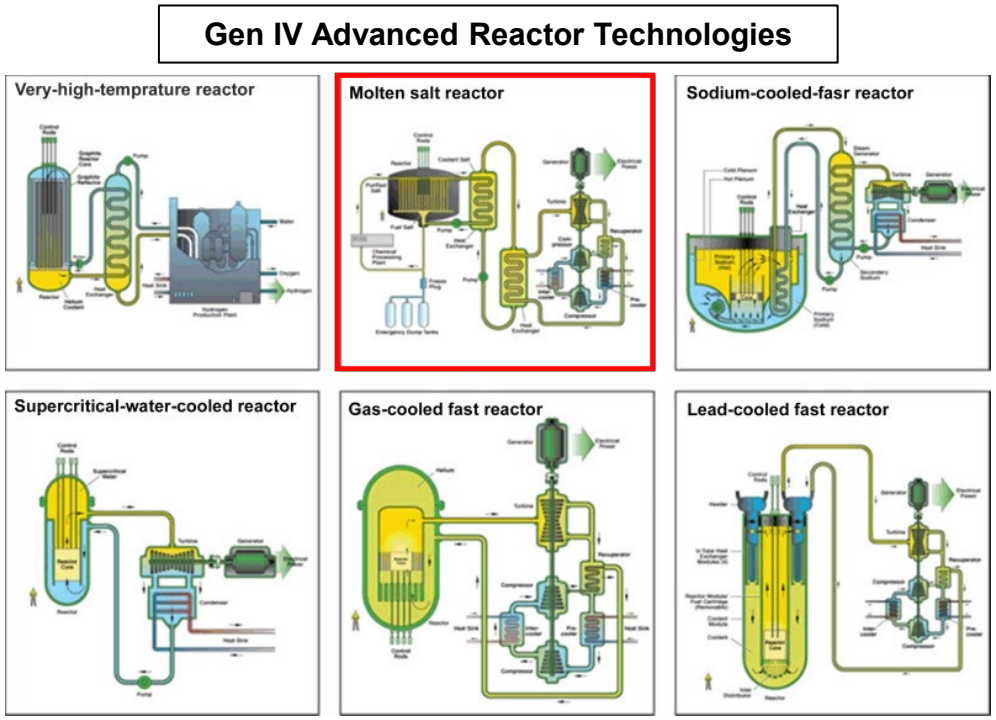
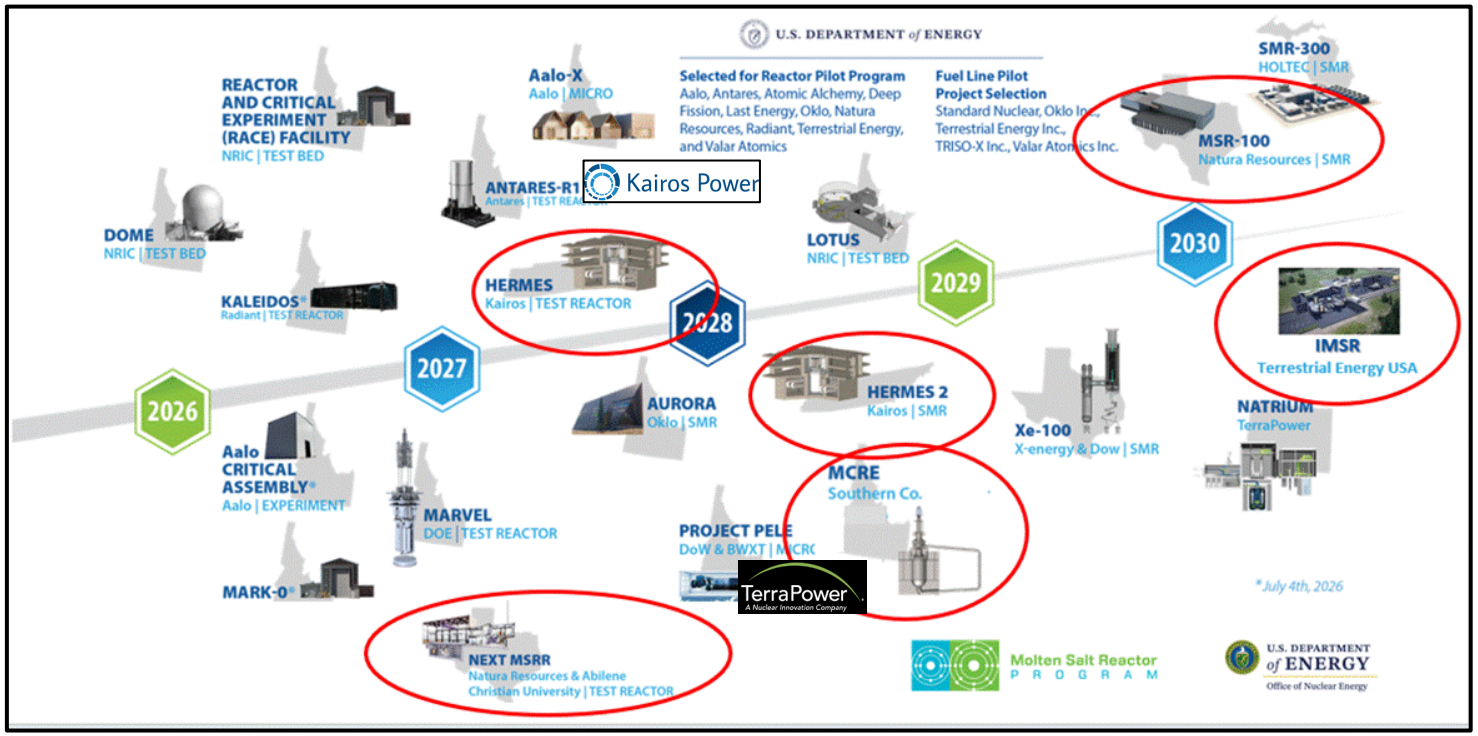
Worldwide efforts to push molten salt reactors toward demonstration and deployment are primarily driven by extensive legacy knowledge



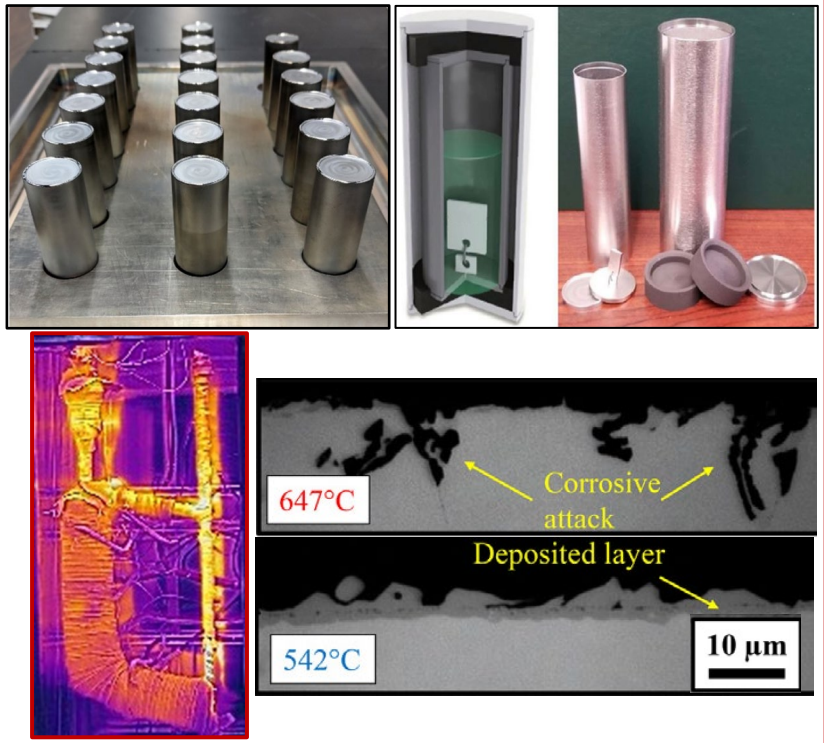


- Impact of long-term operation in different salts?
- Role of impurities?
- Material degradation due to coupled extremes of stress, corrosion and irradiation?
- Enough information to predict material performance over reactor operating lifetimes of 30-50 years?

MSR roadmap image courtesy: Patricia Paviet

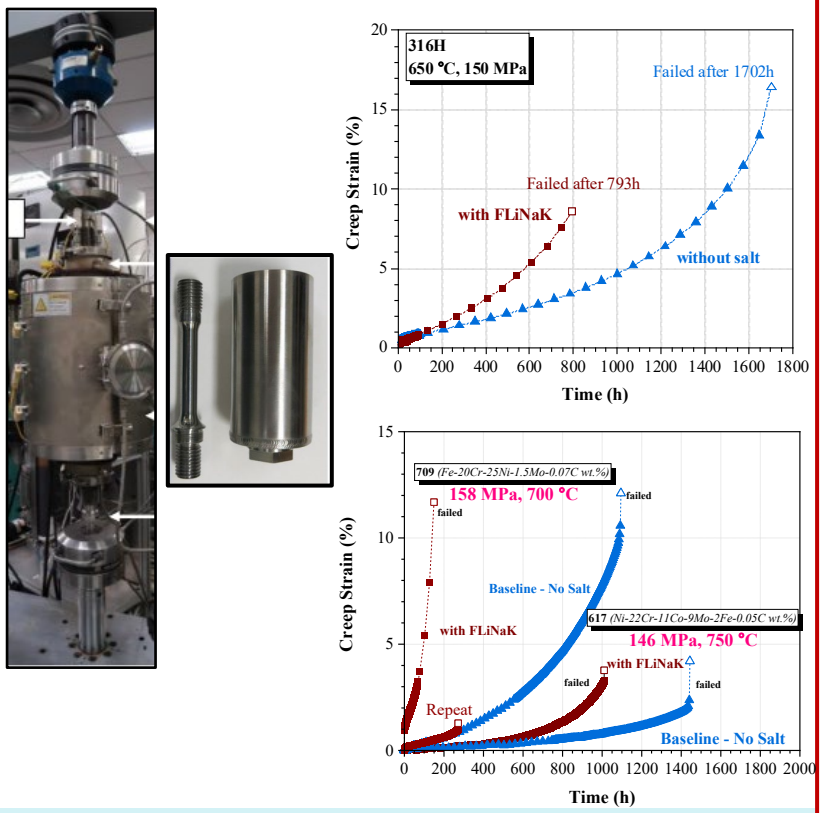
ORNL has been providing critical data and validated predictive models to evaluate structural materials compatibility and lifetime in molten halide salts

Purification+ Corrosion Testing



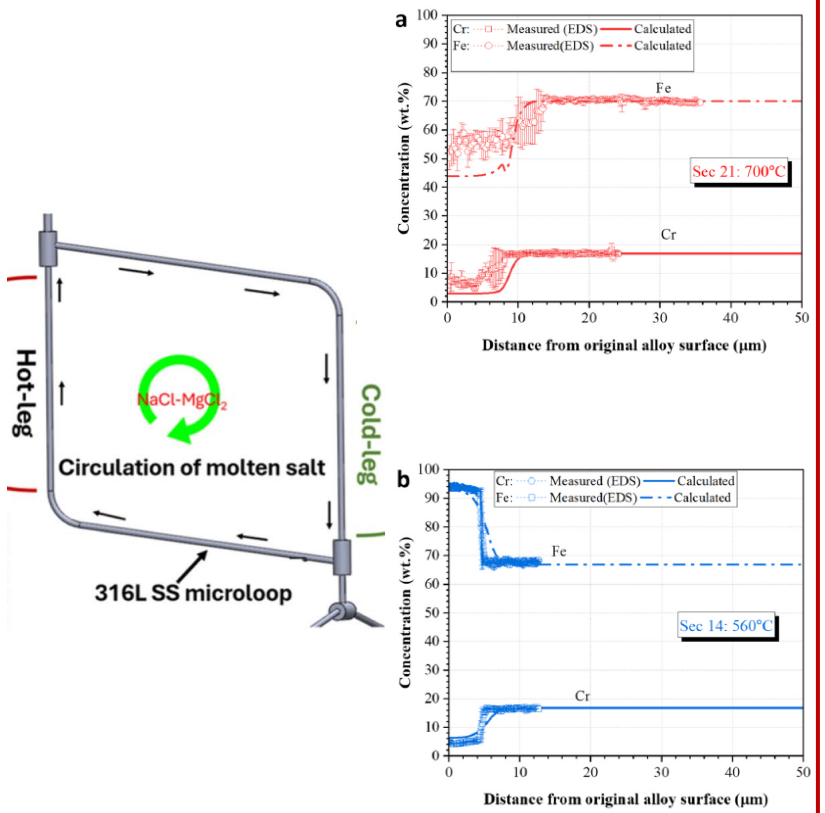
- Static + flowing testing
- Impact of salt chemistry
- Allowable impurities\Redox control
- Long-term material behavior

Combined effects testing



- Mechanical testing in molten salts[1]
- Tensile, creep and fatigue

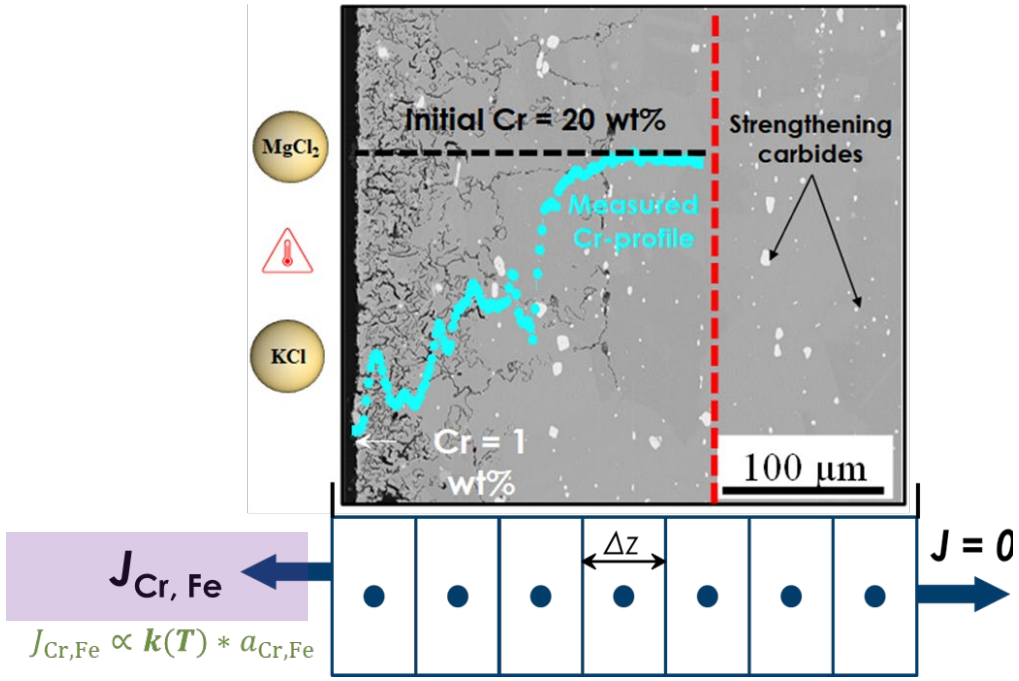
Predictive modeling

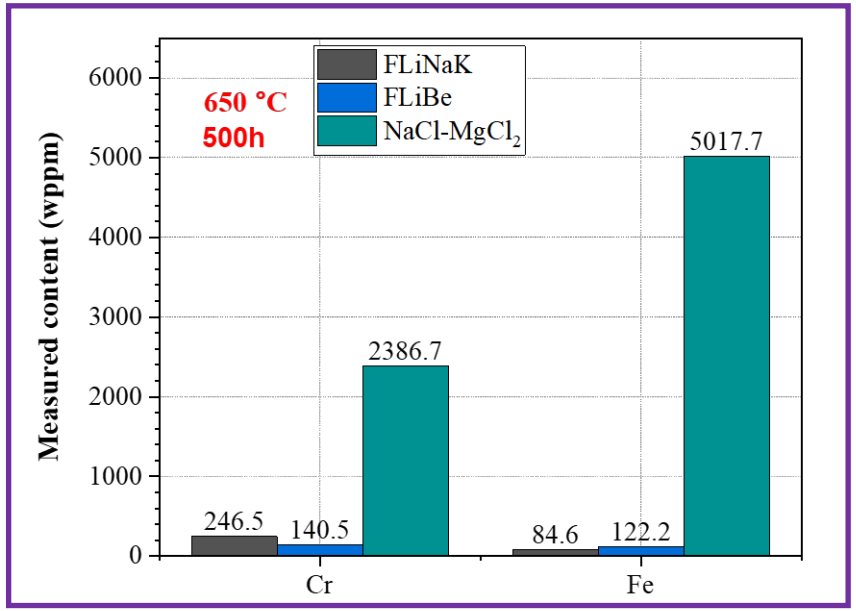


- Accurate prediction of material behaviour during static[2] and flowing[3] testing

[1] Pillai et al. , ASM-EPRI, 2024
[2] Pillai et al. , JOM, 2023
[3] Sure, Pillai et al. , Corrosion Science, 2025

Coupled thermodynamic-kinetic modeling method validated for multicomponent and multiphase alloys with long term static and flowing salt tests





- Using measured concentrations of pure elements after exposure in purified halide salts
- Empirical description of grain boundaries
- Model commercial high temperature alloys
- 30,000h simulation in < 1 week

Calculate thermodynamic equilibrium between salt and alloy*

- Loss of alloying constituents
- Impact of impurities
- Identify optimum redox additions

- Pillai et al., JNM, 546, 2021
- Pillai et al., JOM, 75, 2023
- Sure et al., Corr. Sci. 258, 2025

* FactSage (Pure Substances & SGTE Databases)

A couple of key examples were selected to demonstrate role of alloy chemistry and microstructure on the corrosion behavior and mechanical properties of structural alloys in molten halide salts

Interplay between microstructure and salt chemistry in governing corrosion of alloy 244 in molten chloride salts

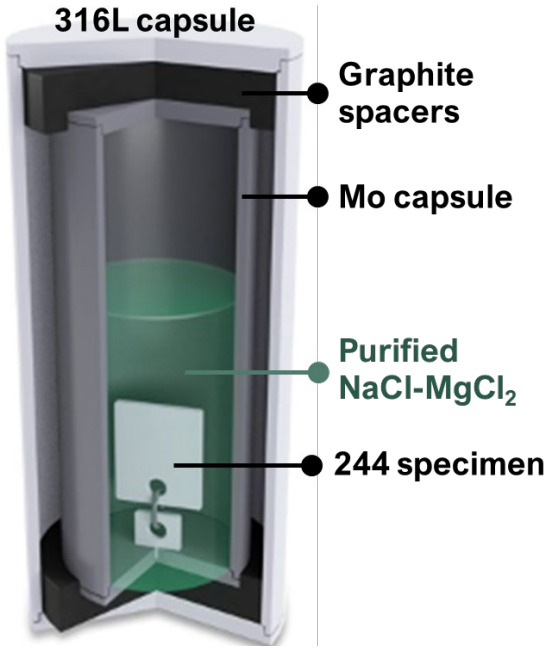
Impact of alloy chemistry and microstructure on creep behavior in molten salts

Static capsule testing for Alloy 244

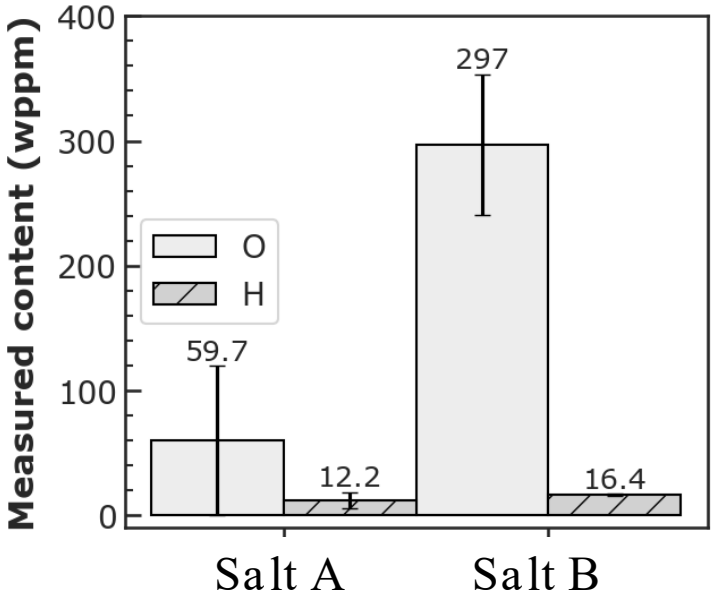
Measured composition in wt.%

Alloy	Ni	Cr	Fe	Mn	Si	Mo	W	C
244	61.9	8	1.1	0.3	-	22.4	6	0.05

Alloys	Temperature (°C)	Times
244 – solution annealed	750, 850	100, 500h



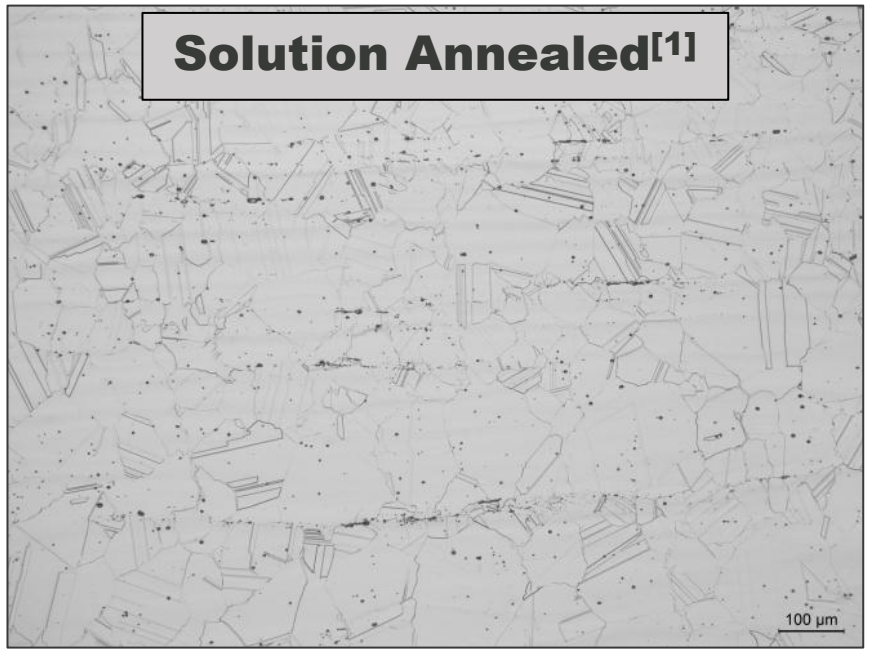
LECO analysis of salts

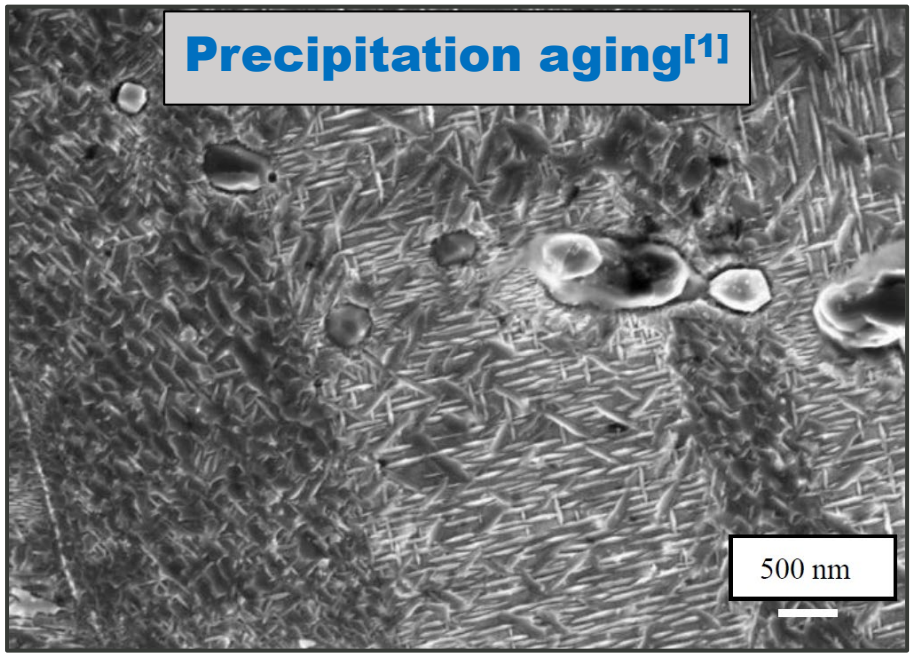


Salt A: Commercial salt
Salt B: Purified using established procedure*

***Young et al. 1993; Chen et al. 1993; Kurley et al. 2018**

Test temperatures chosen here will result in different microstructures for 244



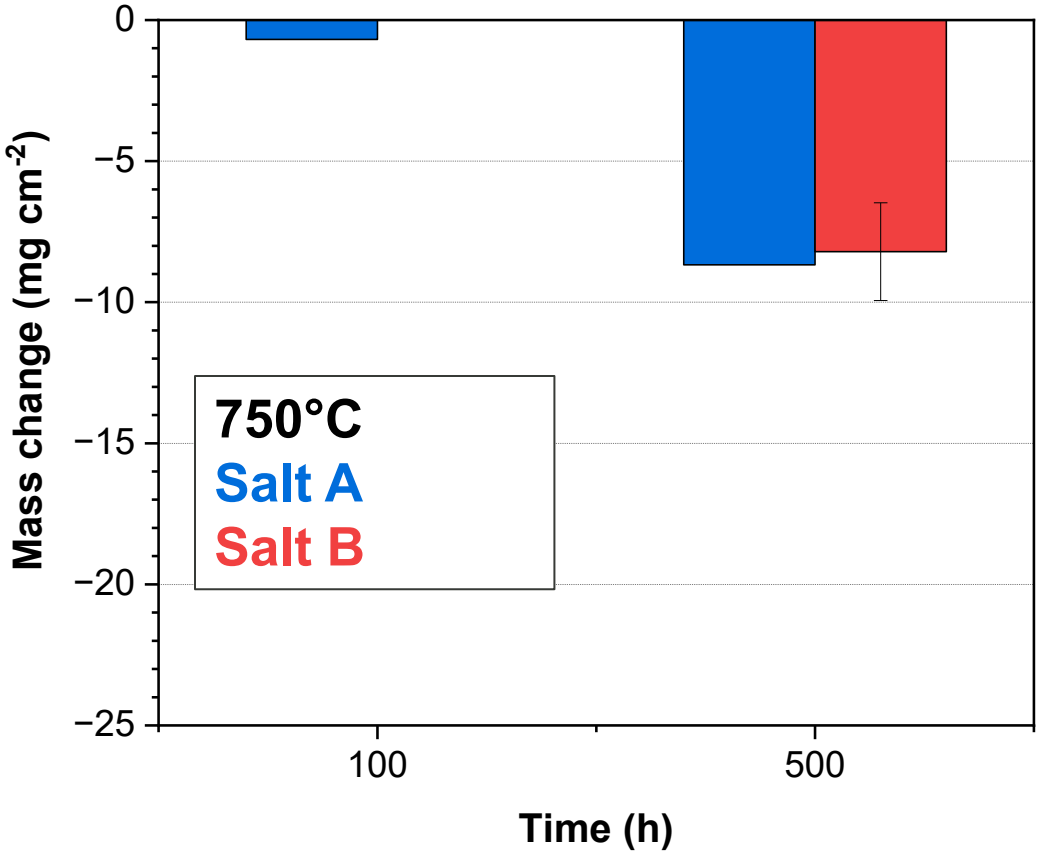


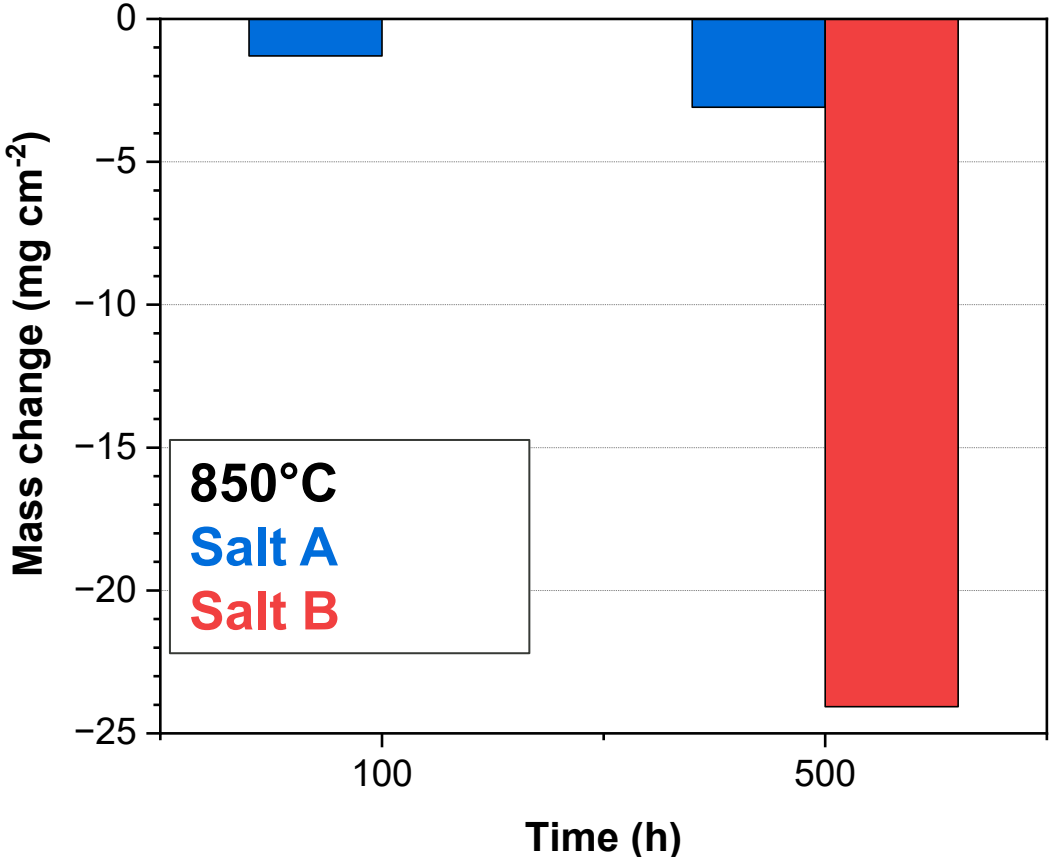
- γ-FCC matrix
- Phase extraction / XRD analyses:
  - **µ-phase:** $Cr_{20}Mo_{43}Ni_{37}$, hexagonal crystal system
  - **P-phase:** $Cr_9Mo_{21}Ni_{20}$,orthorhombic crystal system) phases
  - **M_6C** type carbide

- 16h@760°C → furnace cooling to 32h@649°C → air cool
- $Ni_2(Cr, Mo, W)$ domains (body centered orthorhombic Pt_2Mo structure type)
  - **are not expected to be stable above 770°C**
- (Mo,W)-rich µ-phase
- Long-term aging (1000h) at 760°C → γ-FCC + µ-phase

[1] M. Fahrmann et al., Superalloys 2012

Significantly higher mass loss was observed for exposure in Salt B at 850°C



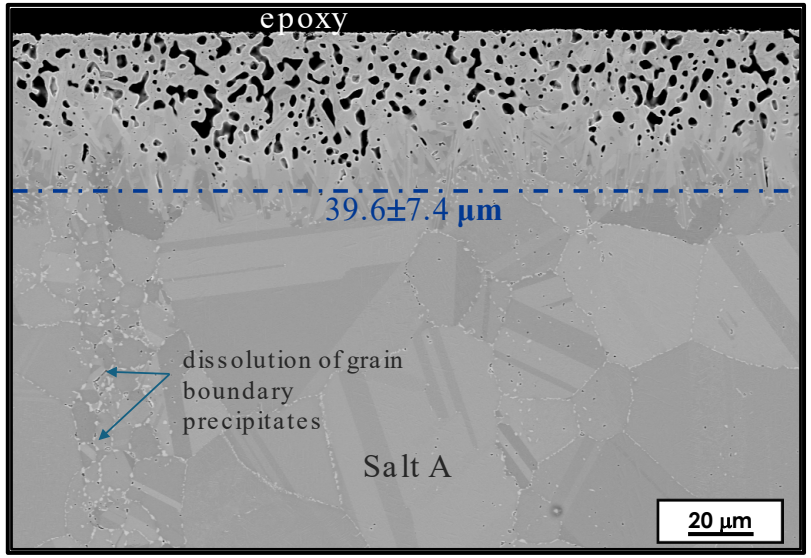


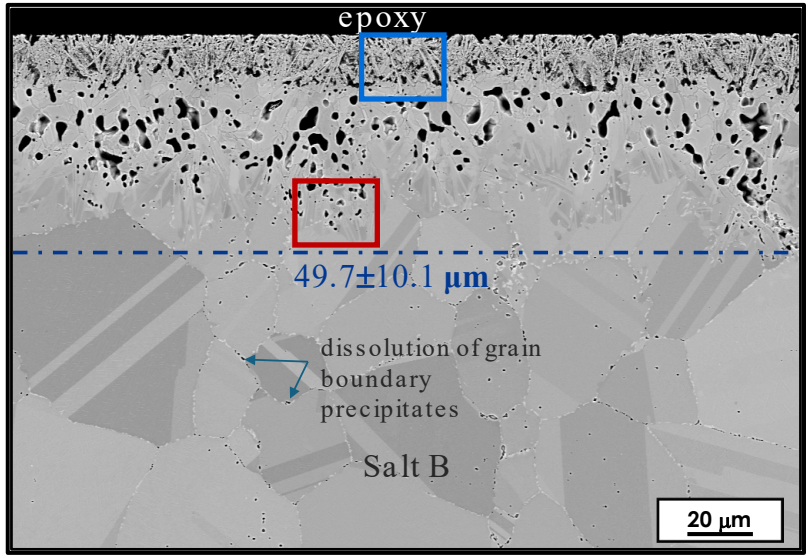
Mass loss was comparable after 500h at 750°C between the two salts

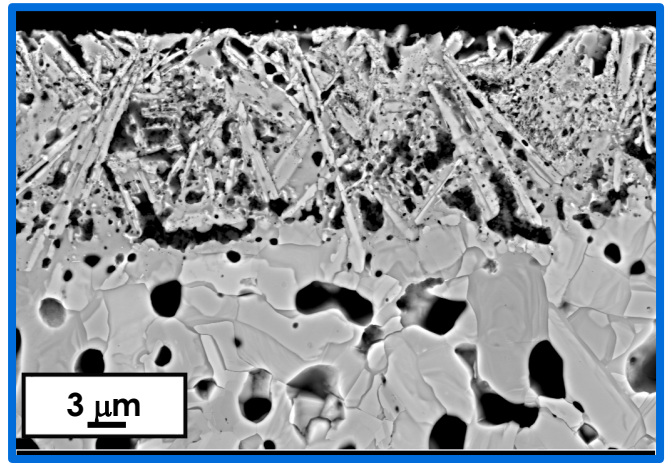
Significantly less attack for exposures in the Salt A (purer salt) after 500h at 850°C

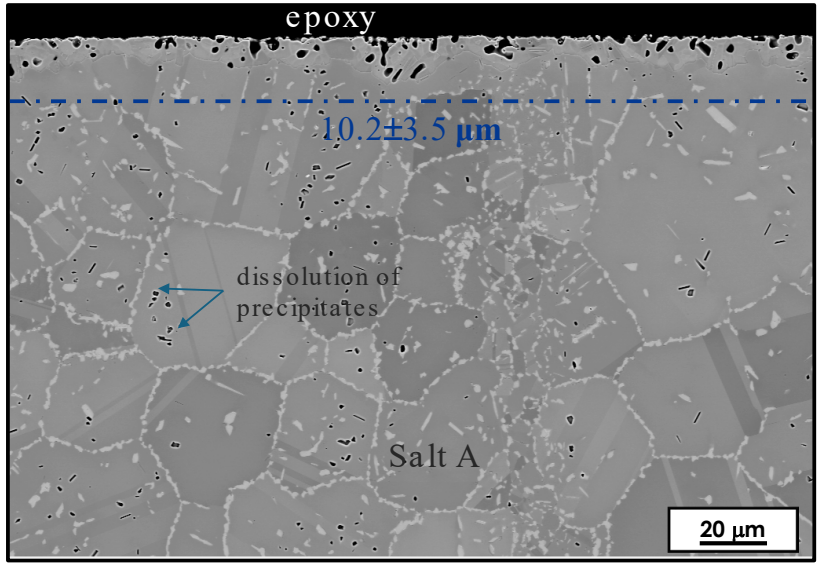
750°C

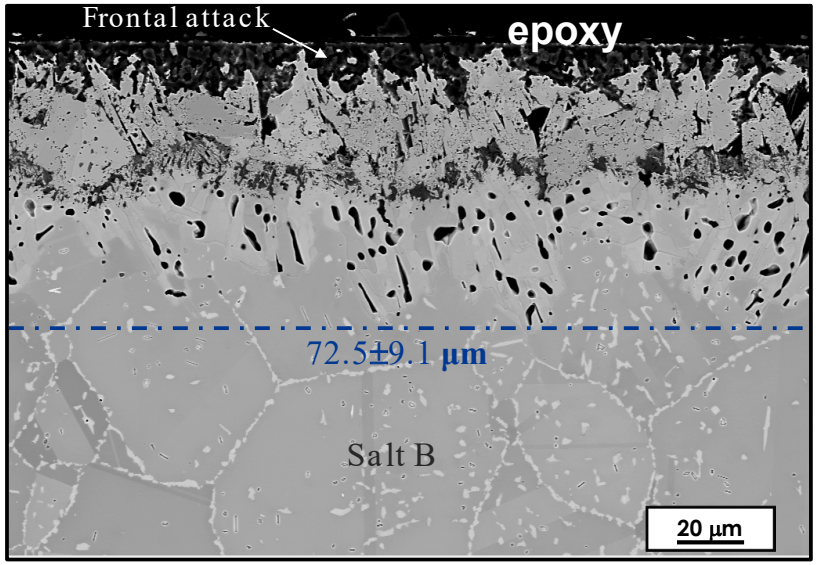
850°C

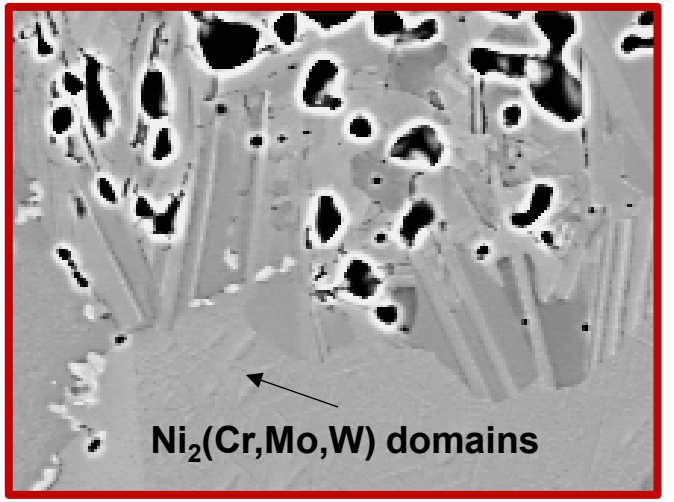






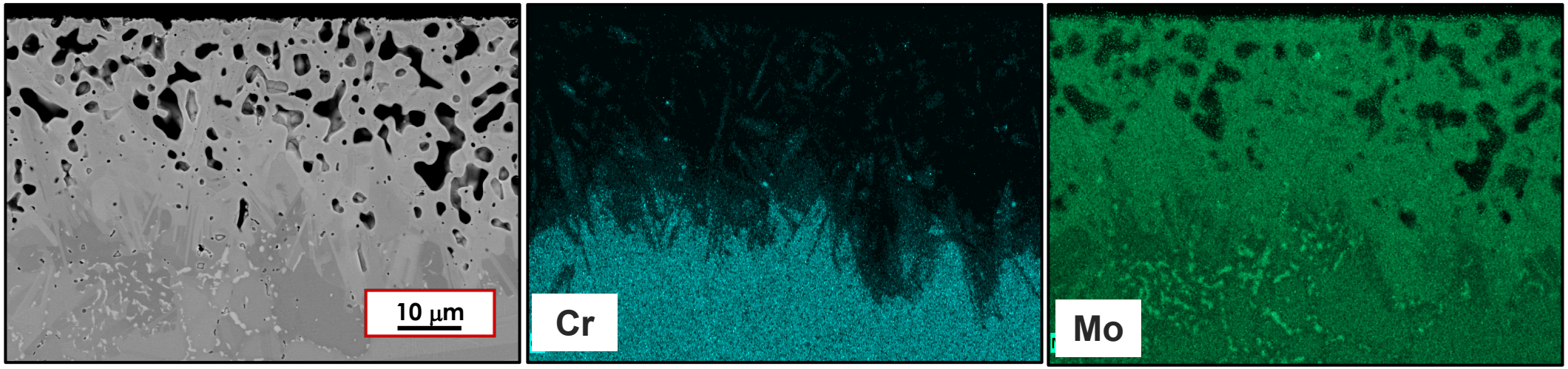




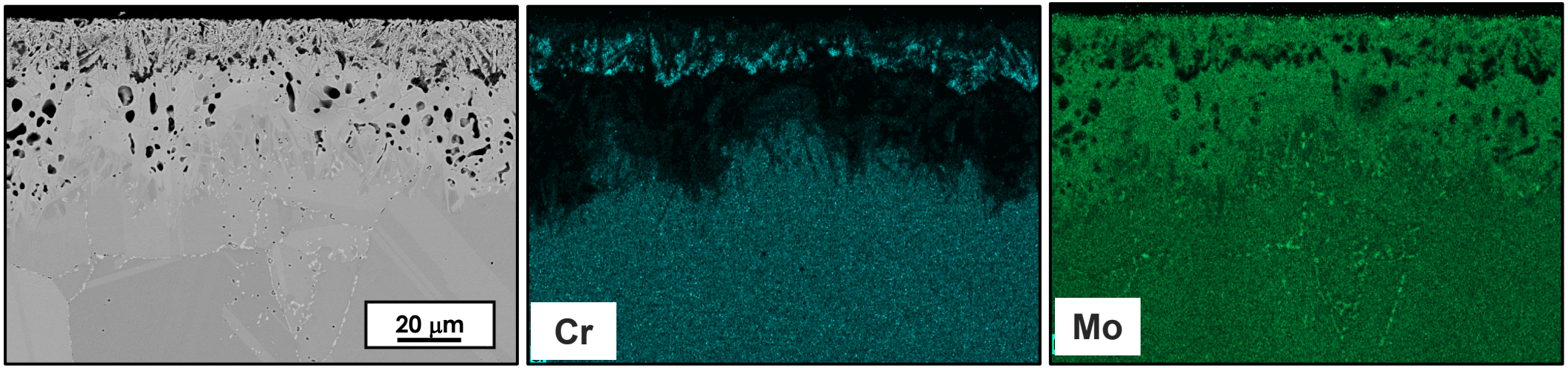


Simultaneous Cr depletion and Mo enrichment in the alloy subsurface is observed for exposures in both salts after 500h at 750°C

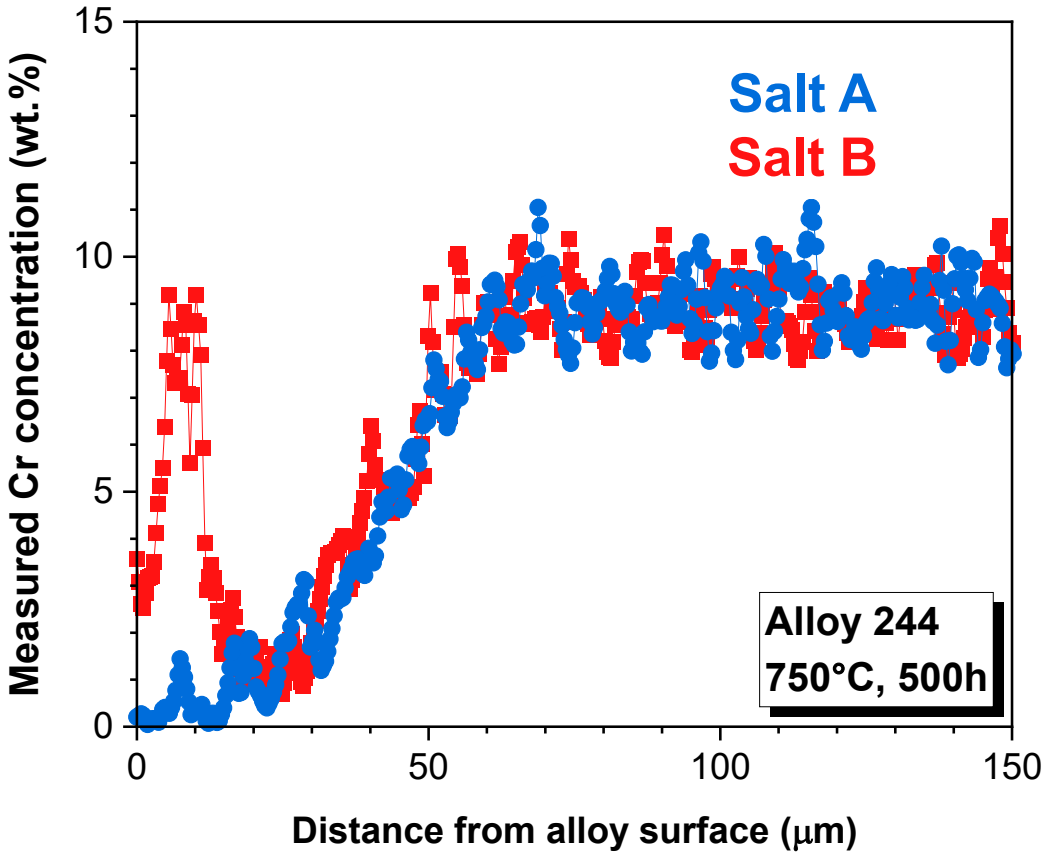
Salt A

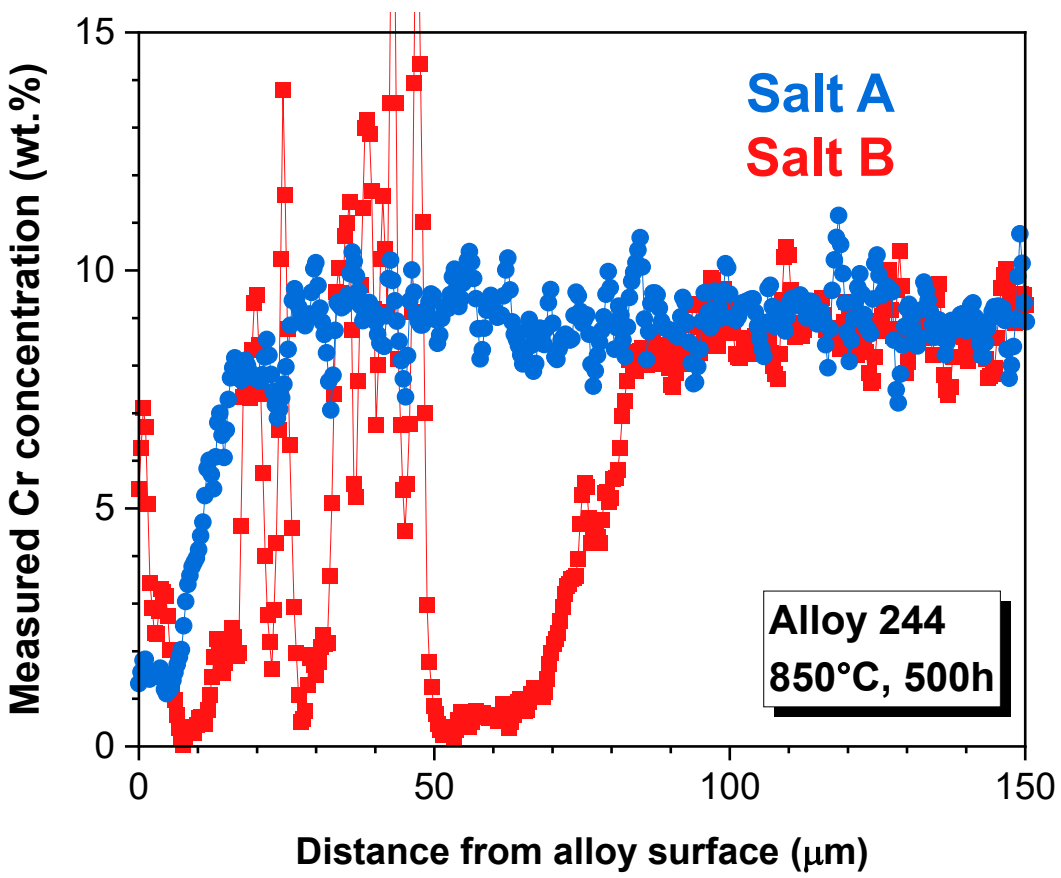


Salt B



Concentration profiles confirm similar Cr depletion in both salts at 750°C but higher Cr depletion in the impure salt (Salt B) at 850 ° C



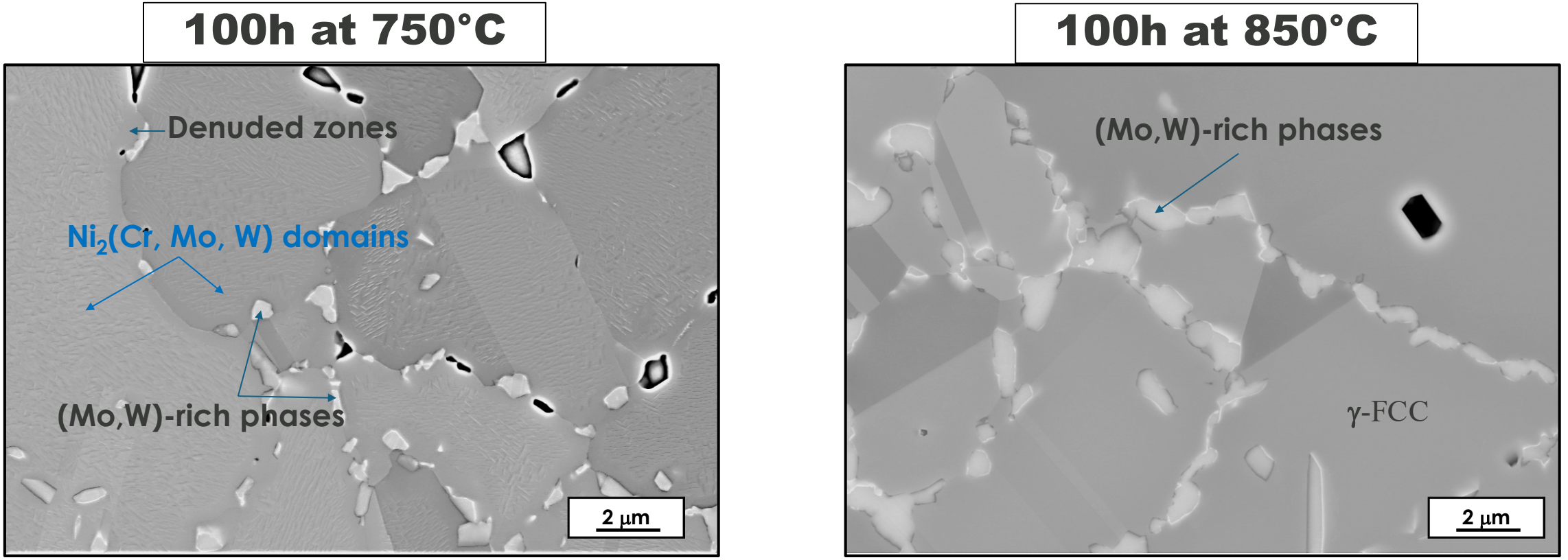


- Measured depths of attack correspond well with observed depths of Cr depletion
- Higher O impurities in the Salt B most likely accelerating corrosion at 850°C

What are the reasons for this anomalous temperature dependence of the corrosion behavior for 244?

750ºC	Increased attack independent of salt impurity level
850ºC	Reduced attack in pure salt

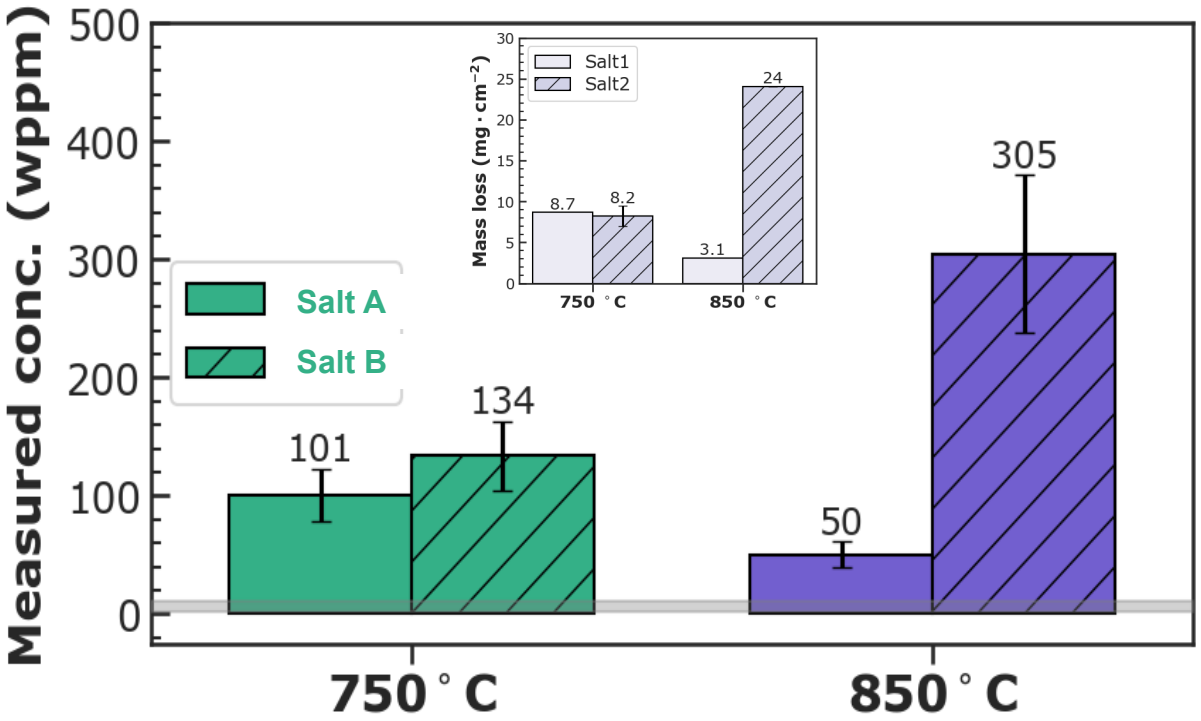
Ni_2(Cr, Mo, W) domains were not stable at 850°C which is in complete agreement with literature

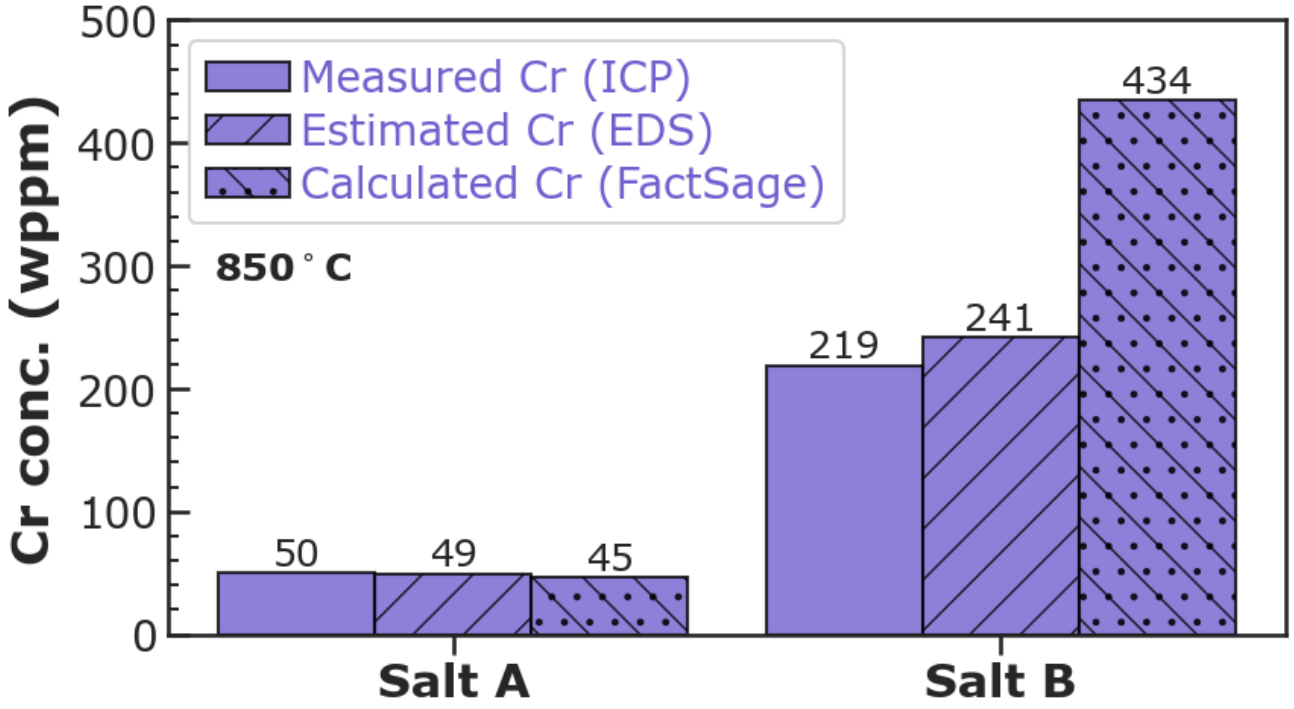


- Ni_2(Cr, Mo, W) {Pt_2Mo-type} domains stability < 790°C[1]
- (Mo,W)-rich phases are most likely M_6C-carbides (confirming with TEM)

[1] Mann. T et al., Acta Materialia (2024)

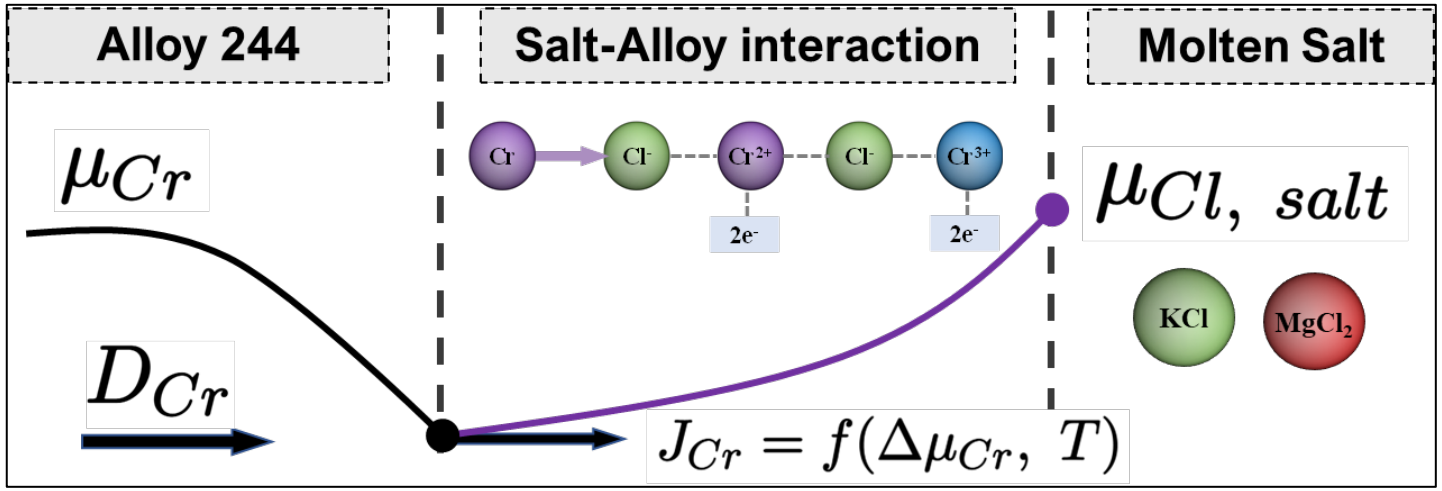
Measured Cr depletion, Cr content in the salt and predictions of Cr content in equilibrium with the salt are in good agreement





- Cr content in salt follows mass loss trend
- Cr lost from alloy (EDS Cr profile) ≈ Cr measured in salt (ICP-MS of salt)
- FactSage (at Thermodynamic Equilibrium, assuming Cr surface activity = 0.125)

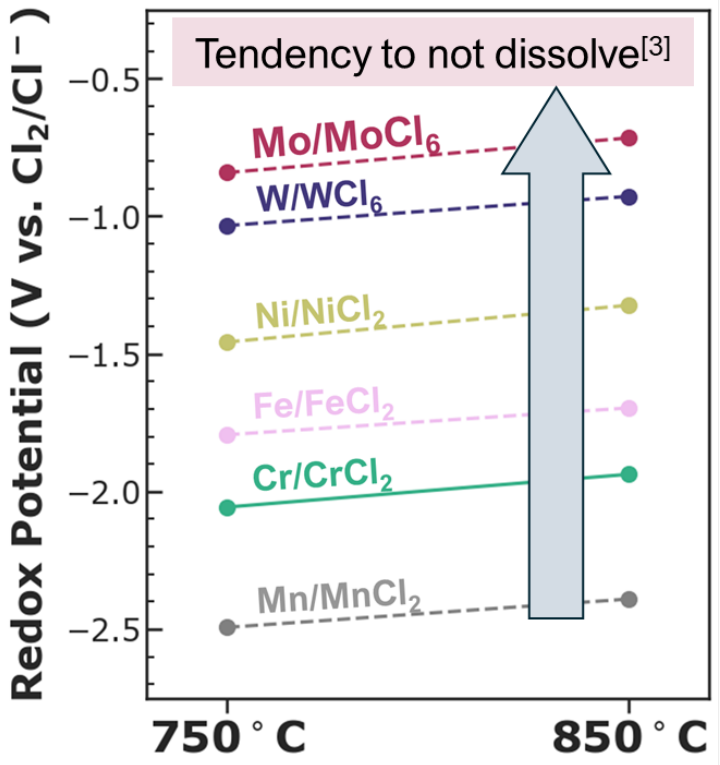
Thermodynamic factors influencing Cr loss in NaCl-$MgCl_2$



μ_{Cl} : *Salt redox potential*

μ_{Cr} : *Activity of Cr*

Calculated redox potential[1]

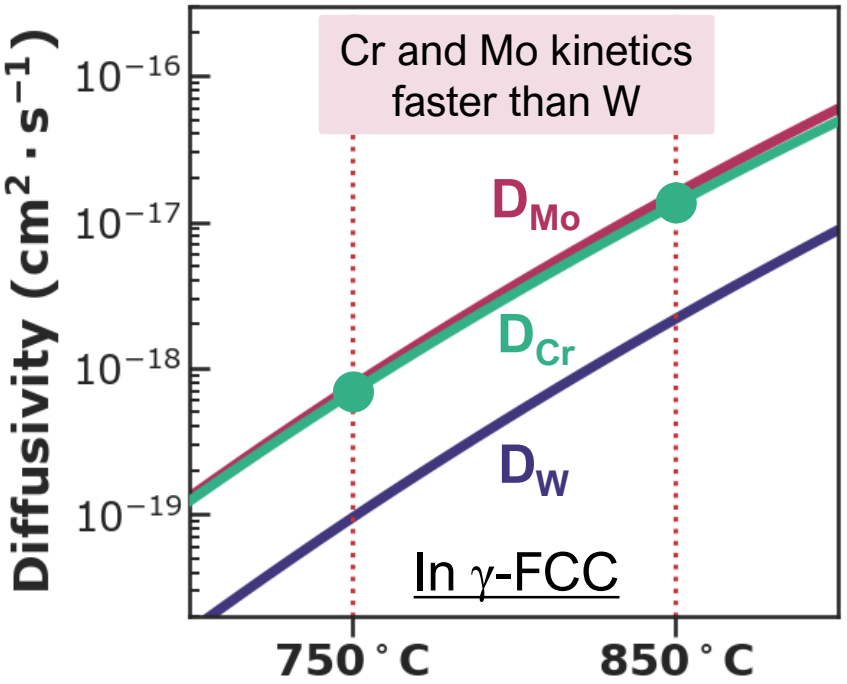


Cr dissolution is proportional to its activity and diffusivity in alloy[2]

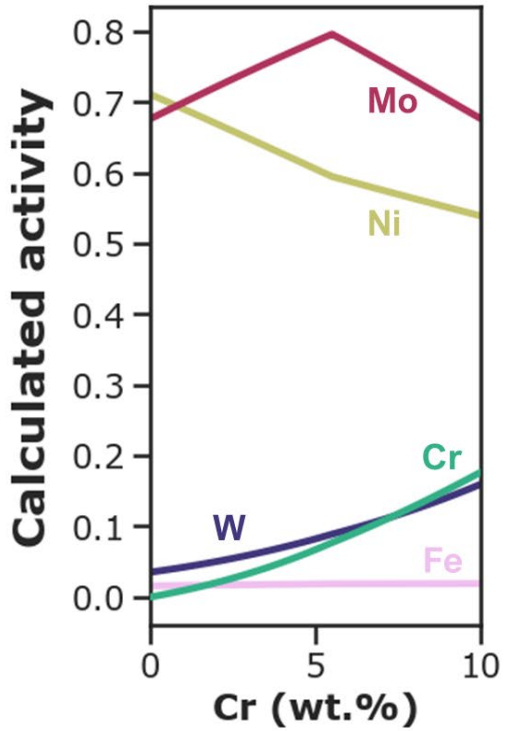
[1] FactSage v8.3, SGTE database
[2] Pillai, R., et al., JNM (2021).

Kinetics: Higher diffusivity of Cr and Mo drive surface activity of W and Cr

Calculated elemental diffusivity[1]



Calculated thermodynamic activity at 850ºC[1]

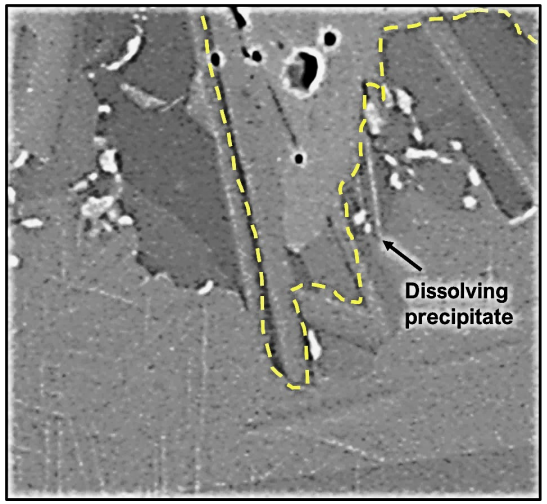


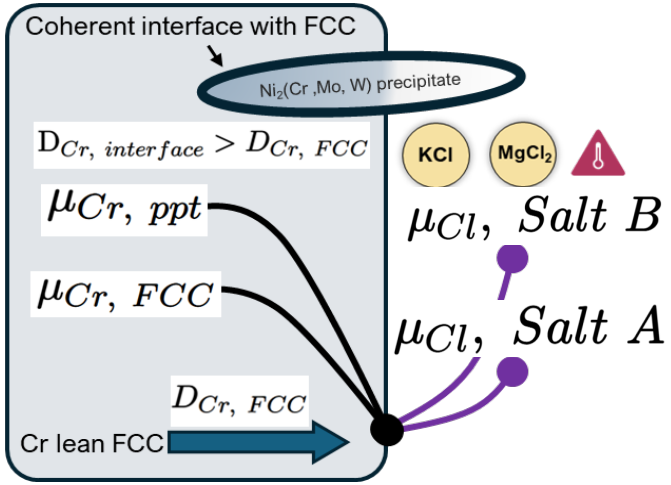
$$Cr\ depletion\ + Mo\ enrichment \rightarrow \uparrow \Delta\mu_W \rightarrow \uparrow \Delta\mu_{Cr}$$

[1]ThermoCalc, TCNI12-MOBNI6 database

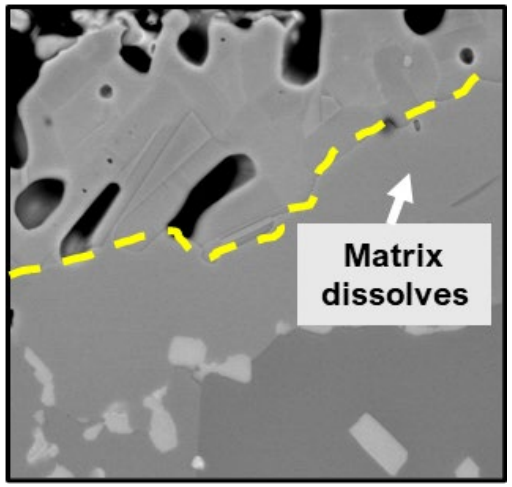
750 vs. 850ºC: $Ni_2(Cr, Mo, W)$ precipitate driven vs. Matrix

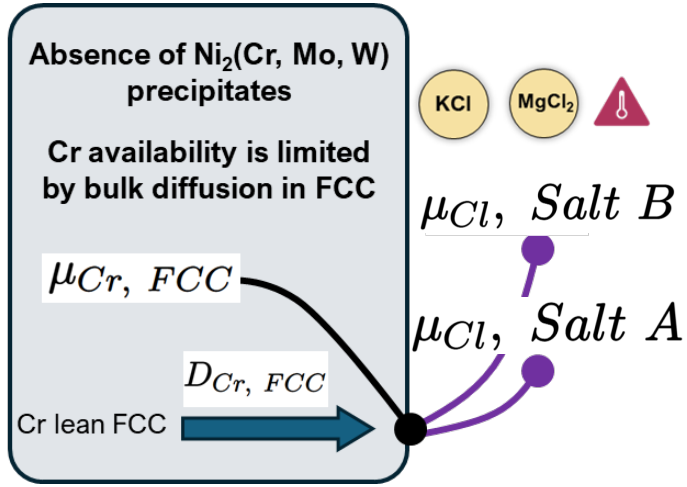
750ºC





850ºC





- Cr source in $Ni_2(Cr, Mo, W)$ precipitates
  → always available at salt-alloy interface → sustained corrosion
- Coherent FCC/precipitate interface
  → fast diffusion pathways → destabilizes precipitate
- Ongoing STEM analysis

- Lower contents of Cr available at salt interface
  → limited by bulk diffusivity of Cr in matrix at 850ºC
- Diffusivity of Cr and Mo ~10 times higher than W at 850ºC
  → increased Cr depletion and Mo enrichment
- Surface Cr activity further increased!

Microstructure governs corrosion behavior < 770°C[1] < Impurities govern corrosion behavior

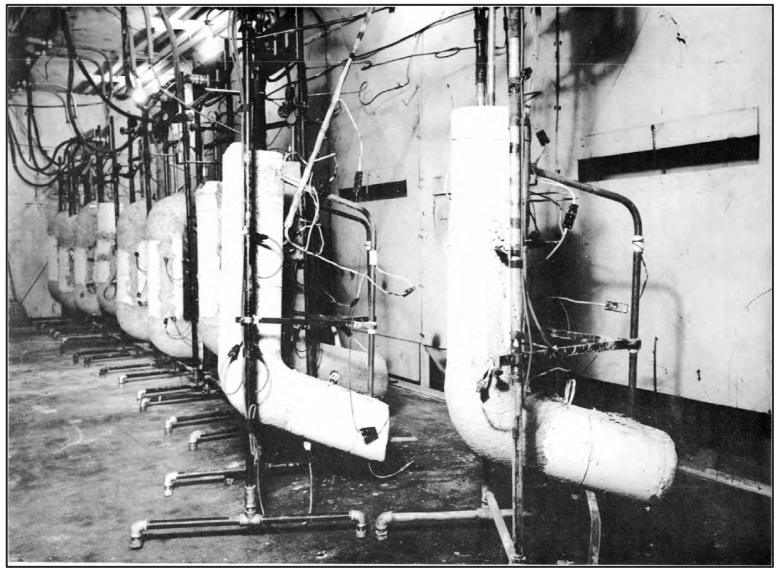
[1] Song, J., et al., *Met. and Mat. Trans. A: Physical Metallurgy and Materials Science*, 2017, *48*(5).

A couple of key examples were selected to demonstrate role of alloy chemistry and microstructure on the corrosion behavior and mechanical properties of structural alloys in molten halide salts

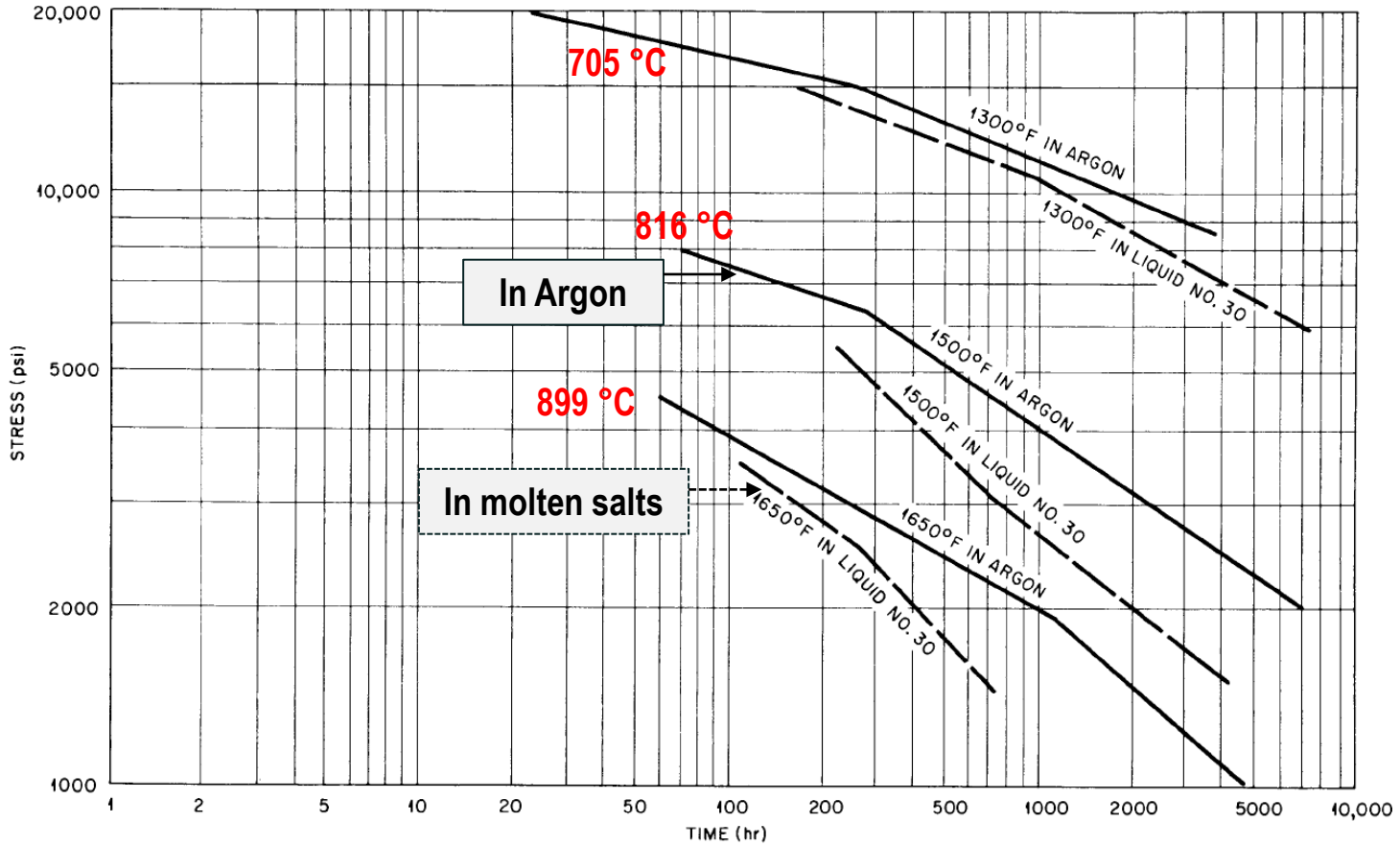
Impact of alloy chemistry and microstructure on creep behavior in molten salts

Impact of molten salt induced corrosion on the creep behavior of structural materials has received limited attention since the Aircraft Reactor Experiment in the 50's

The INCONEL Story*



- **Inconel (Ni-15Cr-7Fe in wt.%)**
- **$NaF-ZrF_4-UF_4$ (50-46-4 mol.%)**
- **500 h, TCL (704-816 °C)**



- Significant decrease in creep rupture times during exposures in molten salts
- Corrosion-induced dissolution of secondary carbides*

* Manly at al., ORNL-2349, 1958

Primary focus was to generate some initial data on the creep behavior of 316H, 709 and 617 in molten fluoride and chloride salts

Measured composition in wt.%

Alloy	Fe	Cr	Ni	Mn	Si	Mo	C	Co	Al	Ti	Other
316H	Bal.	16.6	10.3	1.6	0.3	2.0	0.04	0.2	-	-	Cu 0.4 N 0.03
617	1.6	22.2	Bal.	0.1	0.1	8.6	0.05	11.6	1.1	0.4	Cu 0.04
709	Bal.	20.0	24.6	0.9	0.4	1.5	0.08	-	-	-	Nb 0.2 N 0.2

316H: Solution Annealed
709: Solution annealed at 1150°C, → precipitation treatment at 775°C for 10h
617: Solution Annealed

Salts	Source	Purification
FLiNaK LiF-NaF-KF (46.5-11.5-42 mol %)	**Commercial***	**As-received ~500 wppm O ~30-50 wppm H ~450 wppm Zr**
NaCl-$MgCl_2$ (57-43 mol.%)	**In-house**	**Established 4-step procedure** ~100-200 wppm O**

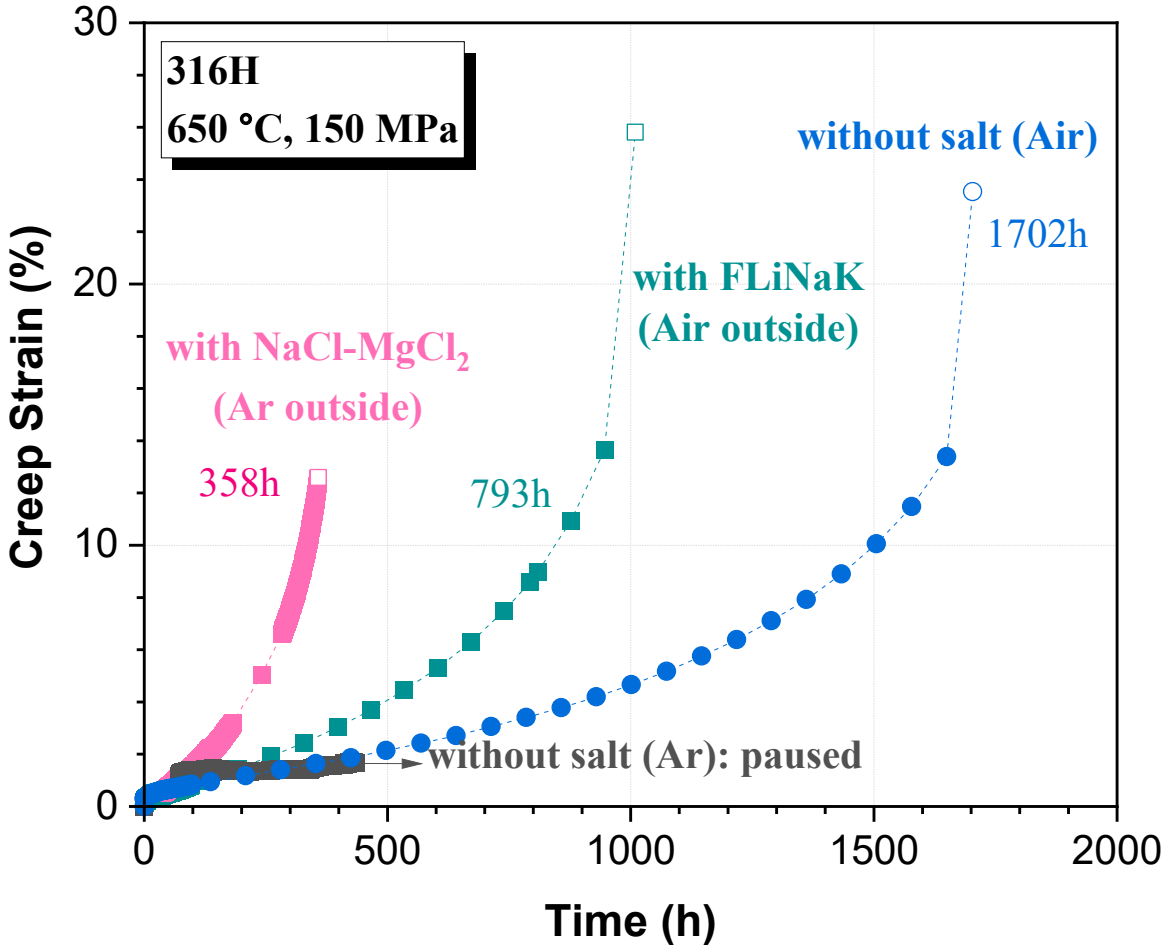
Acknowledgement: 617 and 709 Materials provided by Yanli Wang (DOE-NE ART Materials Program)

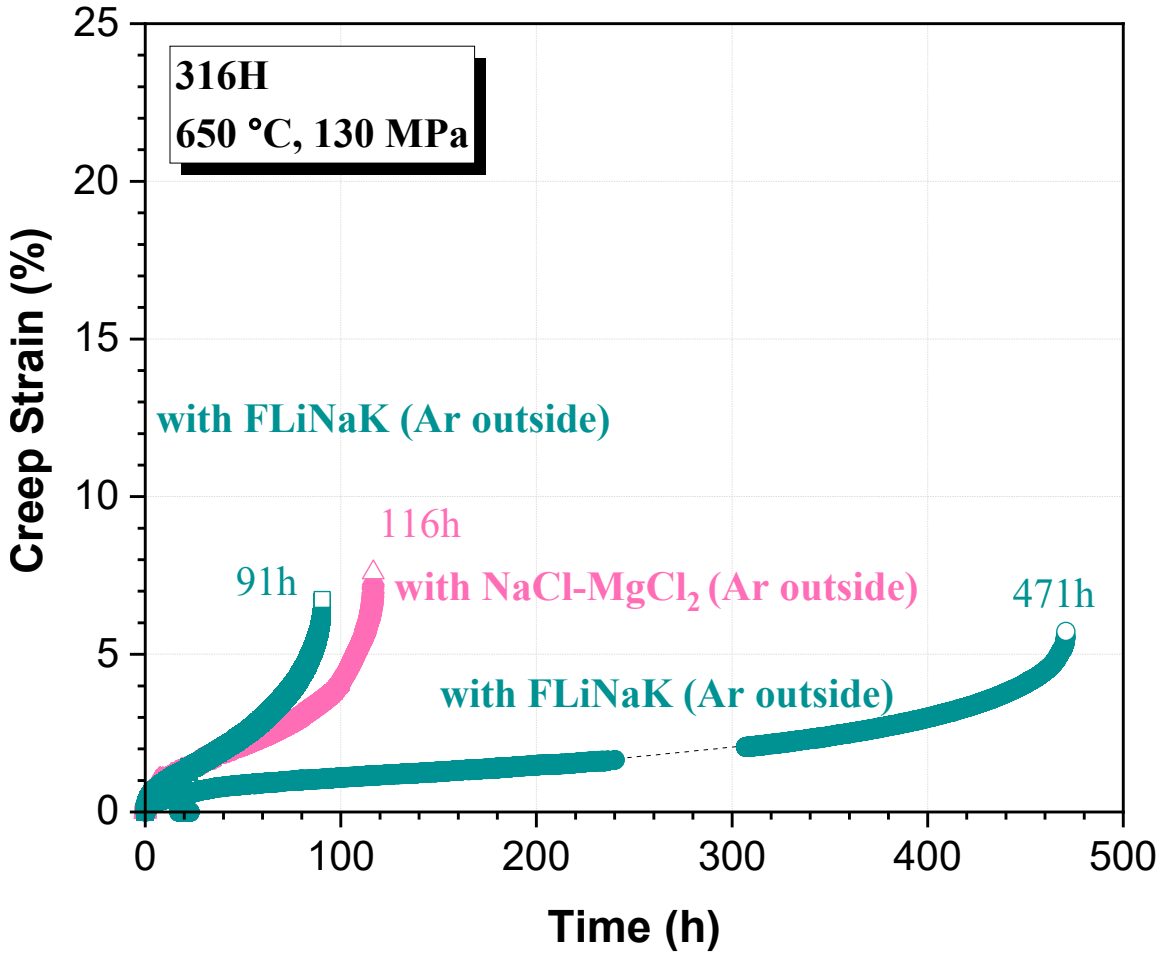
Hollow creep specimen

- Hollow creep specimen filled with purified salts and welded in a glove box
- Outside environment:
  - Air (FY24)
  - Ultra-high purity Ar (FY25)
- Furnace switches off once specimen ruptures
- Stresses chosen for expected creep rupture time between 1000-3000h

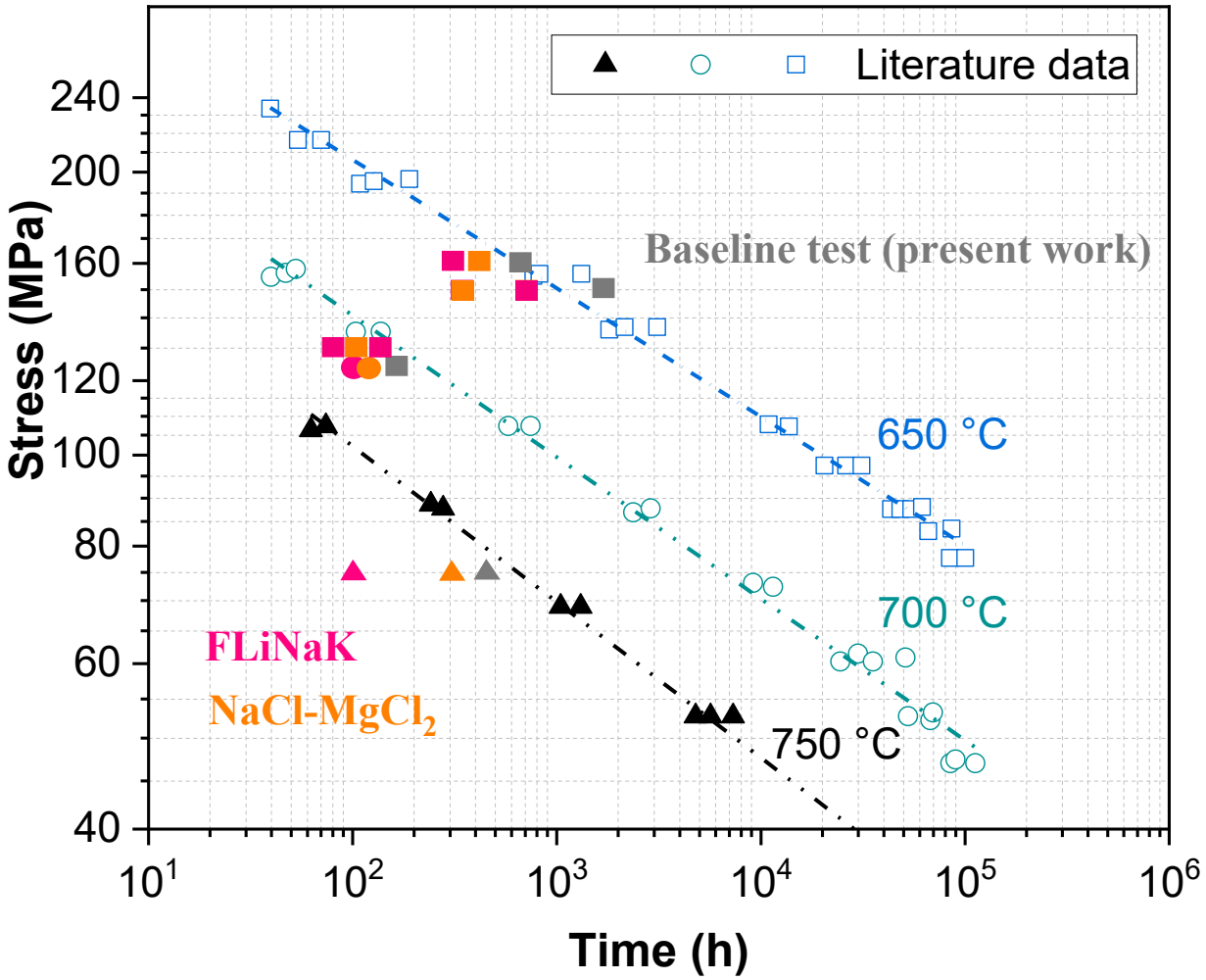
* **ECS (now defunct)**
** **Purified using established procedure: Young et al. 1993; Chen et al. 1993; Kurley et al. 2018**

Considerable impact of molten salt environment on creep behavior of 316H in molten FLiNaK and NaCl-$MgCl_2$





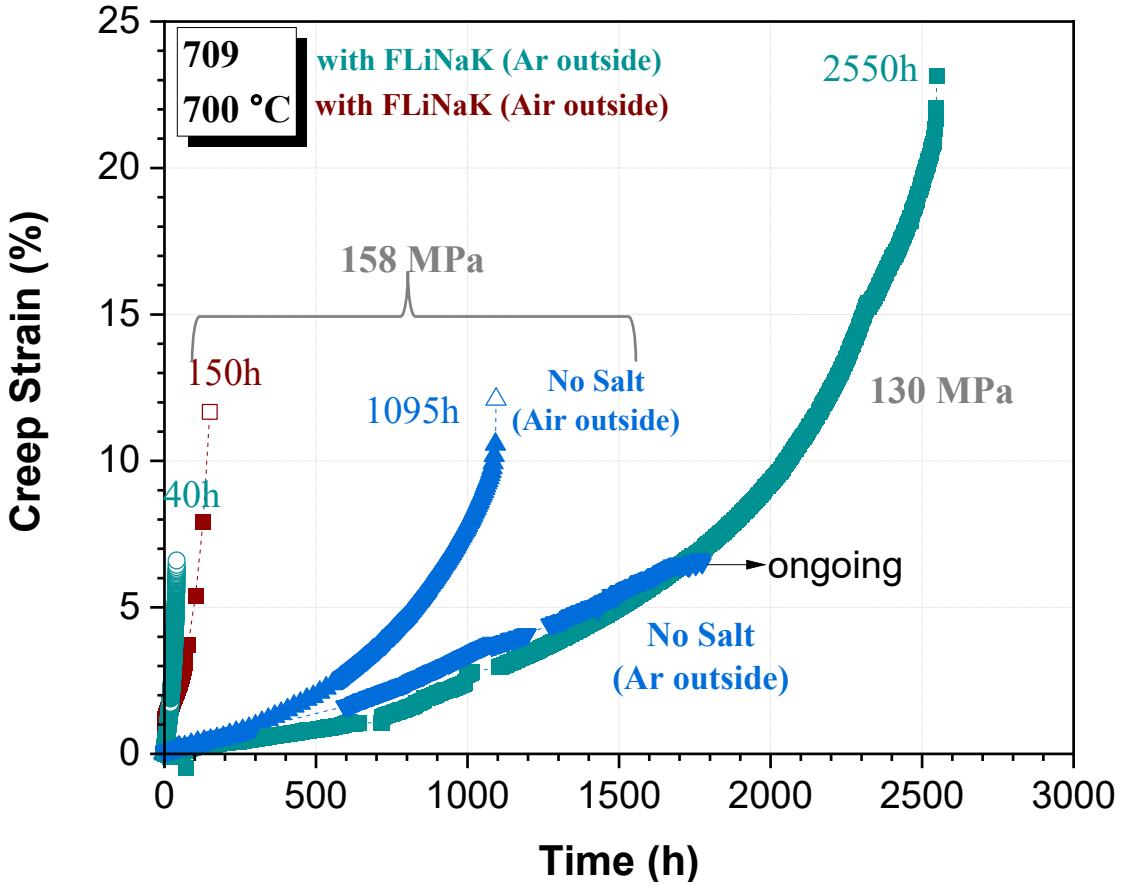
Molten salts have been observed to impact creep behavior of 316H across a wide range of test conditions

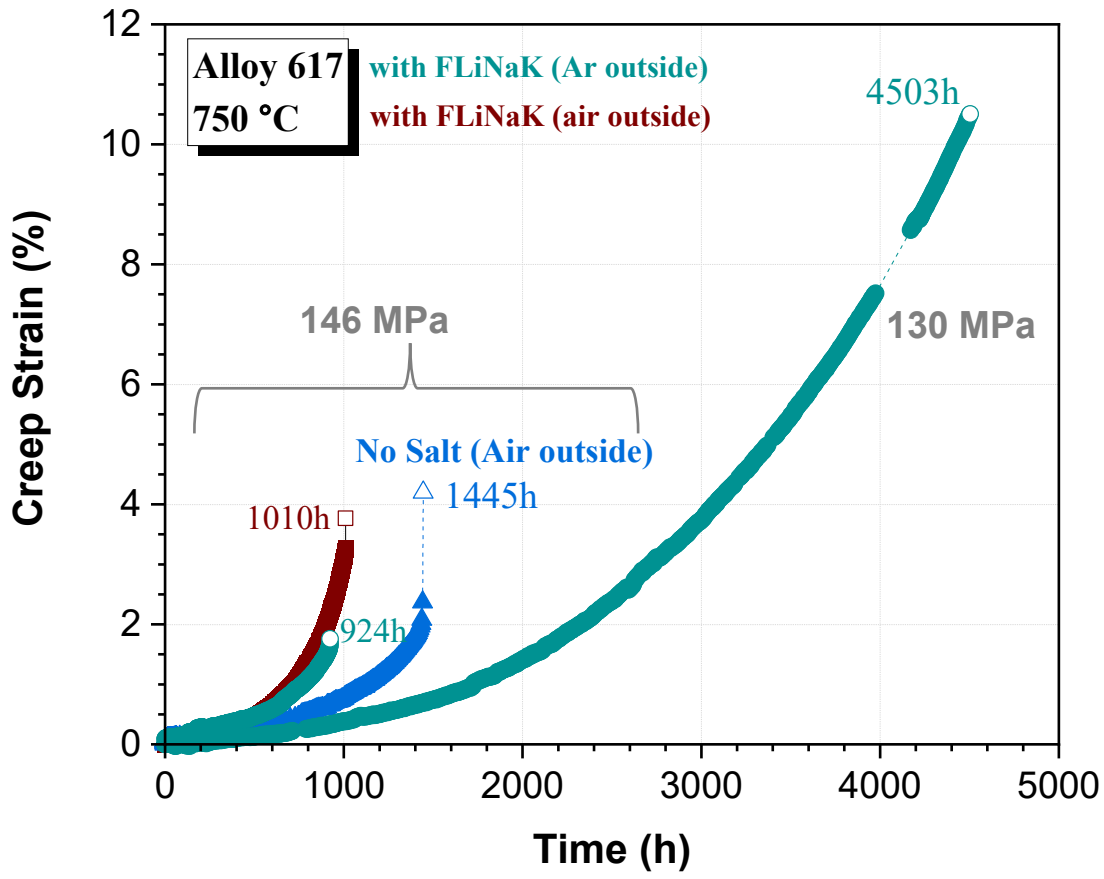


- **Baseline testing agrees with literature data (minimal impact of non-standard specimen geometry)**
- **Consistent decrease in creep rupture life across all temperatures and salts**

Literature source: NIMS Creep Data Sheets no. 6B, 14B and 15B

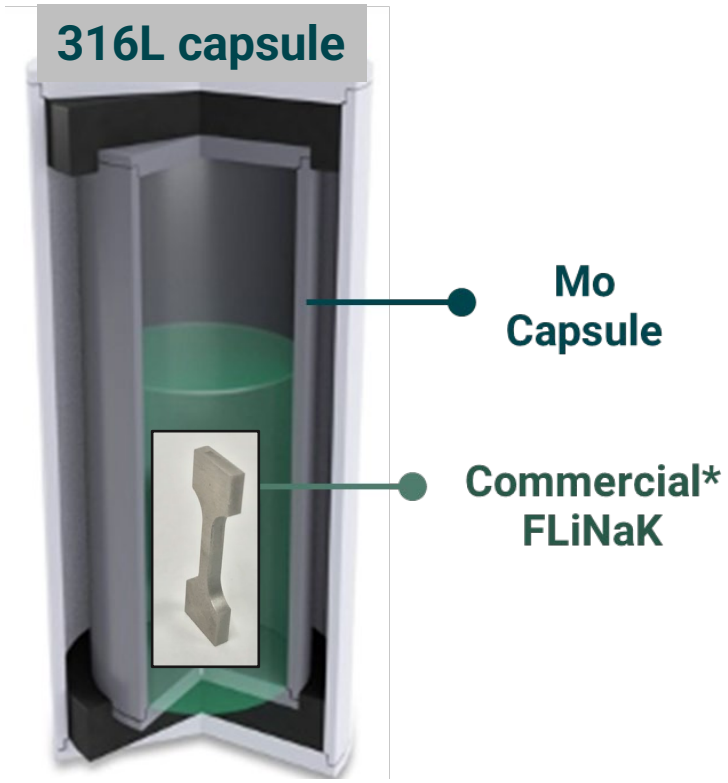
Significant acceleration in creep rupture confirmed for 709 and 617 irrespective of external environment

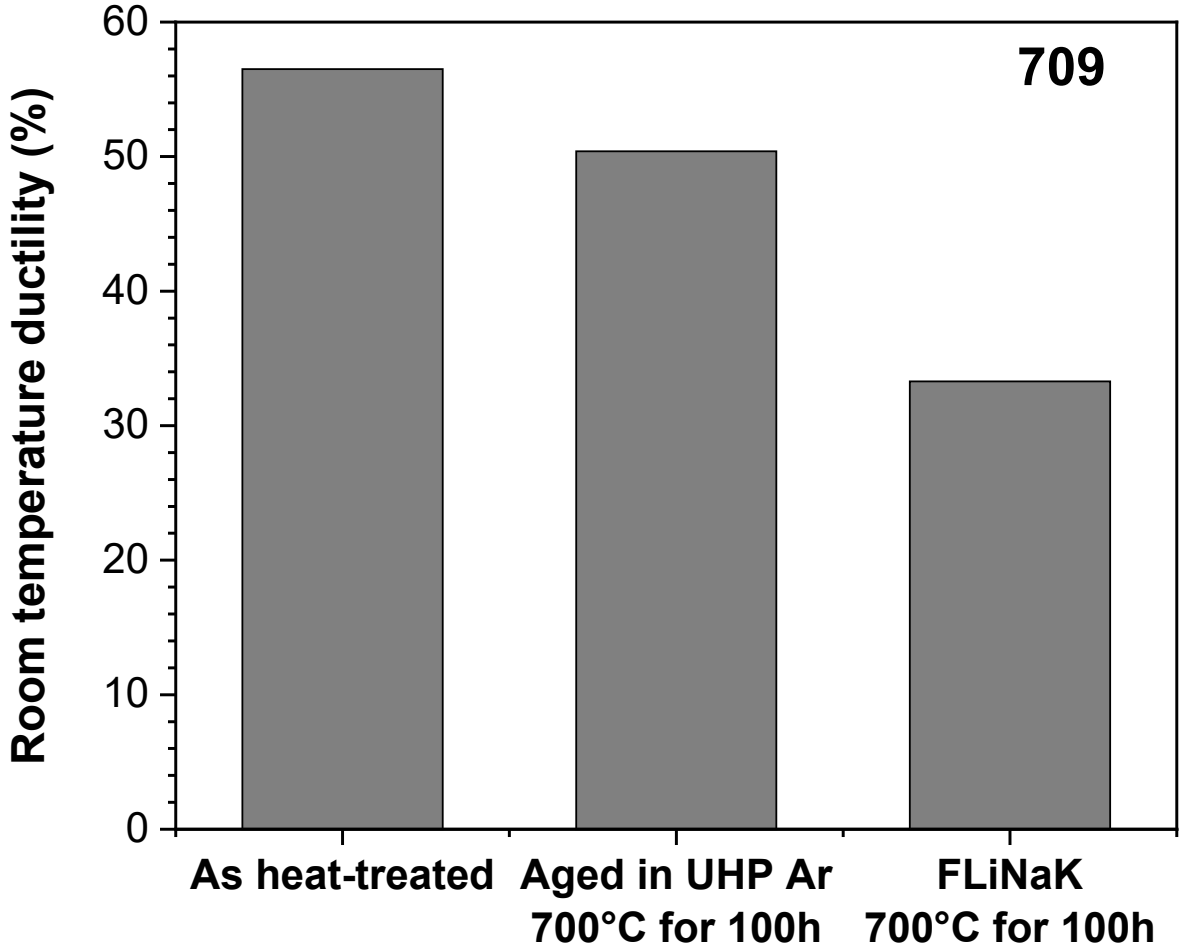




- **Test at lower stress showing similar behavior for 709 (test without salt is ongoing)**
- **Baseline test for 617 is not planned for now (prioritizing FY26 tasks)**

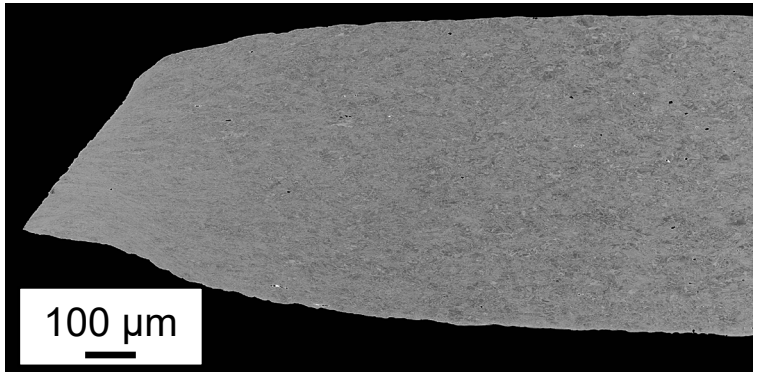
Drop in room temperature ductility after corrosion testing for 100h at 700°C in FLiNaK

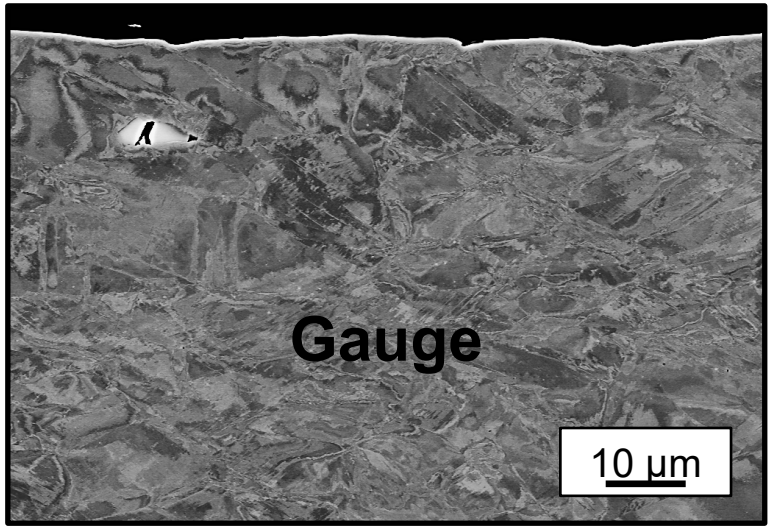




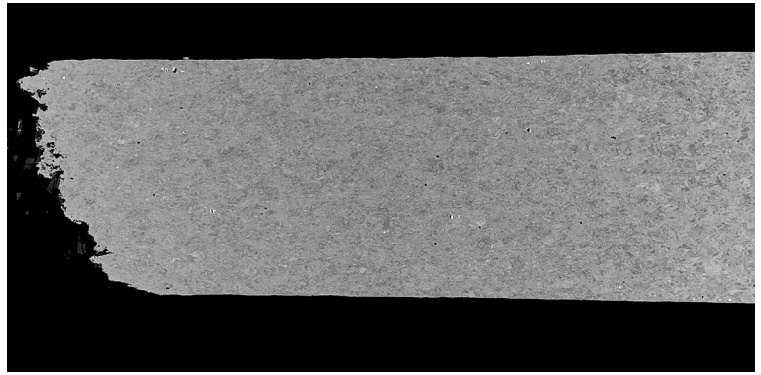
Evident trends in observed fracture mode across different environments

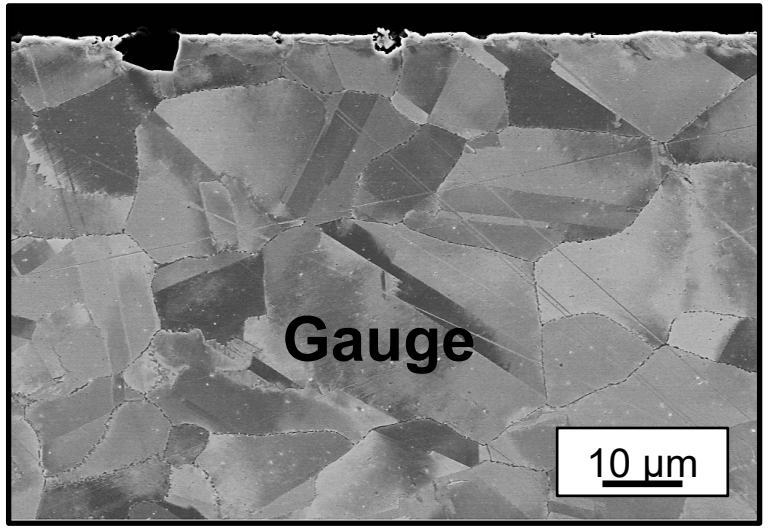
Solution annealed



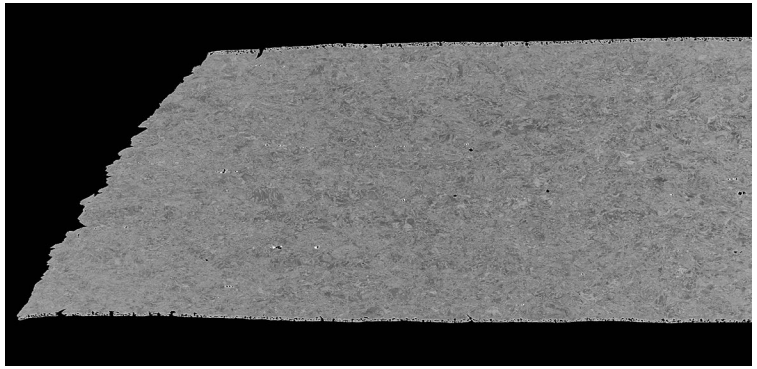


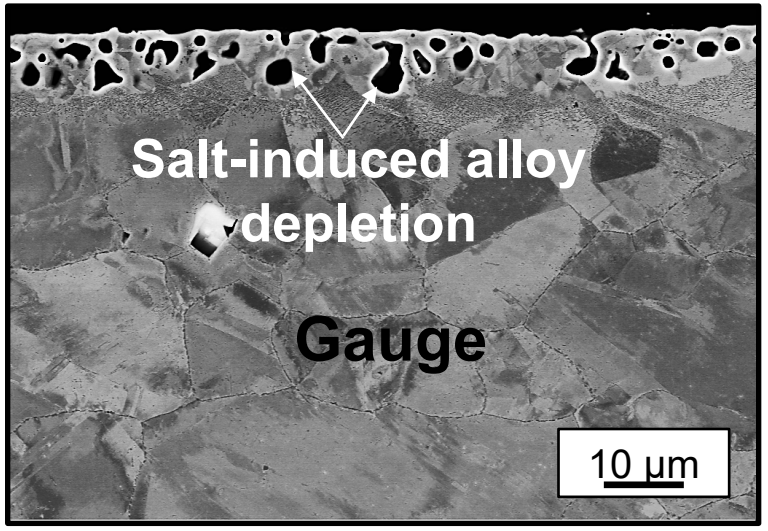
Aged in UHP Ar, 700°C-100h





FLiNaK, 700°C-100h

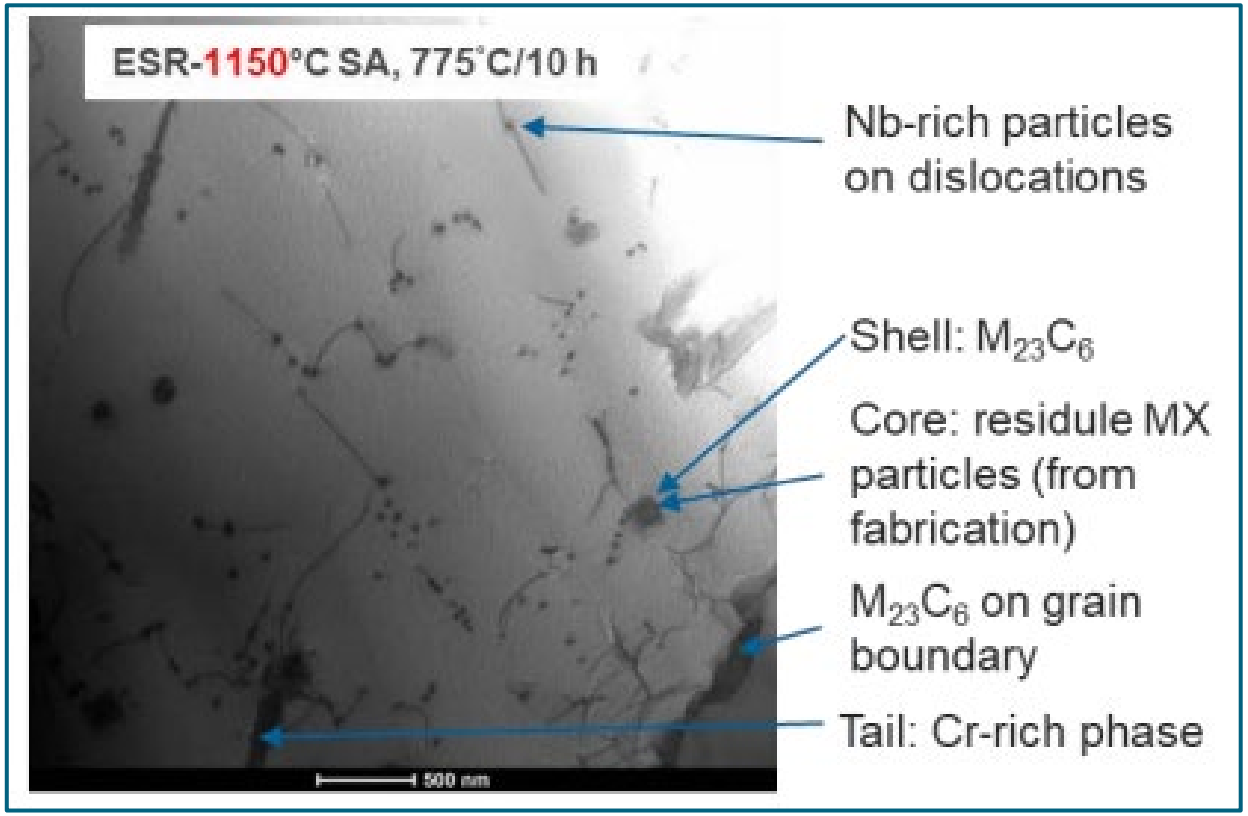




How is corrosion due to molten salts impacting creep rupture behavior?

Initial Microstructure of 709 is austenitic with carbides and nitrides as strengthening phase

- Cr-rich $M_{23}C_6$ with substitutions from Ni, Mo, Fe[1]
- Dislocations have fine Nb-rich precipitates

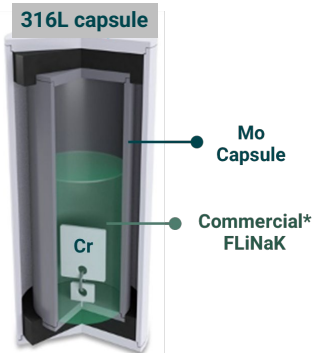


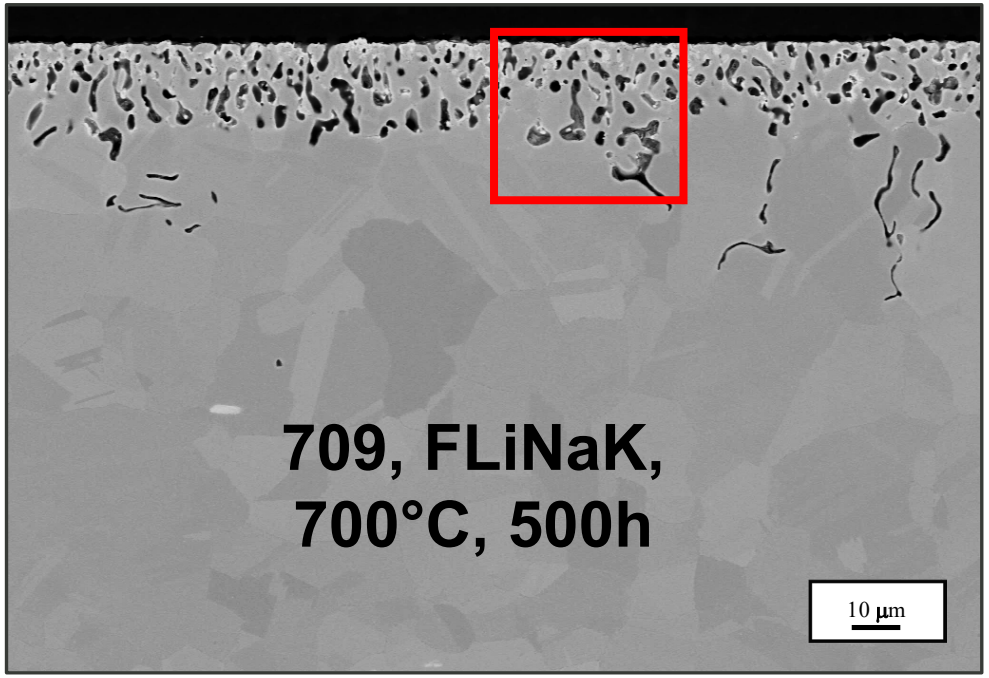
Aging effects[2]

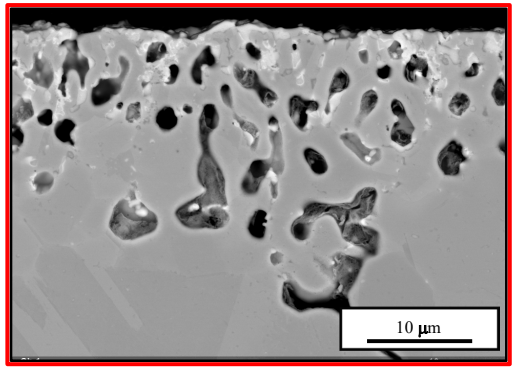
- Nucleation of θ ($(Cr,Mo)_3(Ni,Fe)_2SiN$) phase at GBs after aging at 650-750°C
- Increasing fraction of Z-phase (Nb,Cr)N with aging time was observed

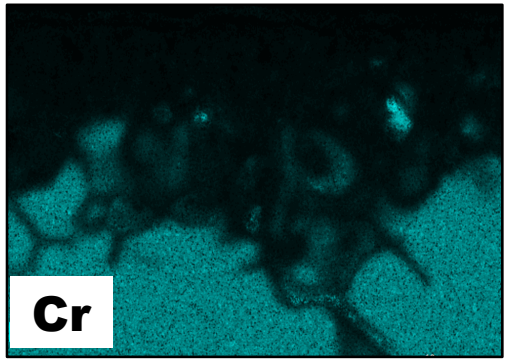
[1] Zhang and Sham 2020 ; [2] Ding et al., 2019

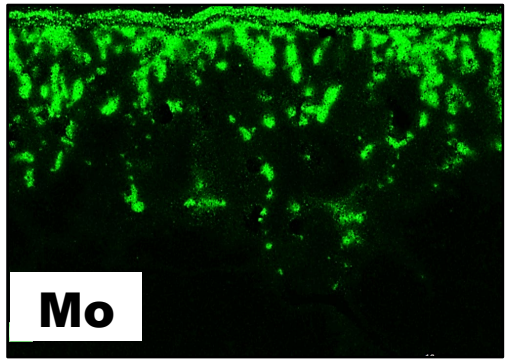
Significant porosity was observed and provided partial evidence for the presence of Mo-rich intermetallic phase in the corrosion affected zone



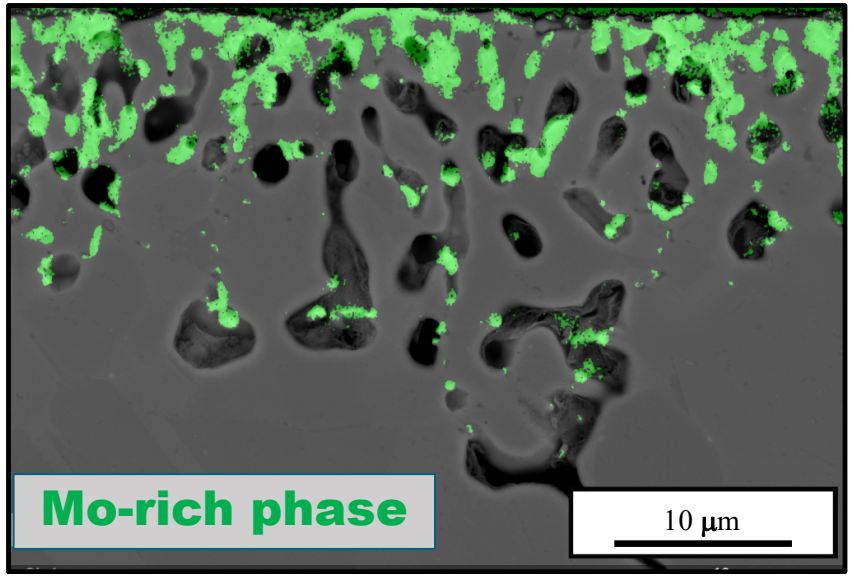






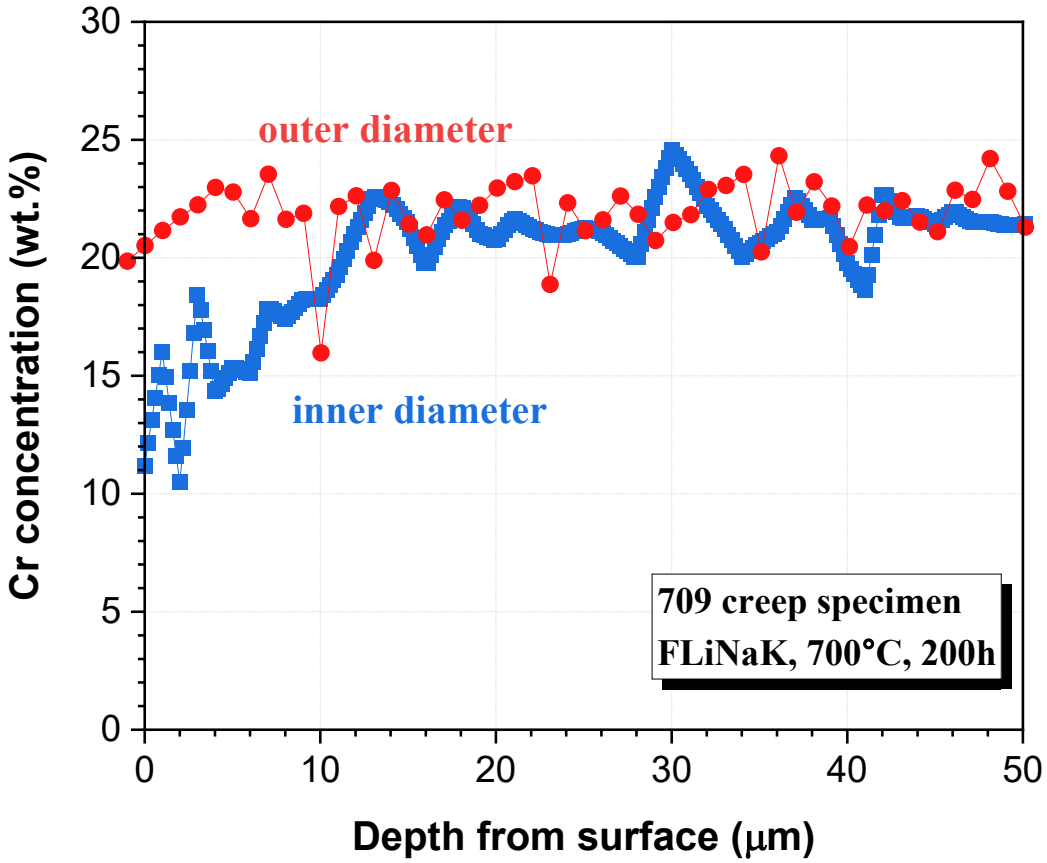


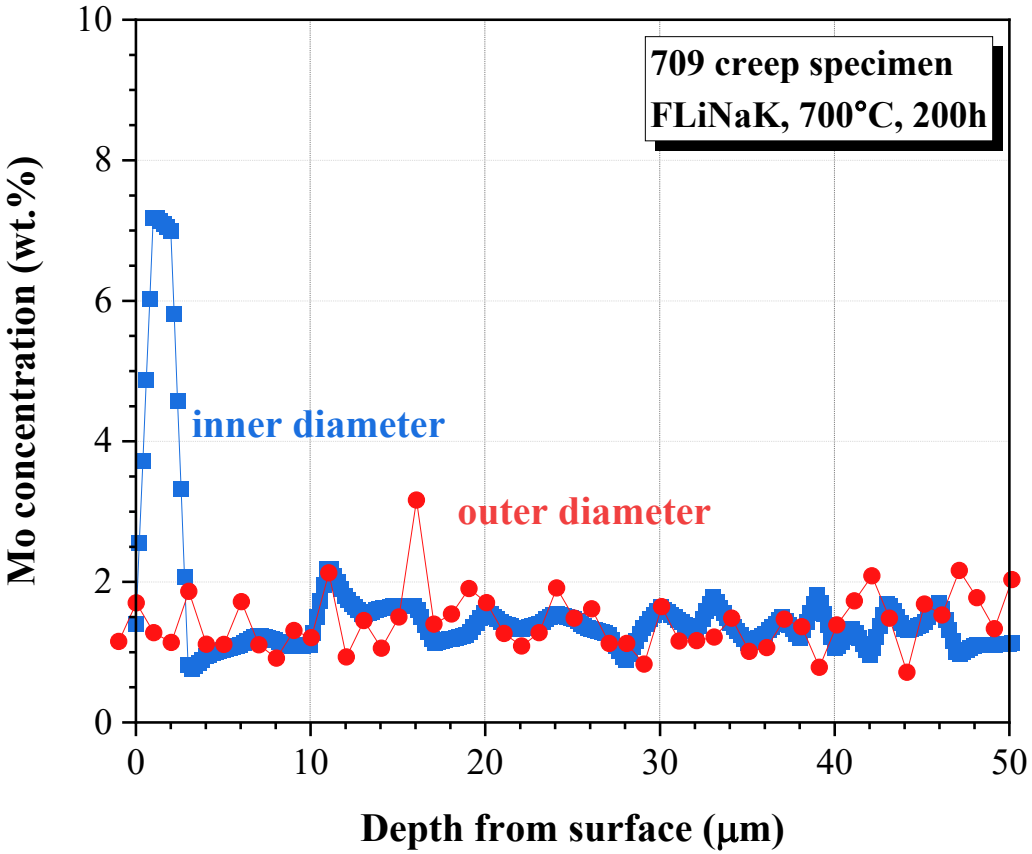
Mo map overlap on BSE image



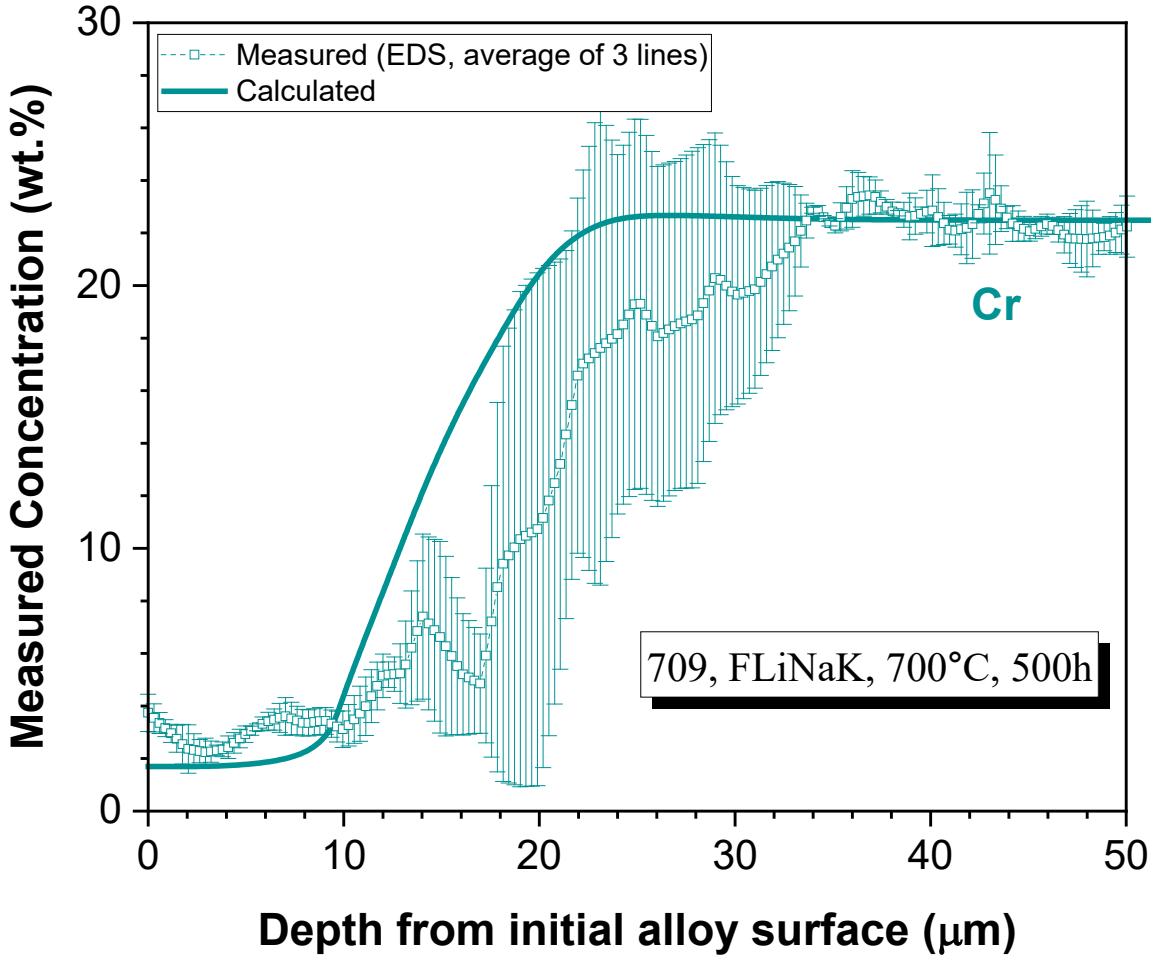
Unloaded creep specimen: Higher Cr depletion and Mo enrichment on the inner diameter (salt-facing) than the outer diameter (air-facing)

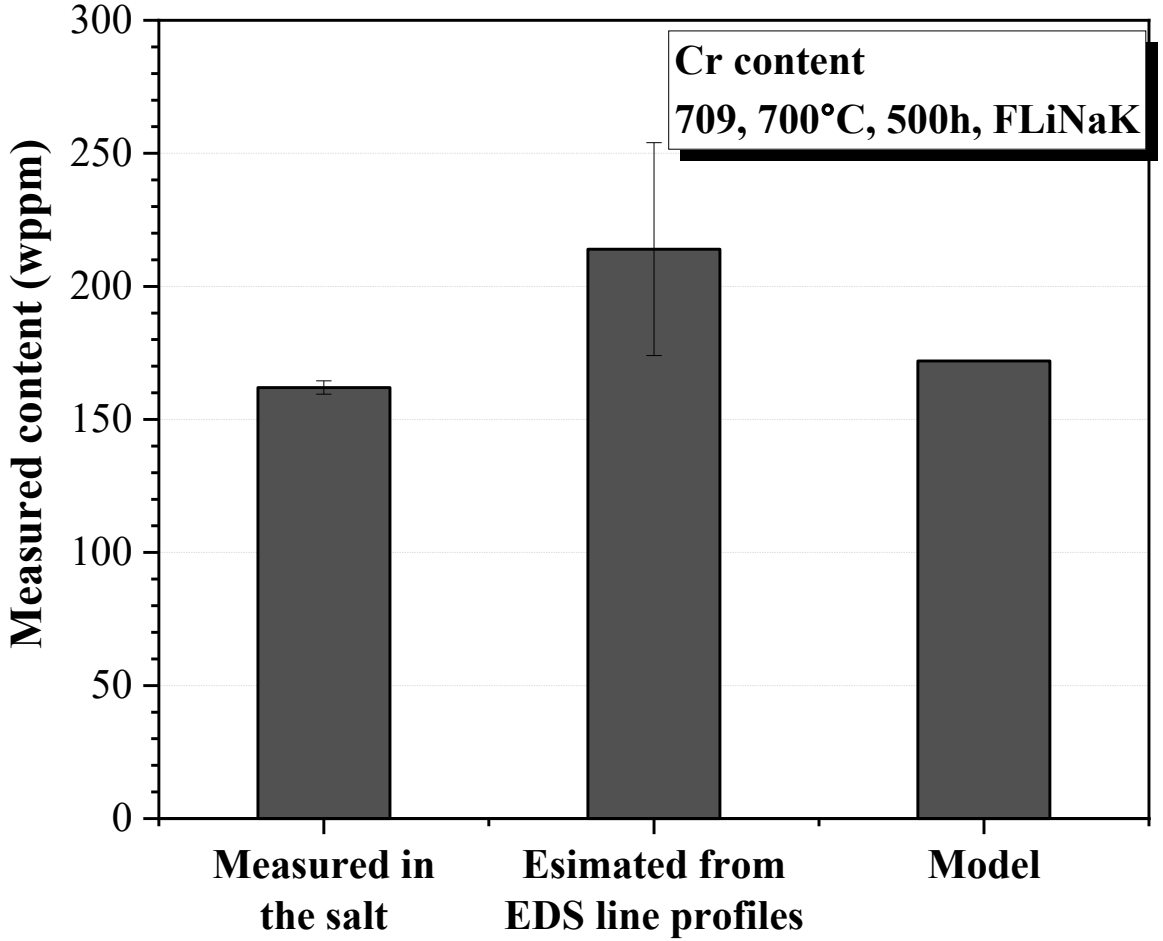
Static testing of creep specimen without loading





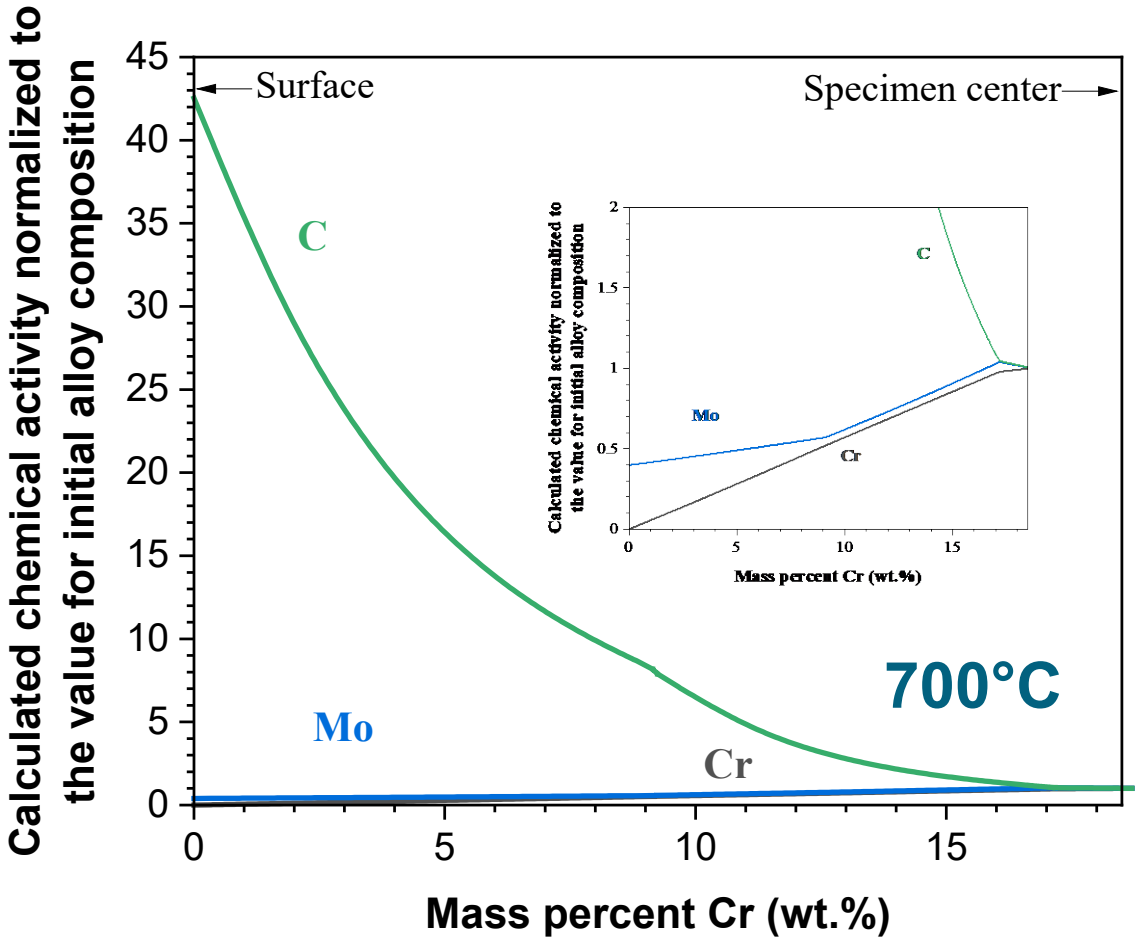
Excellent agreement between measured and predicted depletion of Cr from 709 after 500h in commercial FLiNaK at 700°C

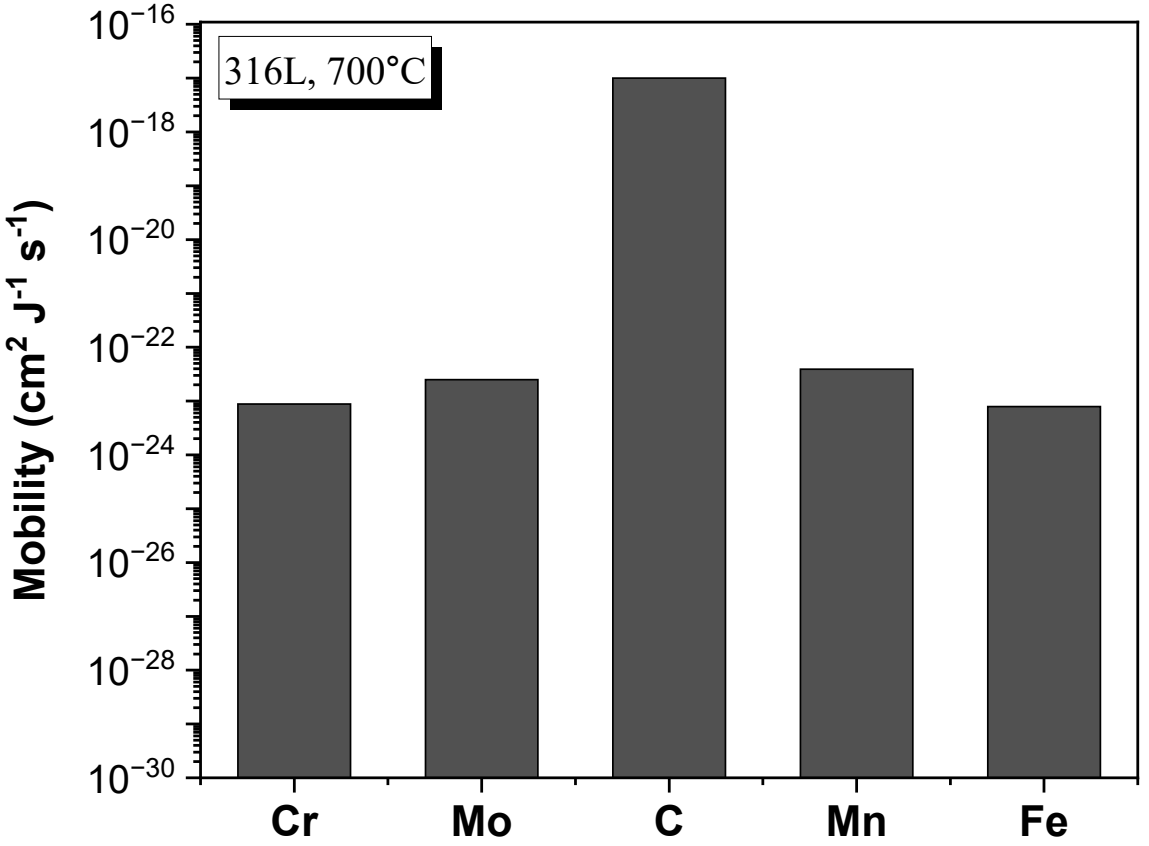




What is the impact of these compositional changes on the phases in the alloy?

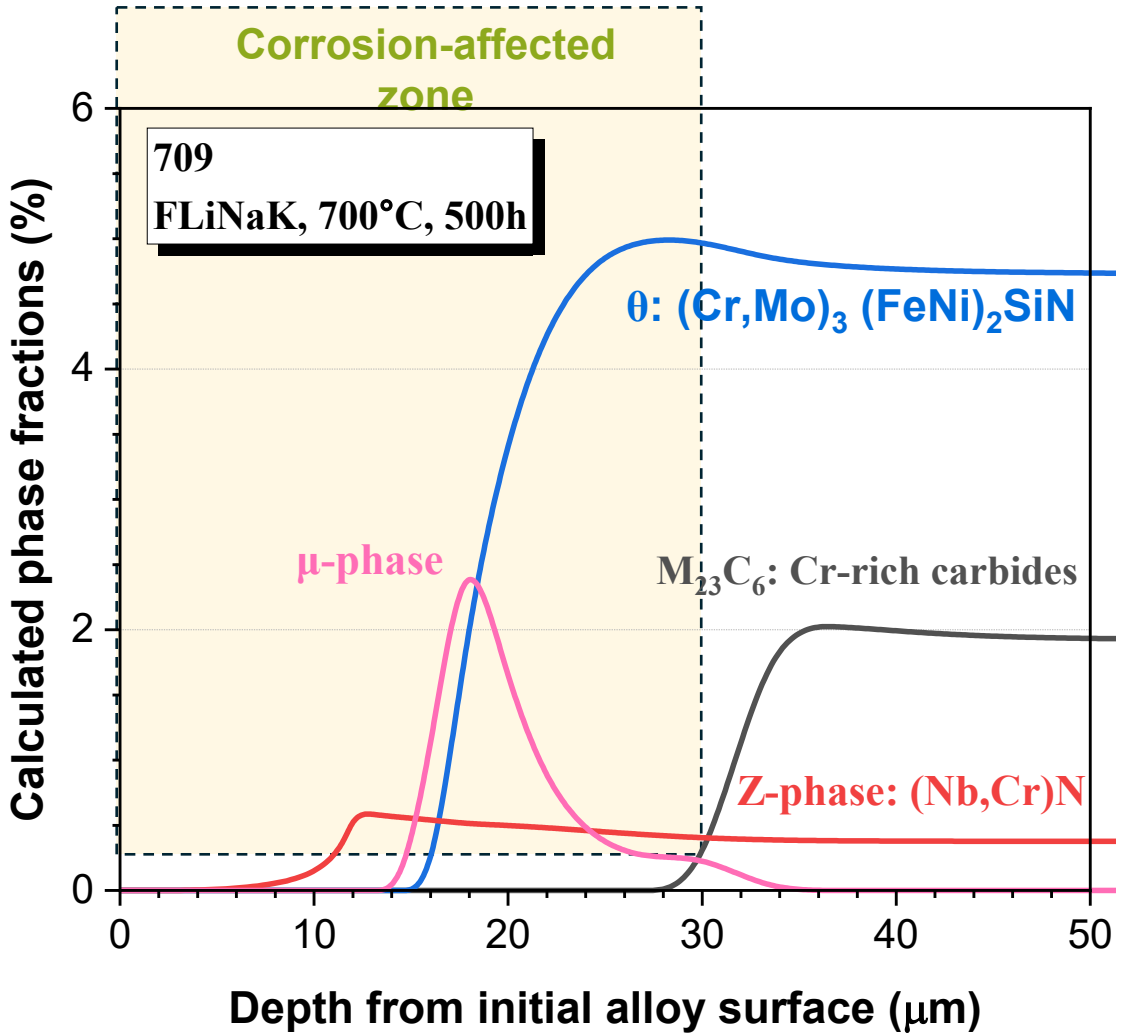
Corrosion-induced Cr depletion increases subsurface C activity and drives it back to the specimen center





C diffuses ~4 orders of magnitude faster than substitutional elements and will govern phase stabilities

Predicted phase distributions suggest the precipitation of the μ–phase in the corrosion-affected zone



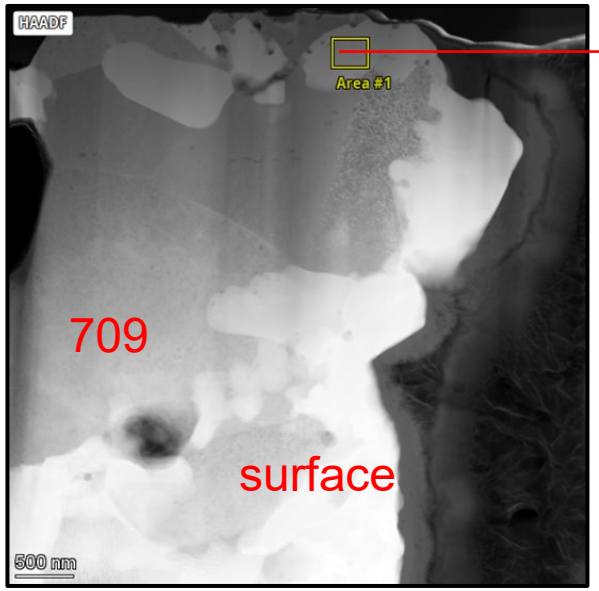
- Cr dissolution ↑ C and N activity

  → *Back diffusion of C and N to the alloy center*

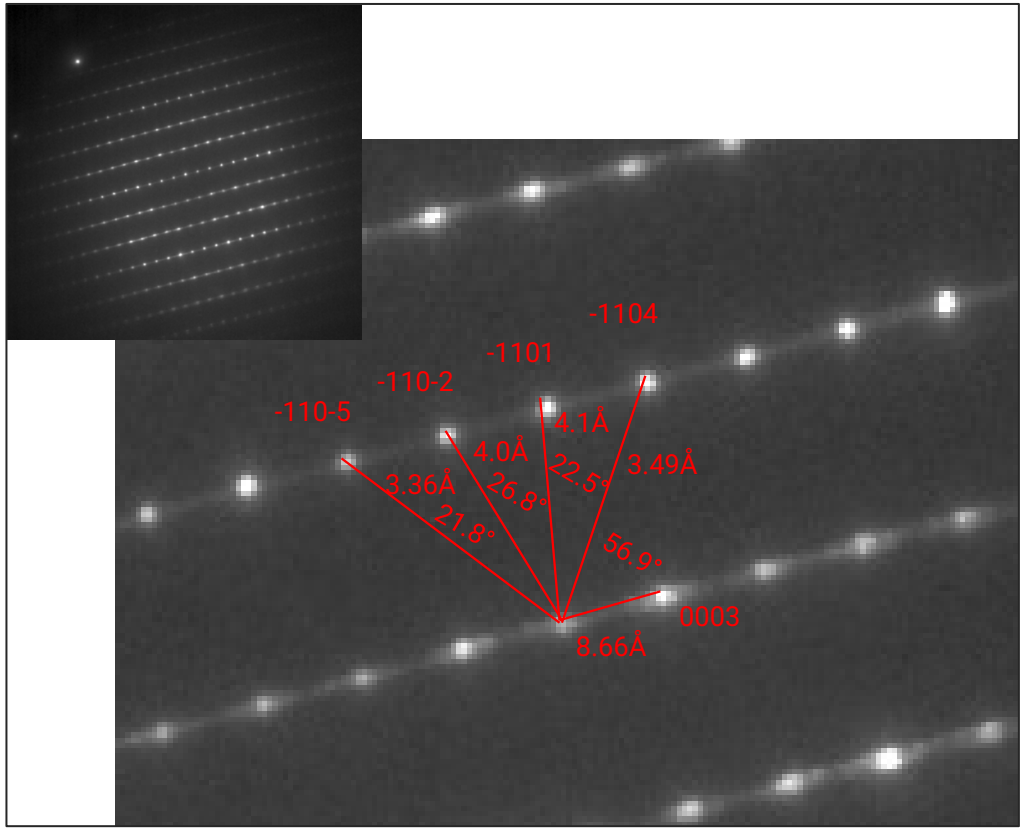
  → ***Dissolution of Carbides, θ and Z-phase***

- **Simultaneous enrichment of Mo stabilizes μ-phase**

Compositional analyses and selected area diffraction confirm the presence of the μ-phase



Element	at%
C	0
N	0
O	2.35
Si	0.38
Cr	0.94
Mn	0
Fe	40.35
Ni	10.72
Nb	0.31
Mo	44.81
W	0.15

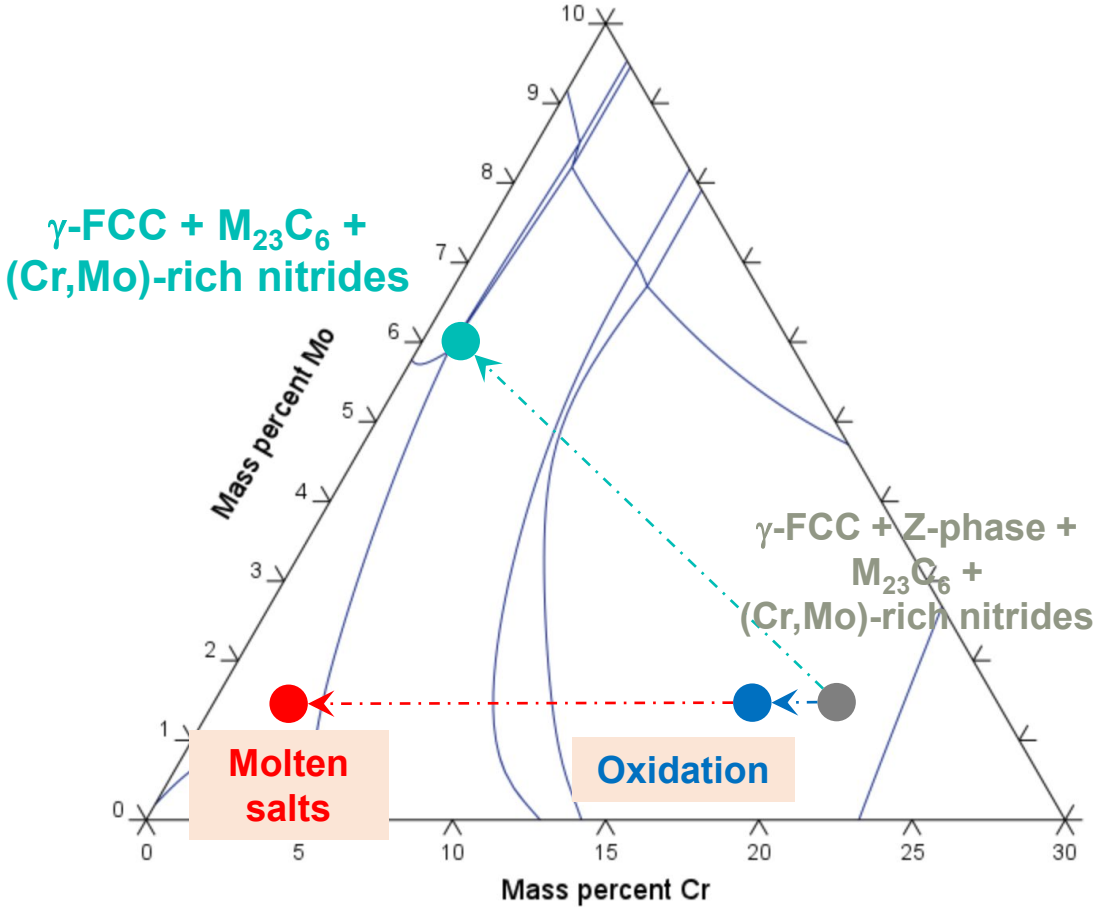


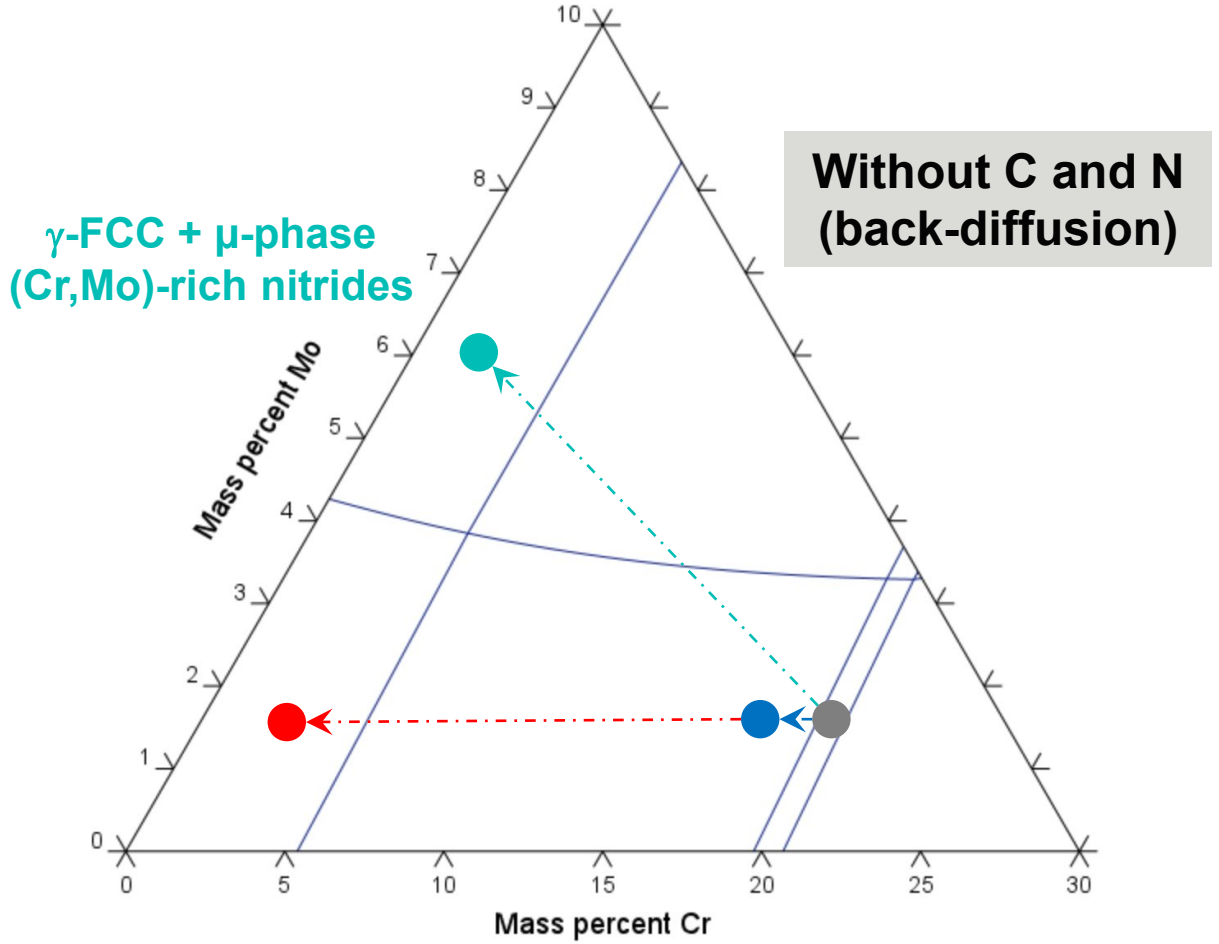
μ-phase structure
d_{0003}=8.66Å
d_{-1104}=3.48Å
d_{-1101}=4.07Å
d_{-110-2}=3.93Å
d_{-110-5}=3.23Å

μ–phase is known to potentially degrade mechanical properties in austenitic materials[1]

[1] Tawancy, J. Mater. Sci., 31, 1996

Pseudo-ternary phase diagram (Fe-Cr-Mo) at 700°C: Significant Cr depletion in molten salts results in distinct phase transformations compared to air oxidation





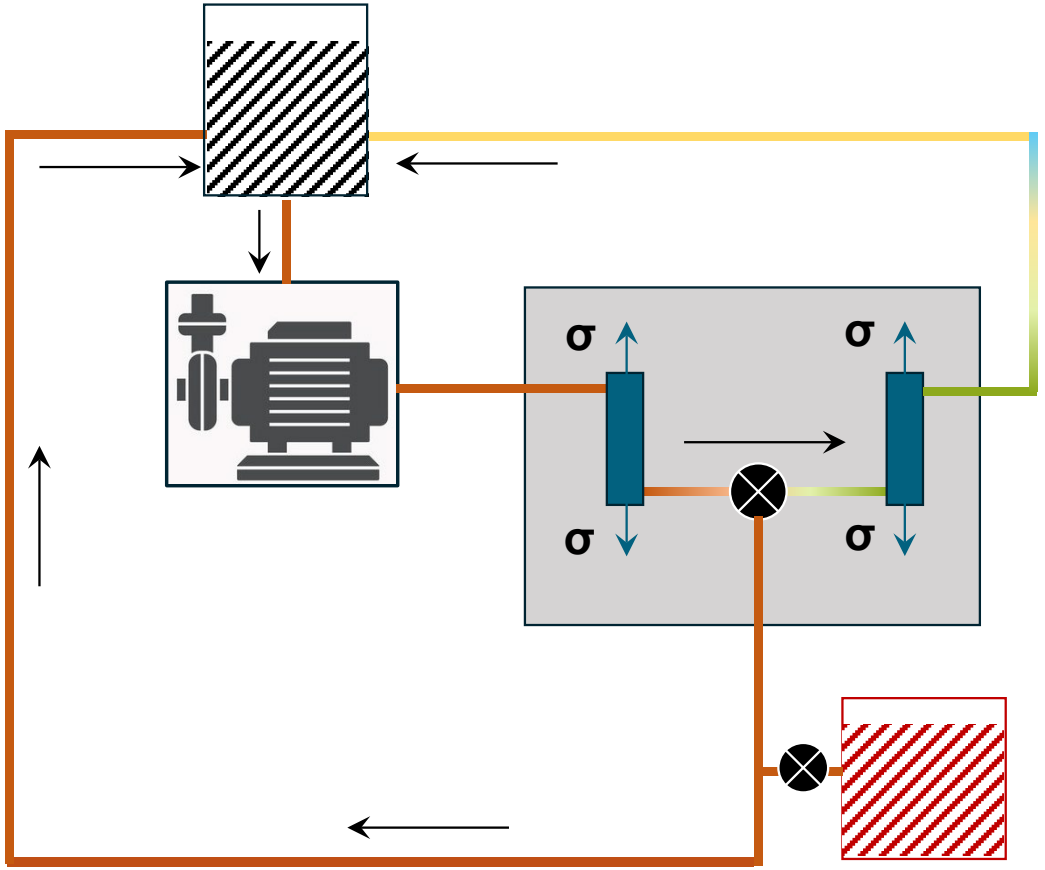
Simultaneous dissolution of strengthening phases might be having a compounding effect

Continuing gaps

- Longer creep tests (at lower stresses) are needed to provide key data to reactor developers and vendors
- Impact of salt chemistry on creep behavior
- Time dependent evolution of microstructure
- Behavior under flowing conditions?

Continuing FY26 activities and milestones

- **Measure impact of molten halide salt on creep and fatigue behavior of 625**
  - Test specimens being machined for creep and fatigue testing
  - Testing expected to begin in May
- **Establish a test capability to enable the creep testing of candidate materials in flowing molten salt**
  - Design of the Pump system for flowing the salts was completed
  - The pump and other peripherals are expected to arrive in early June
  - System setup is planned to be completed by early July
- **Measure impact of molten halide salt on creep behavior of additively manufactured 316H**
  - Material received end of March and test specimens being machined



- ❑ Creep (Up to 1000°C)
- ❑ **Alloys: wrought 316H**
- ❑ **Environments: FLiNaK**

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