



Corrosion mitigation strategies in TES utilizing molten salts and liquid metals

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A. Bonk, T. Bauer, M.C. Galetz

Acknowledgements



RAISELIFE (Raising the Lifetime of Functional Materials for CSP technology)

LIMELISA (Liquid Metal and Liquid Salt Heat Storage System)



Funding Horizon 2020
Grant No: 686008



Funding BMWK
03EE5050A

Components' and Materials' Performance for Advanced Solar supercritical CO₂ Powerplants

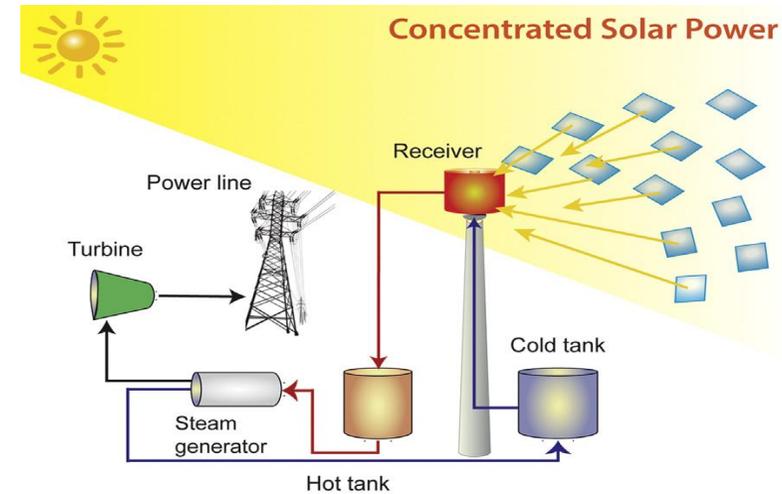


Funding Horizon 2020
Grant No: 958418

Molten salt based TES: CSP plants



Noor Power Station (580 MW) in Ourzazate, Morocco
Second largest plant in the world
Construction cost: 9B USD [SolarPACES]



A. Dorcheh & M.C. Galetz, *Sol. Energ. Mat. Sol. Cells* 146 (2016)

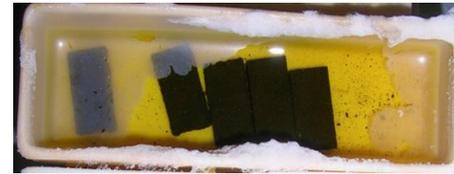
Superhot molten salts leak at giant solar plant to cost owner \$47m

Container holding superheated salt used to store energy has burst at CSP facility, causing outage that will last until November

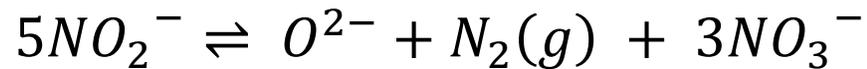
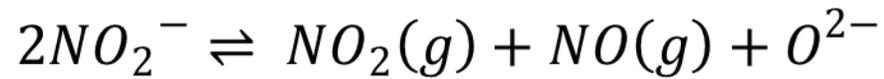
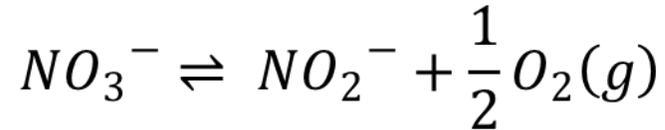
Published 25 March 2024, 11:53 [Recharge News]

- Current trend: Central tower systems with thermal energy storage (TES) via molten salts
- State of the art: Solar salt (60 wt.% NaNO_3 – 40 wt.% KNO_3)
- \approx 10 hours of thermal energy storage \rightarrow higher flexibility
- **Higher corrosion rate for structural materials compared to direct steam generators (DSG)**

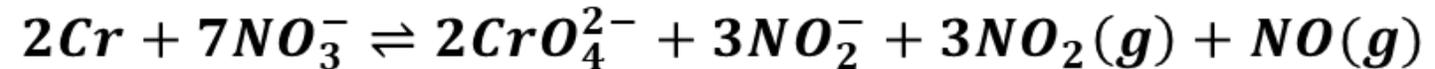
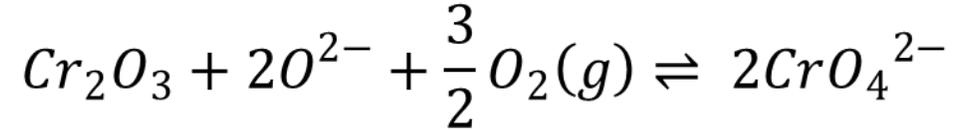
Corrosion in molten nitrates



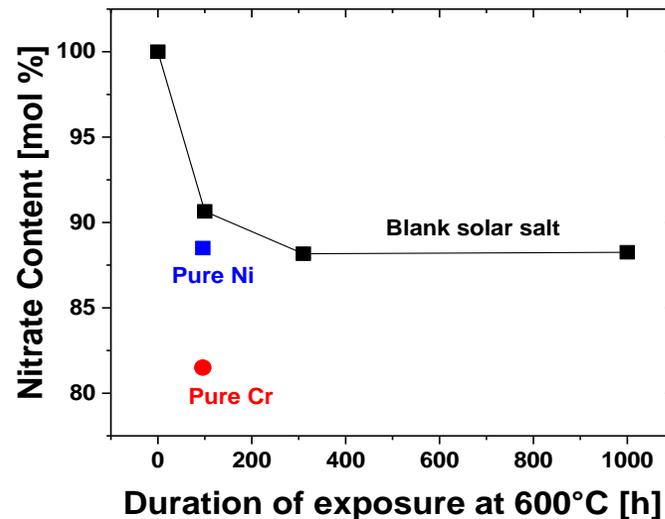
Decomposition of nitrate salts [1]



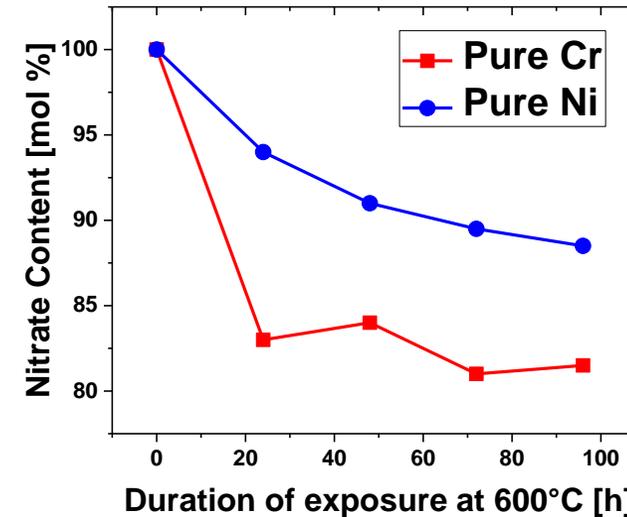
Dissolution of Cr [2]



Anion chromatography conducted at DLR



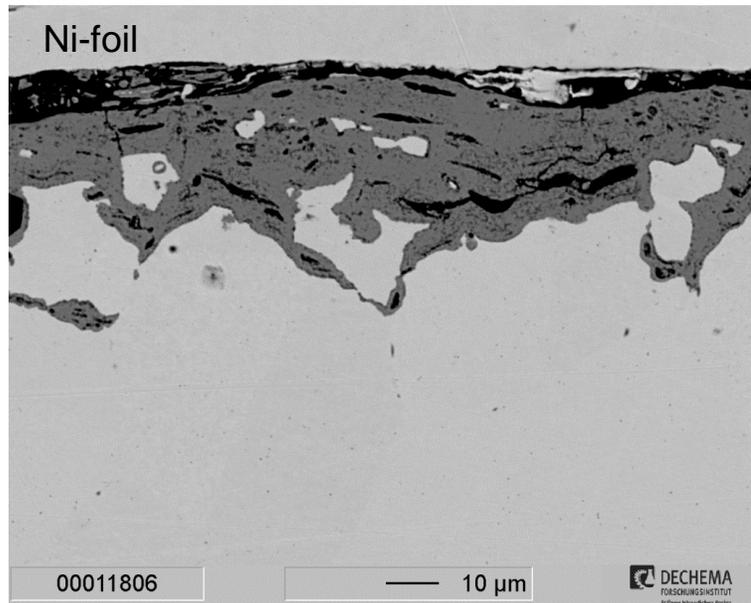
Anion chromatography conducted at DLR



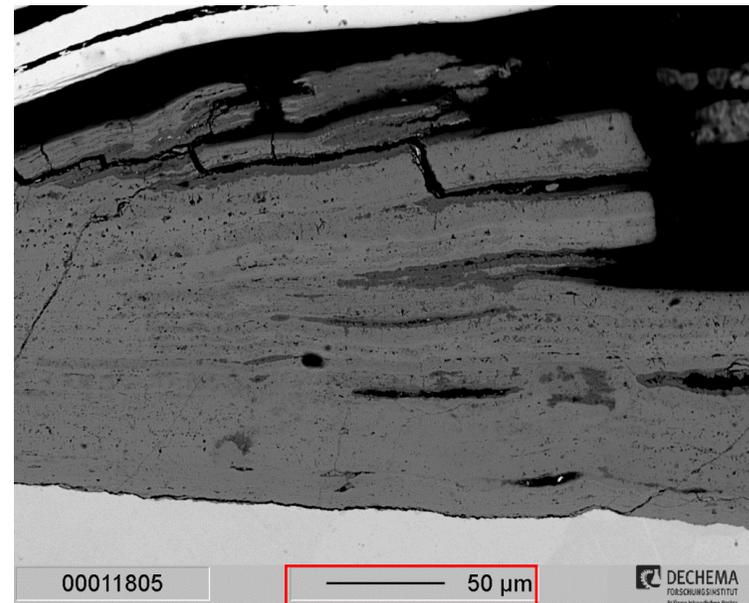
Pure metals in molten nitrate salts

After 98 hours of immersion in molten solar salt at 600°C

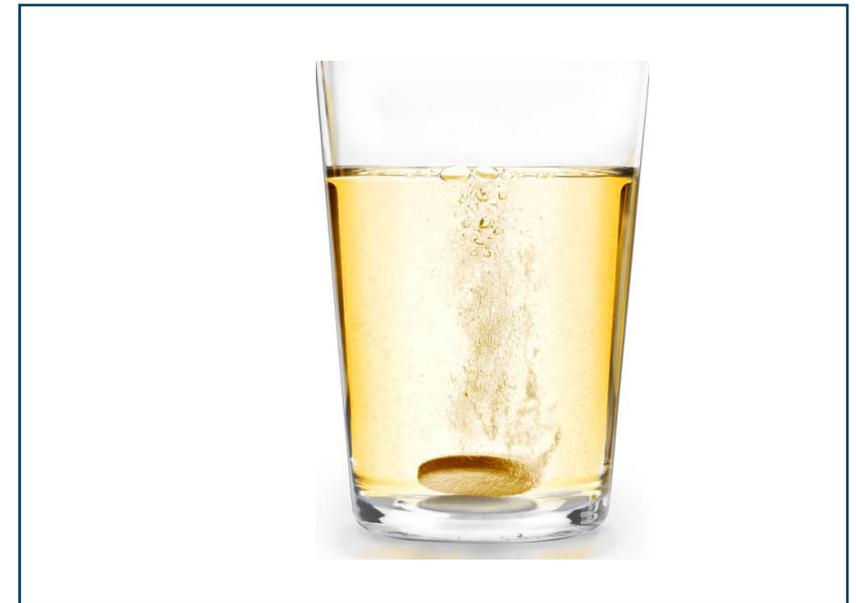
Pure Ni (>99.8 %)



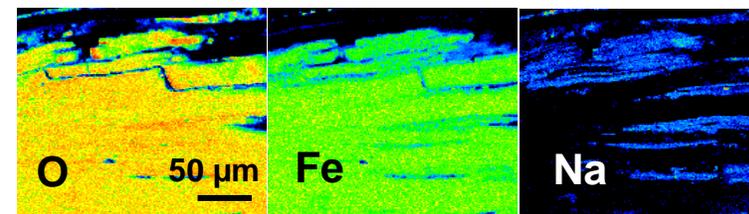
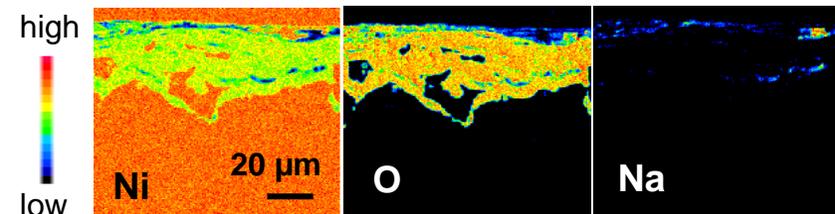
Pure Fe (>99.8 %)



Pure Cr (>99.9 %)

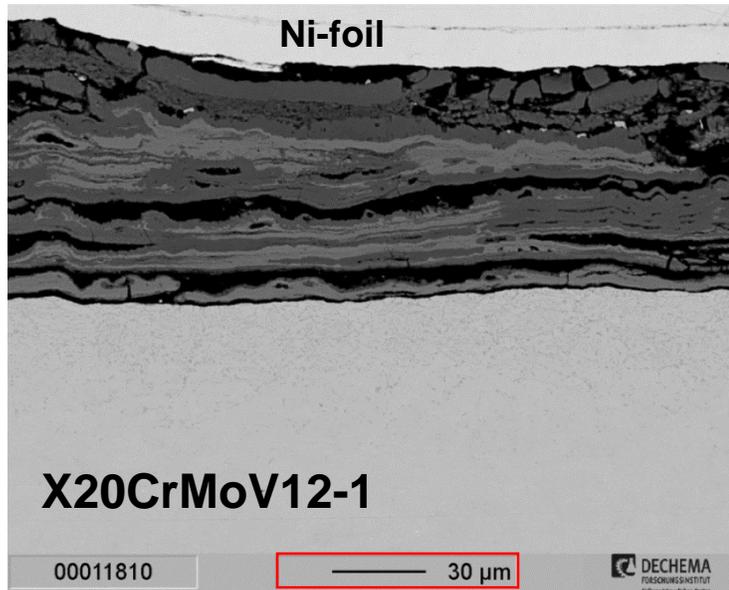


Sample completely dissolved after a few hours

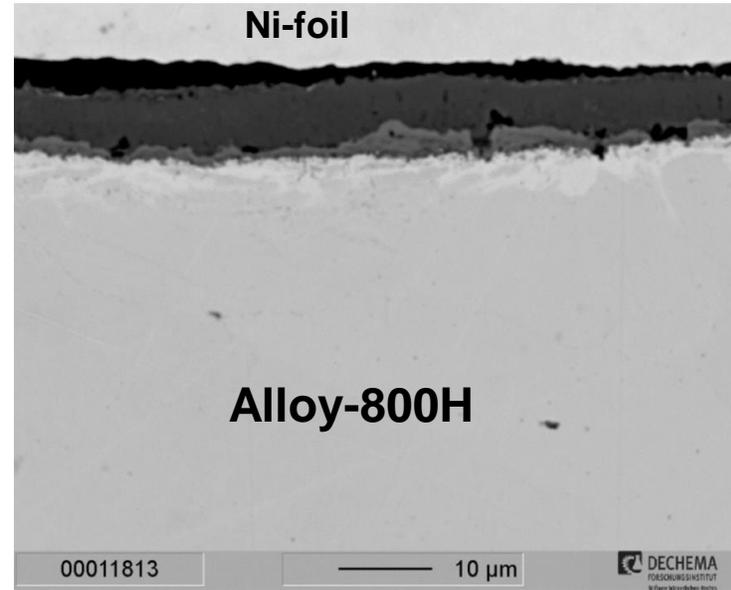


Corrosion behavior of commercial alloys

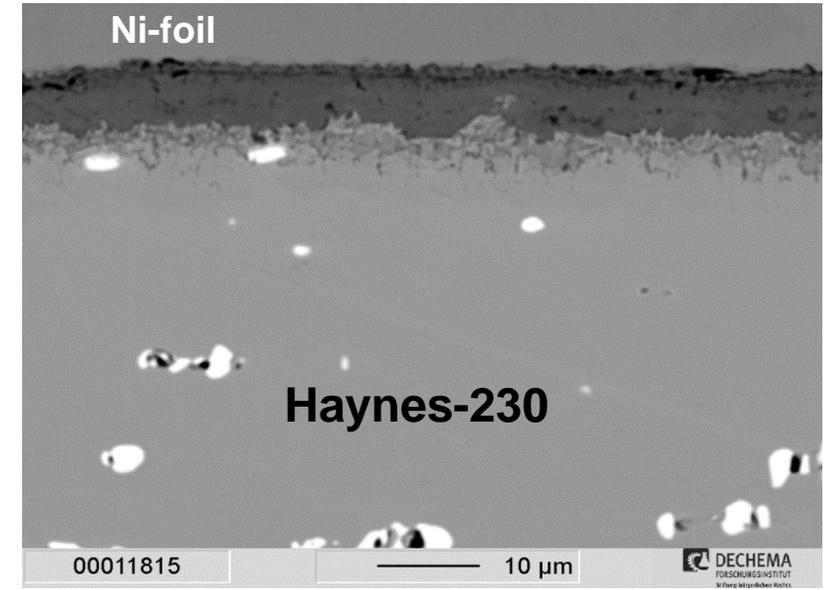
After 1000 h of immersion in solar salt at 600°C



Martensitic steels



Austenitic steels

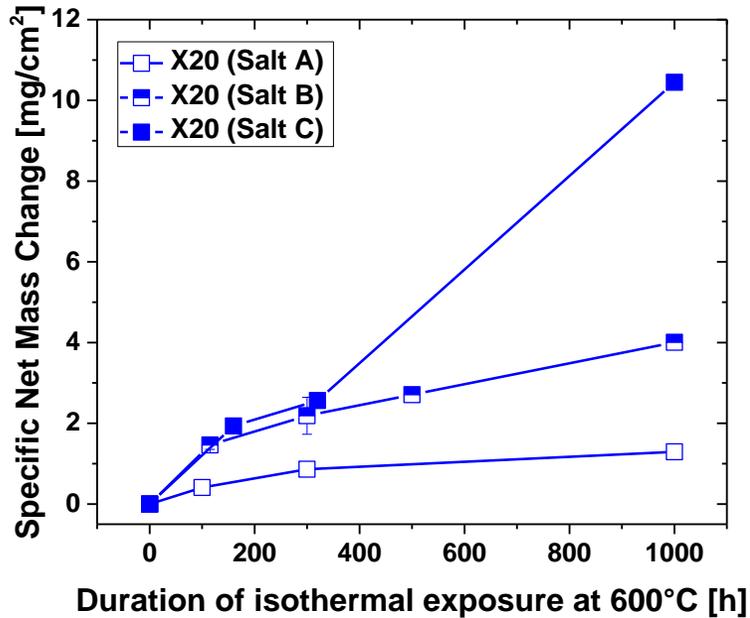


Ni-based alloys

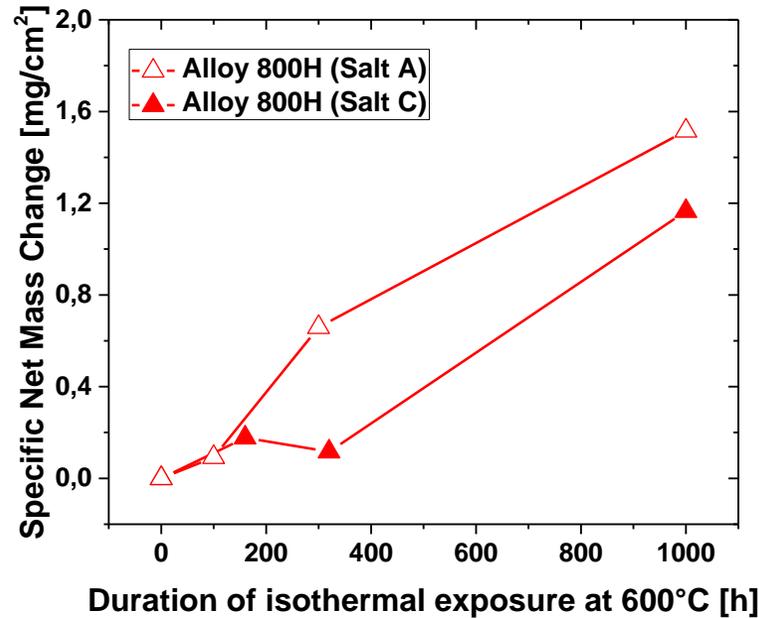
Increasing Ni-content, price and corrosion resistance

Influence of chloride impurities

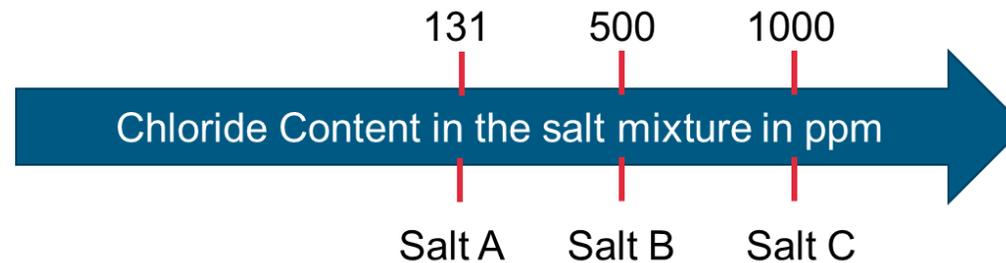
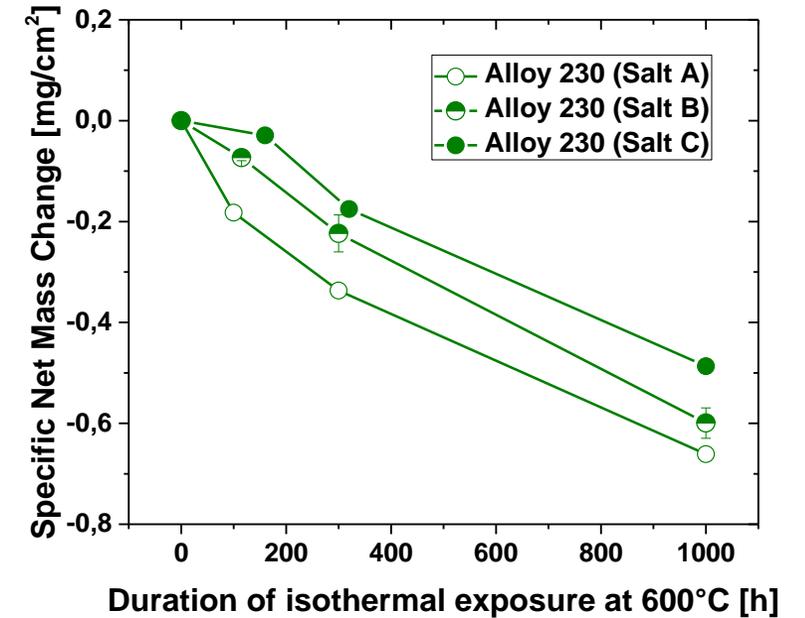
X20CrMoV12-1



Alloy 800H

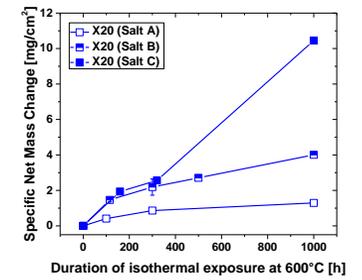


Alloy 230

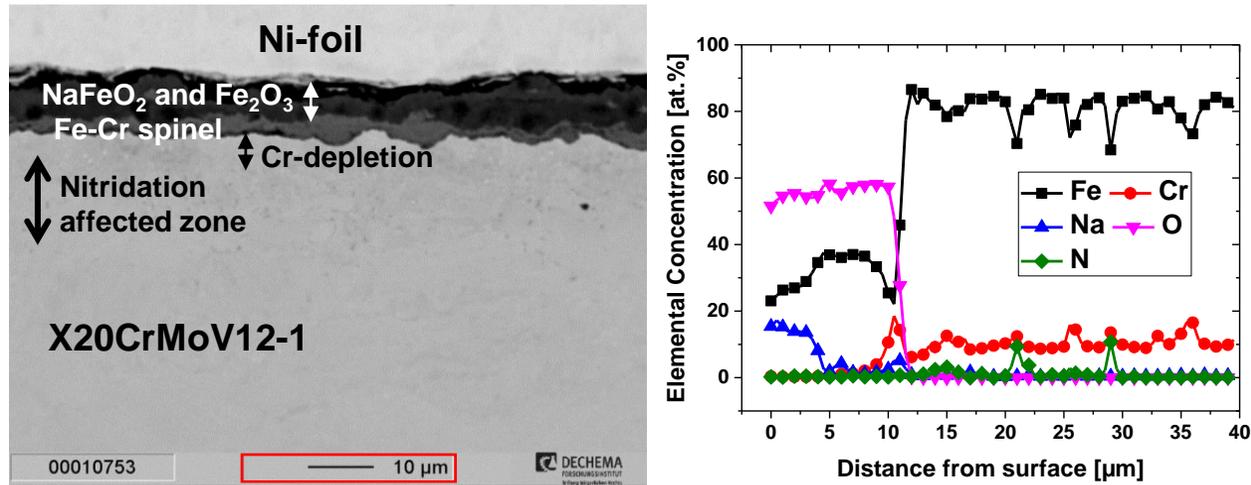


X20CrMoV12-1

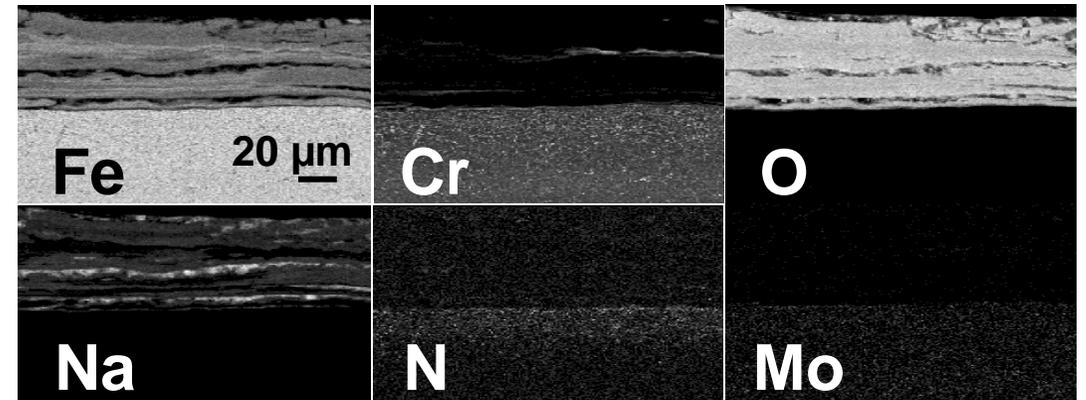
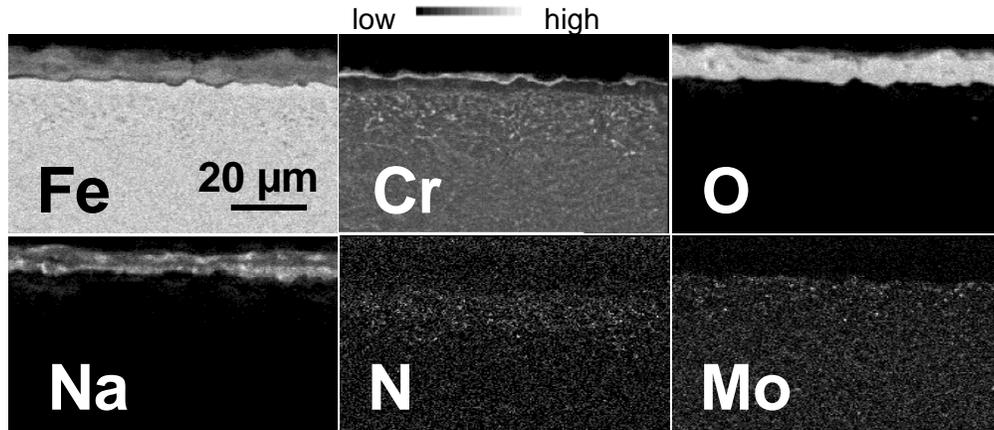
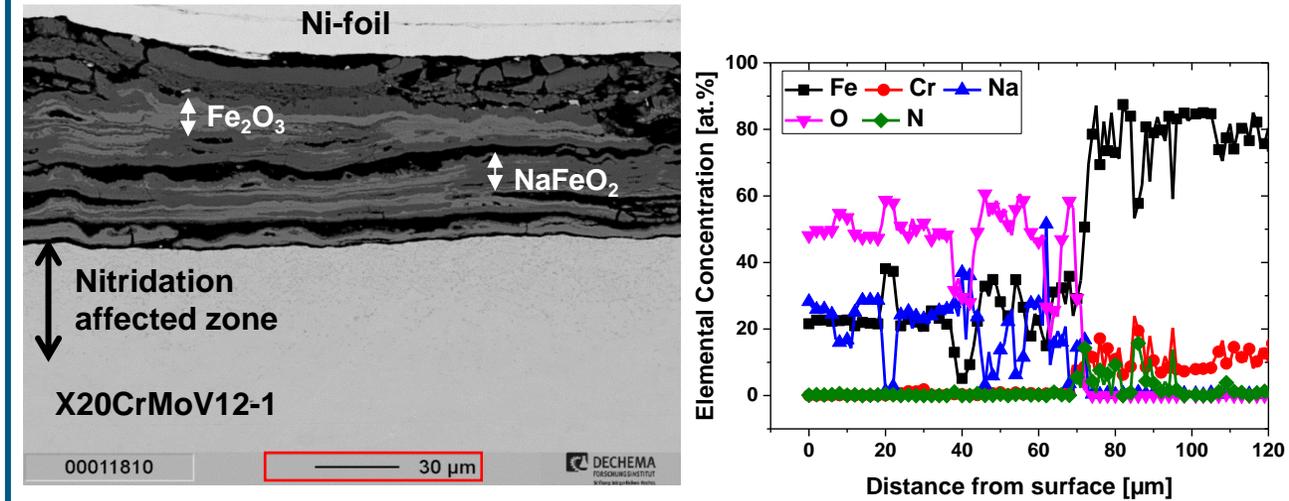
Static immersion at 600°C for 1000 h



Salt A (131 ppm Cl⁻)

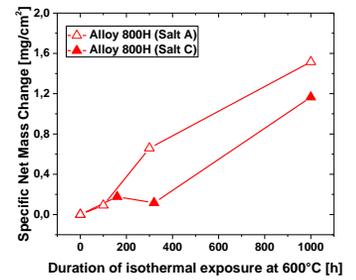


Salt C (1000 ppm Cl⁻)

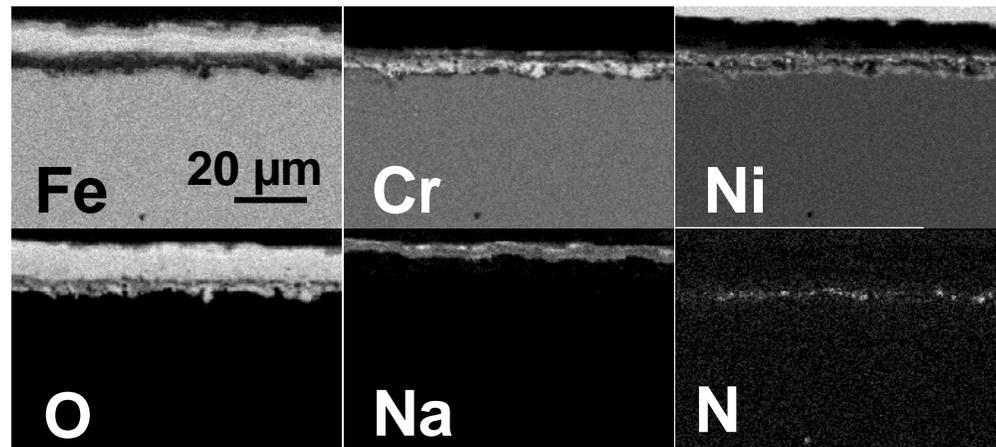
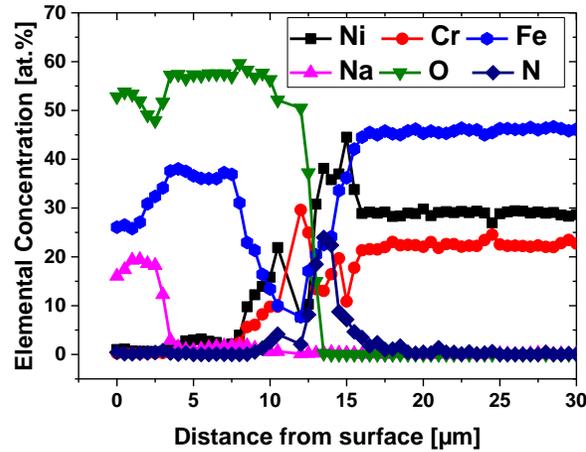
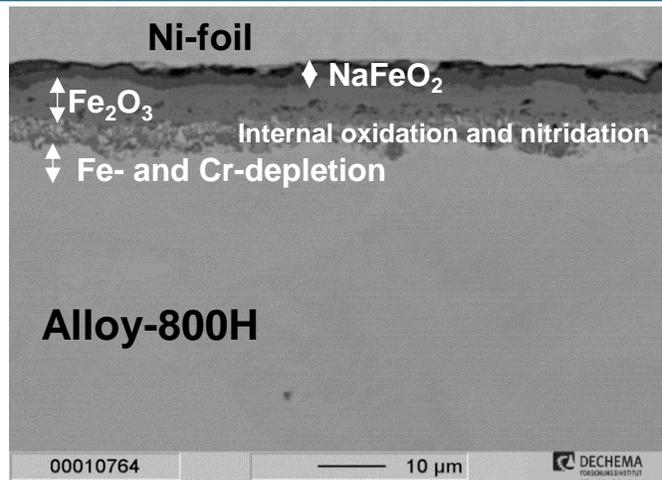


Alloy-800H

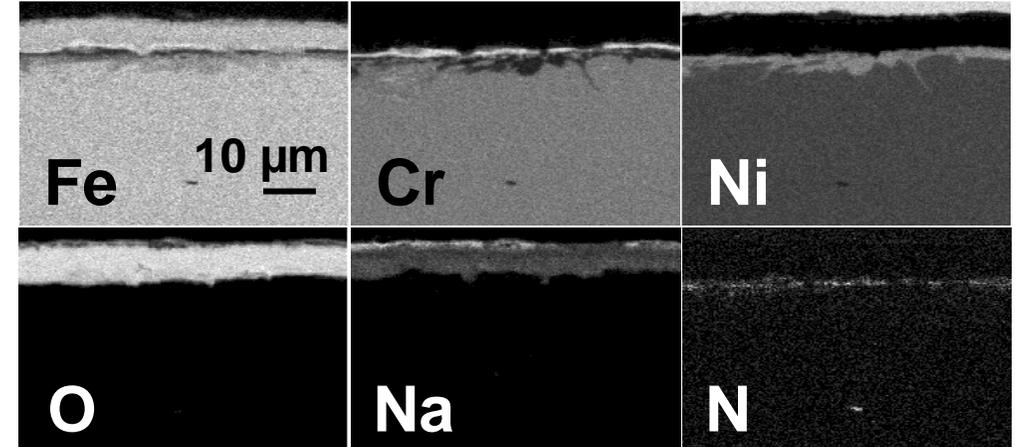
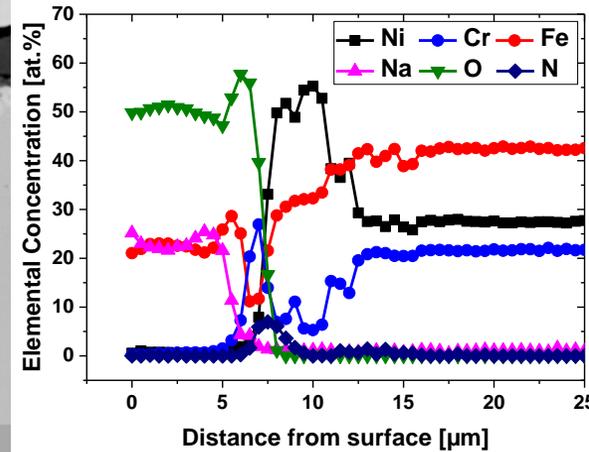
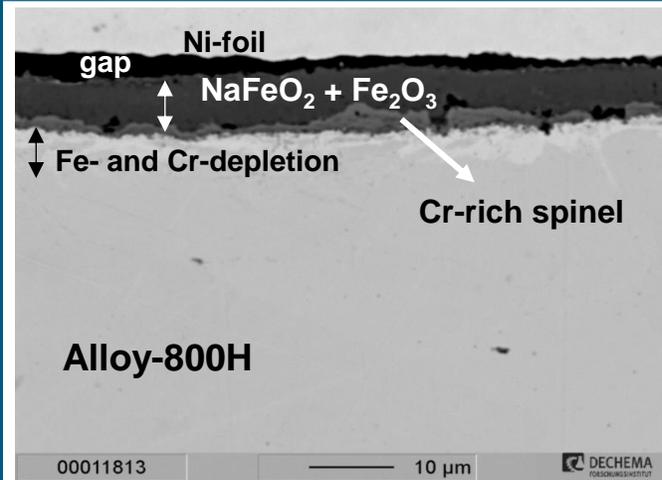
Static immersion at 600°C for 1000 h



Salt A (131 ppm Cl⁻)

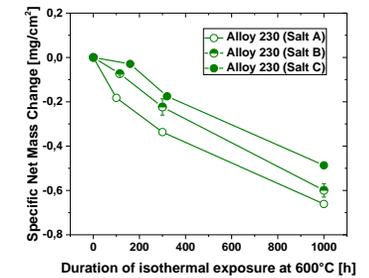


Salt C (1000 ppm Cl⁻)



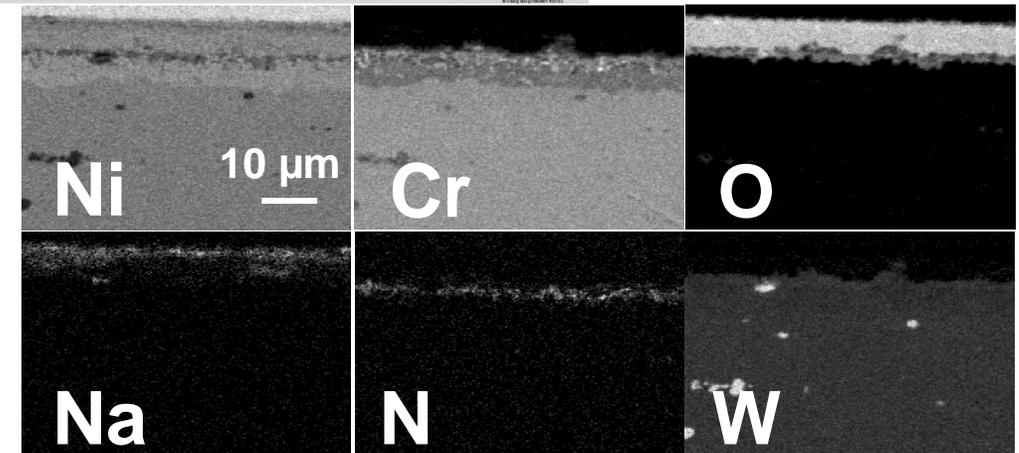
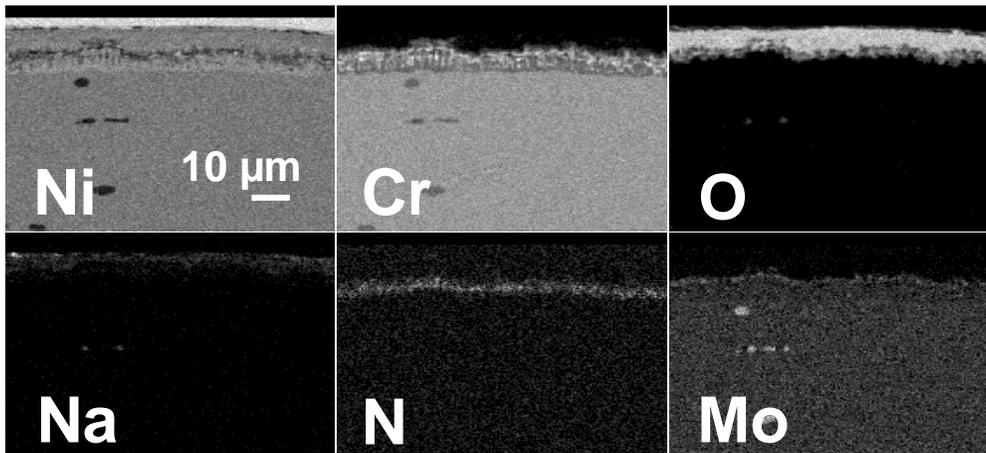
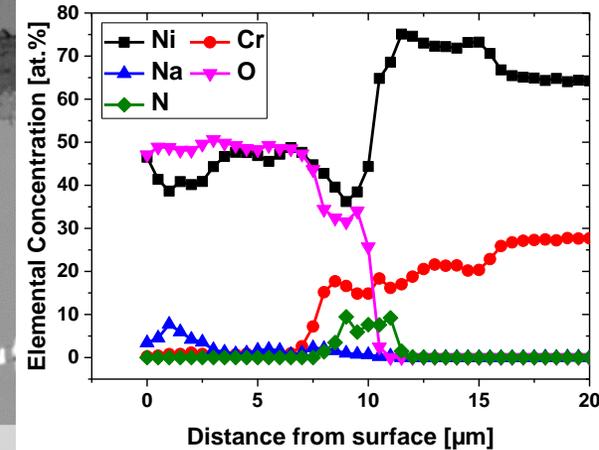
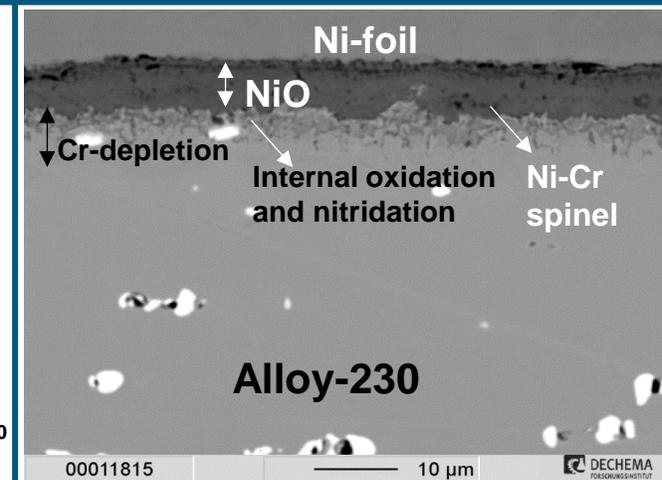
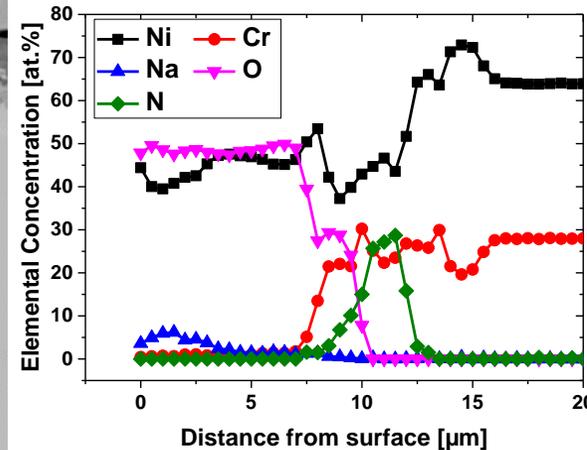
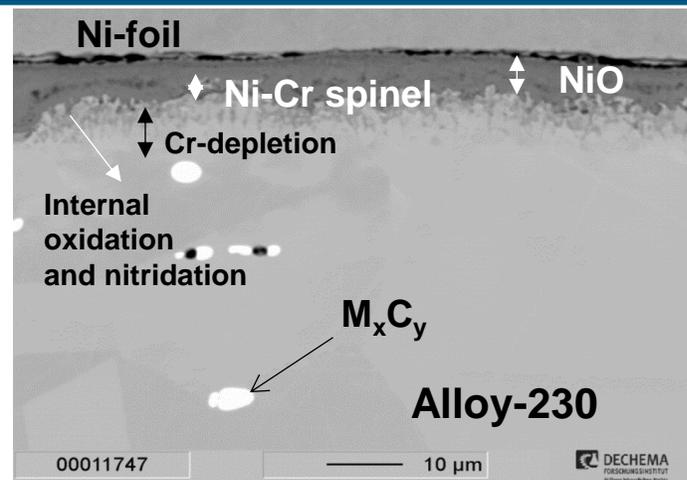
Alloy-230

Static immersion at 600°C for 1000 h

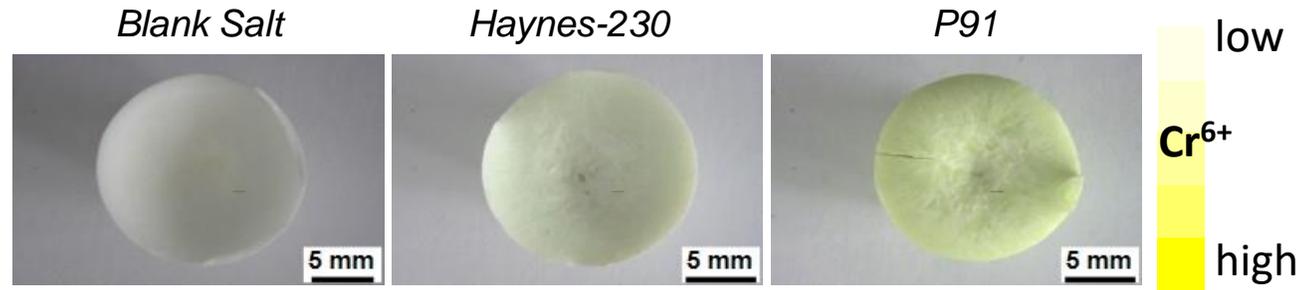


Salt A (131 ppm Cl)

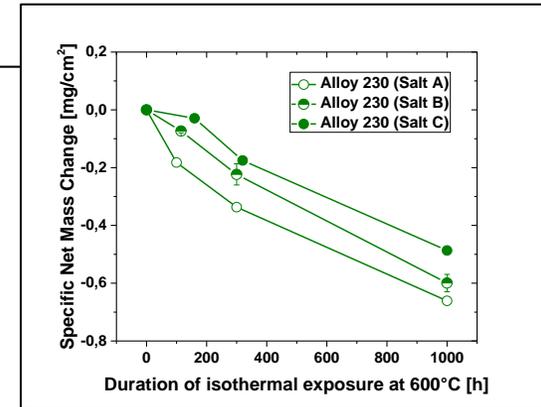
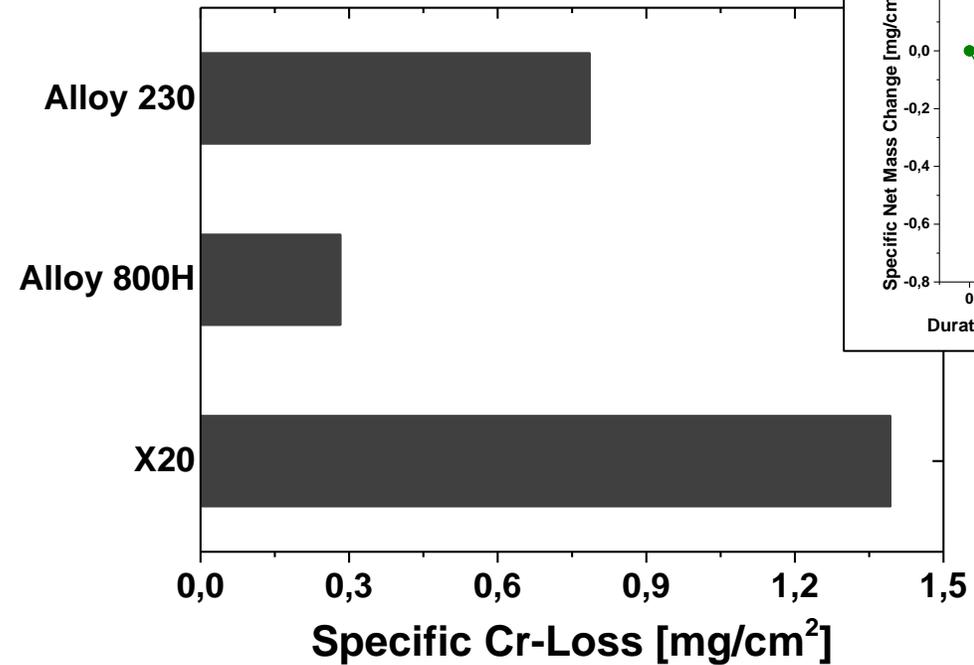
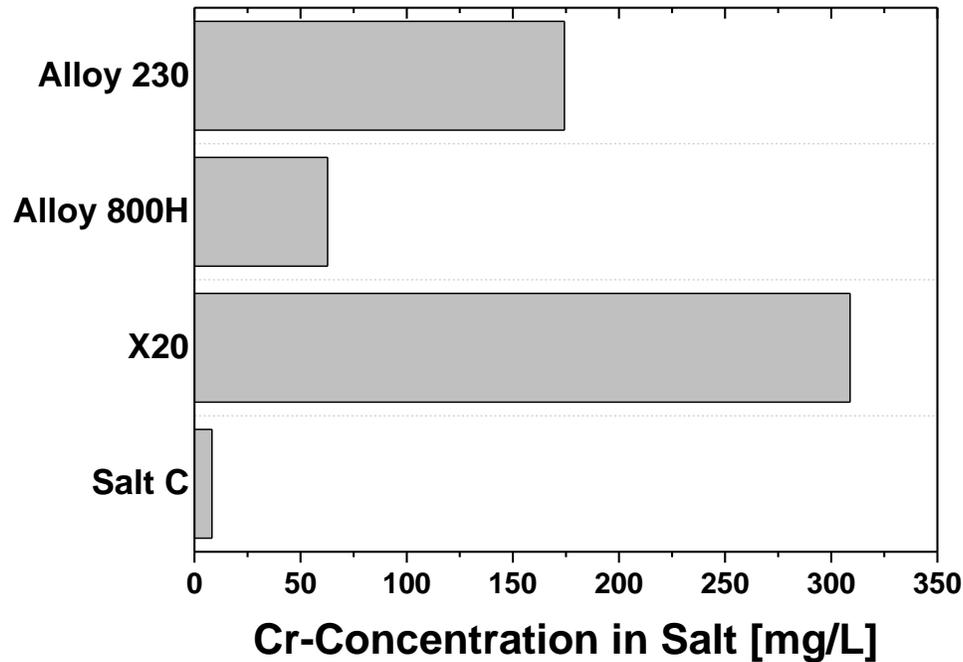
Salt C (1000 ppm Cl)



Cr-Dissolution



After 1000 h exposure in Salt C at 600°C

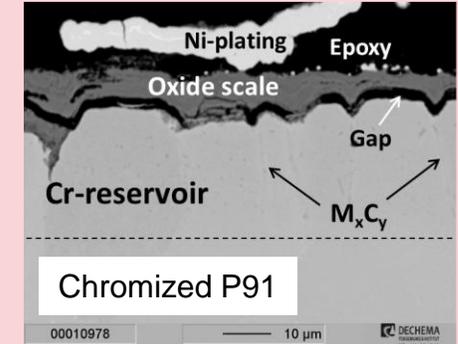
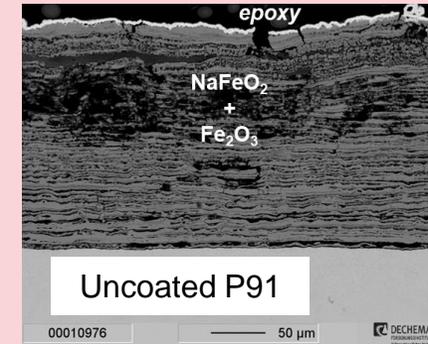


**For Noor power station (580 MW total capacity) → 140k tons of solar salt [ESCF] → ≈ 75k m³
 → 30 olympic swimming pools → 13 kg/h Cr⁶⁺ for Alloy 230 (for 1000 h exposure)**

Coating strategies for molten salt based TES

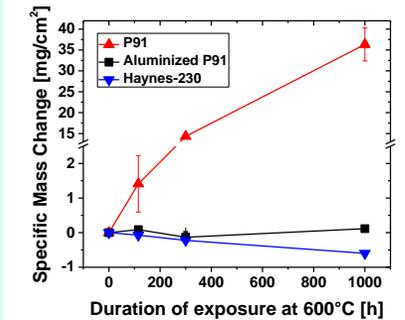
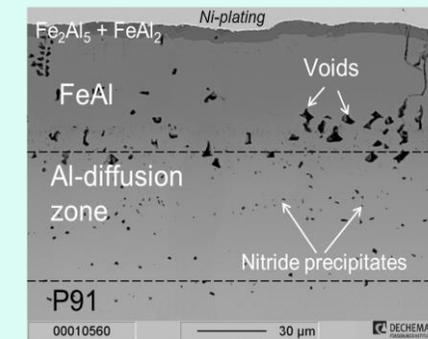
Cr-Enrichment

- ✓ Cr-rich spinel formation → protective behavior
- ❖ Counterproductive for reducing or hindering chromate formation



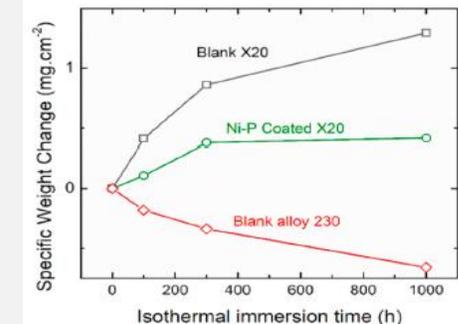
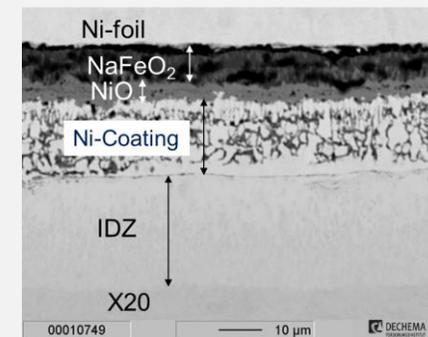
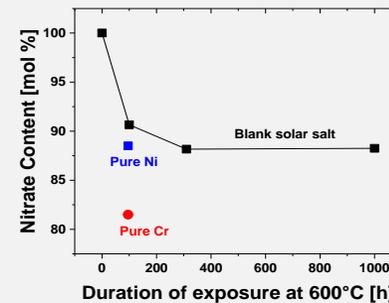
Al-Enrichment

- ✓ Al-rich scales → reducing Cr-dissolution
- ✓ Applicable via pack cementation or slurry deposition
- ❖ Optimization of Al-content necessary



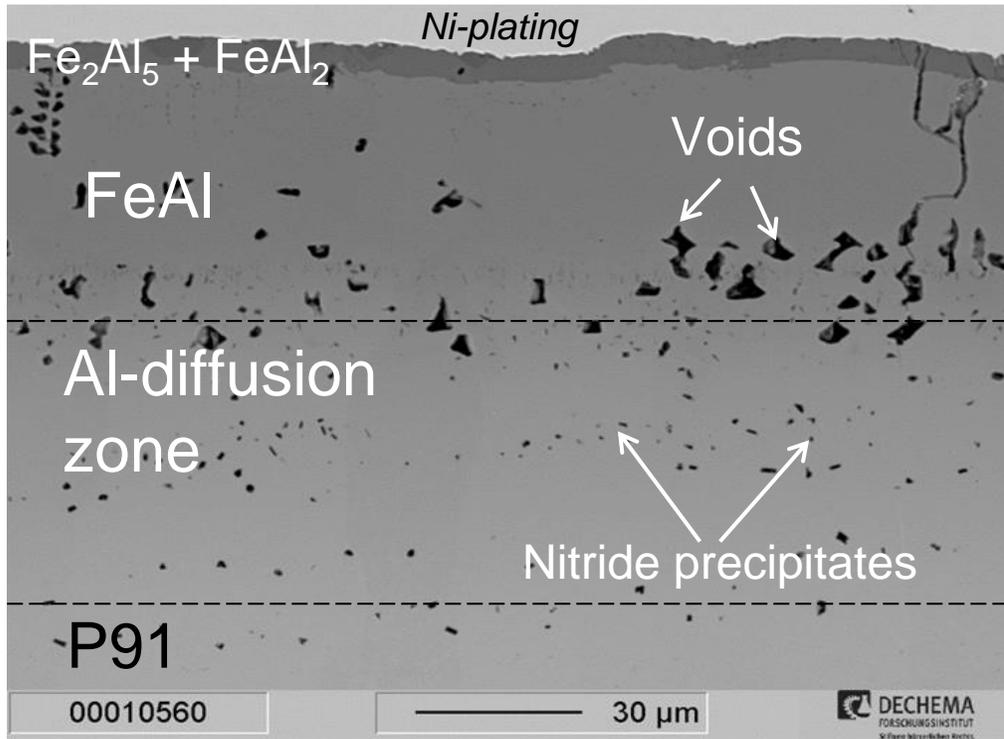
Ni-Enrichment

- ✓ NiO is stable in molten nitrates at these temperatures
- ✓ Applicable via galvanic or **electroless deposition**

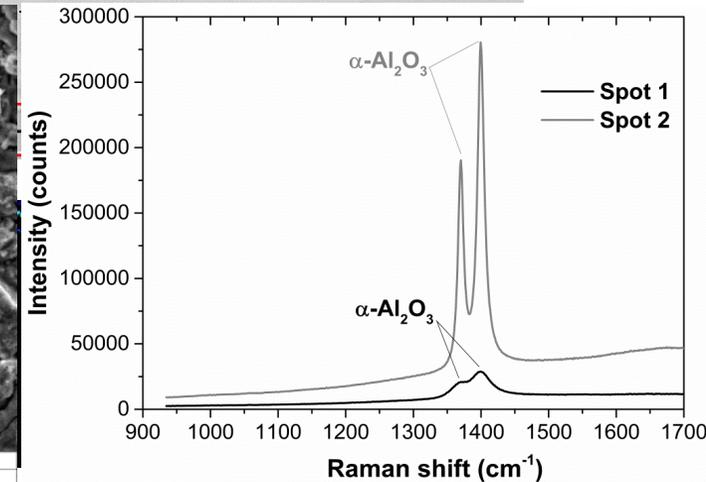
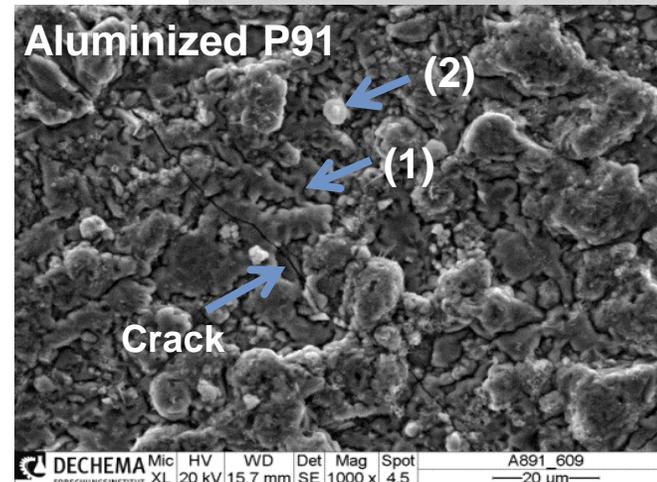
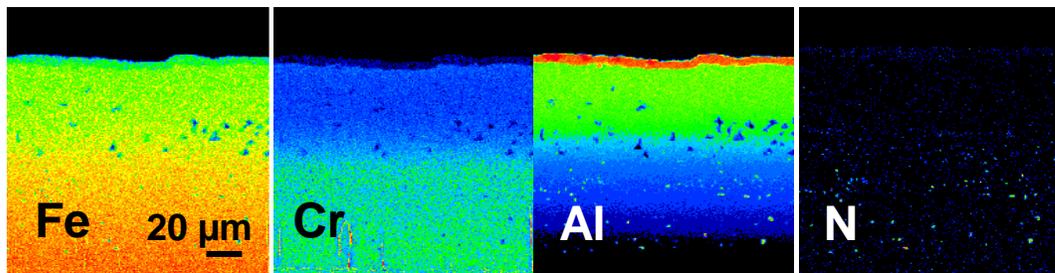
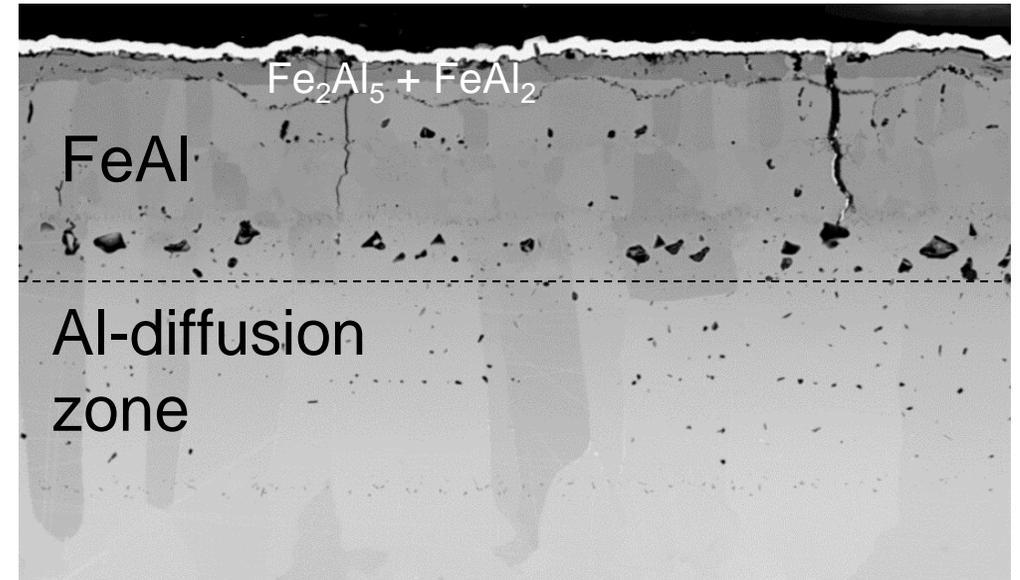


Aluminide diffusion coatings

As-aluminized P91



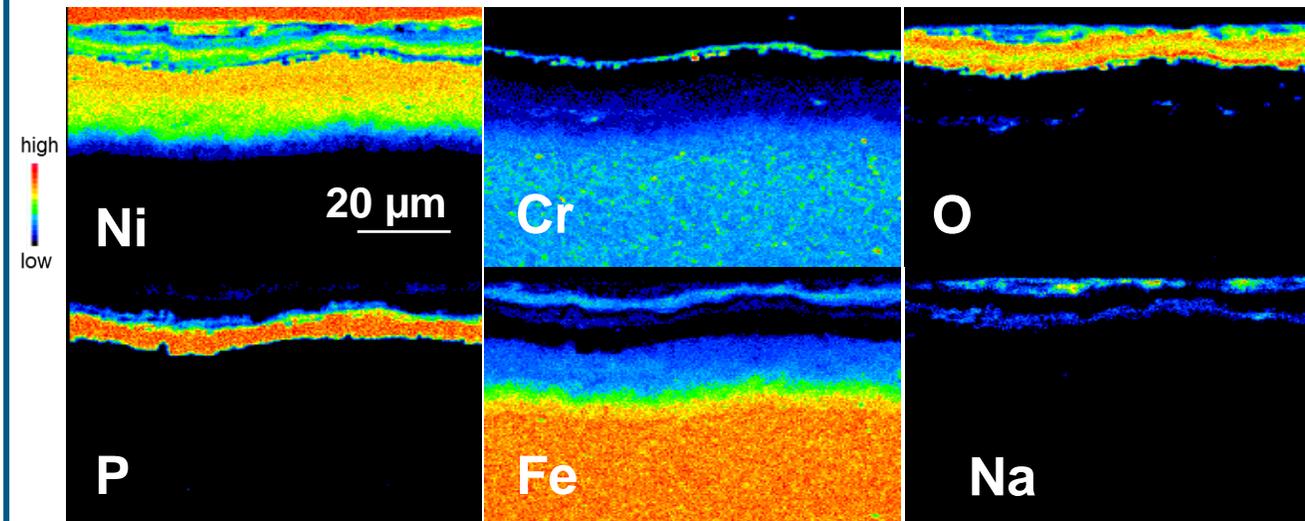
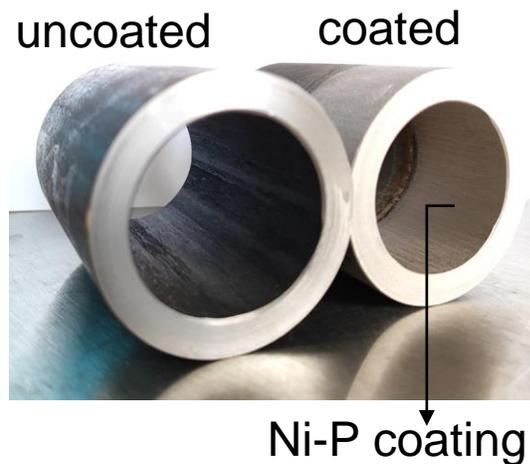
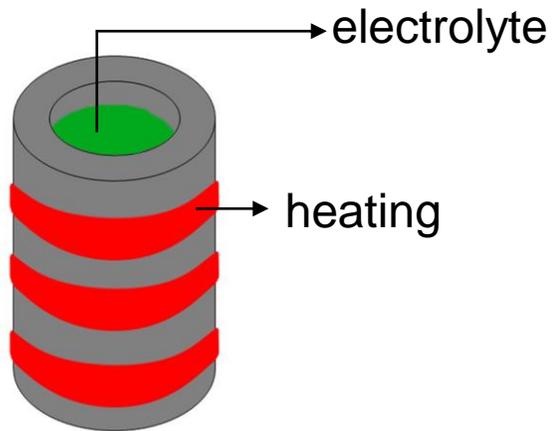
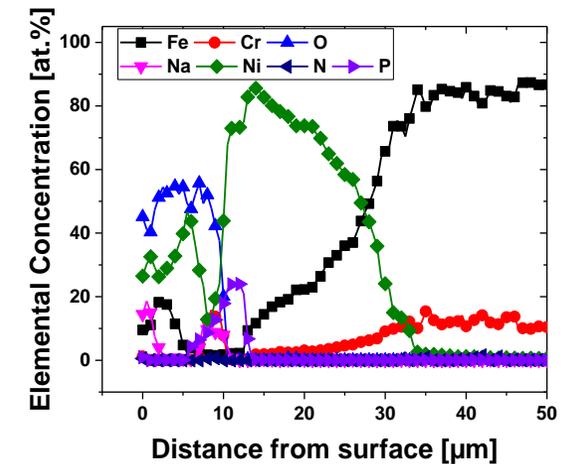
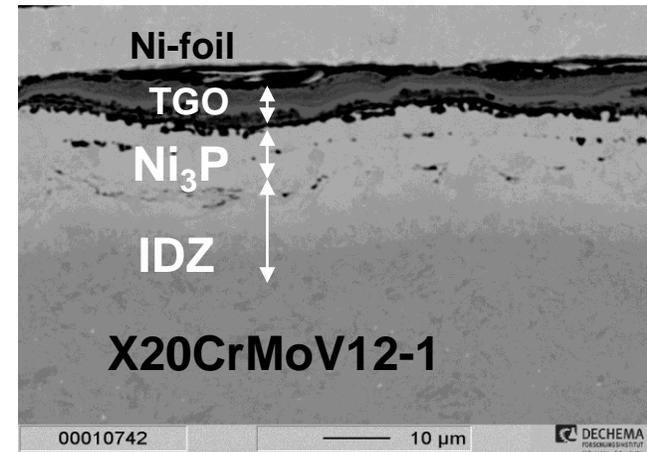
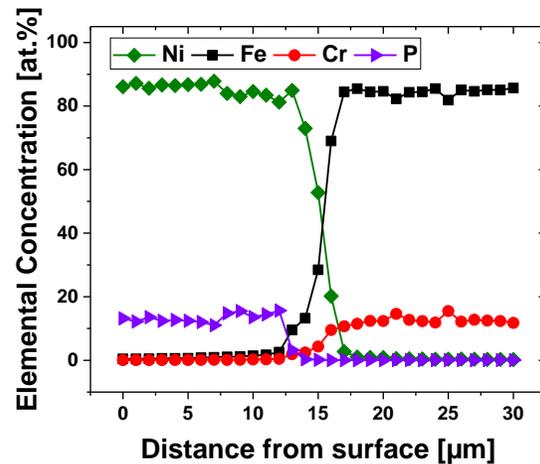
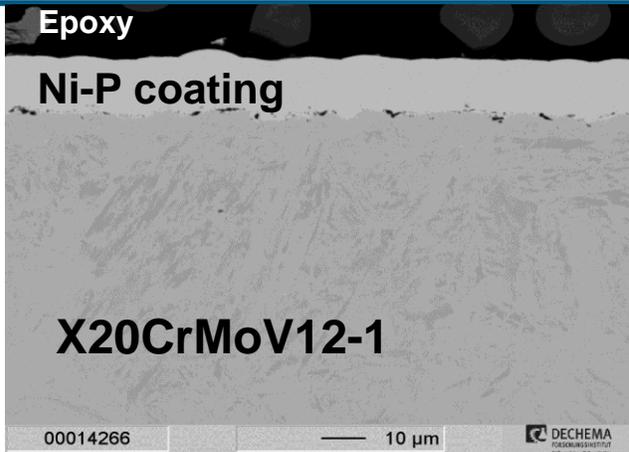
After 1000 h in solar salt at 600°C



Corrosion behavior of Ni-P coatings

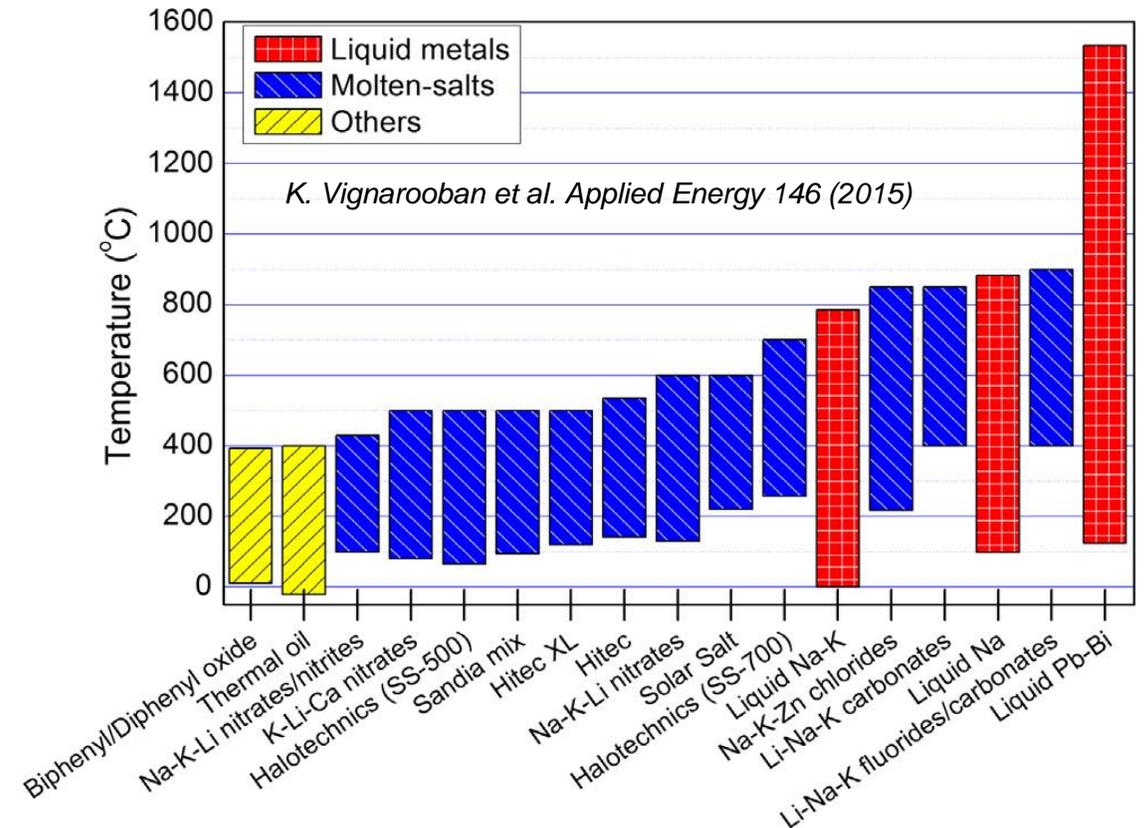
As deposited Ni-P coating

Ni-P coating after 1000 h in Salt C at 600°C



Liquid metal based TES

- State-of-the-art CSP plants with TES → Solar salt (60 wt.% NaNO_3 – 40 wt.% KNO_3 → $T_{\min} > T_{\text{liquidus}} \approx 250^\circ\text{C}$, $T_{\max} < T_{\text{stability}} \approx 570^\circ\text{C}$ → Rankine cycle
- Brayton sCO_2 cycle possible with → Ternary LiNaK carbonates, Ternary NaMgK chlorides or solid particle heat transfer media → higher ΔT
- **Liquid metals such as Na, Pb or Pb-Bi as heat transfer media → higher ΔT**



Liquid Pb based TES

Pros

Abundant and relatively cheap ≈ 2 USD per kg (LME)

Low melting temperature (327°C)

High boiling temperature (1749°C)

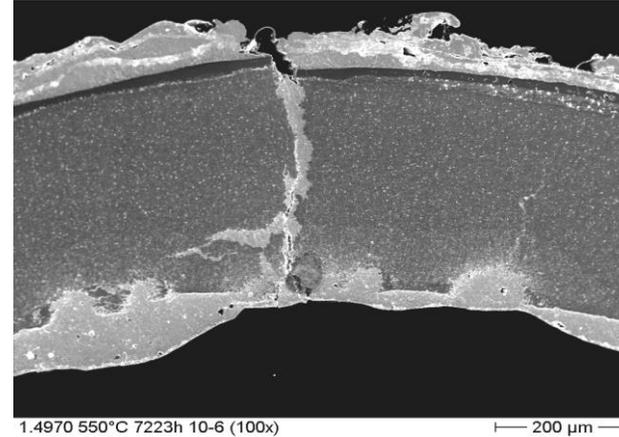
No intense reactivity with water or air

Cons

Toxic

High density $\approx 11.4 \text{ g/cm}^3$

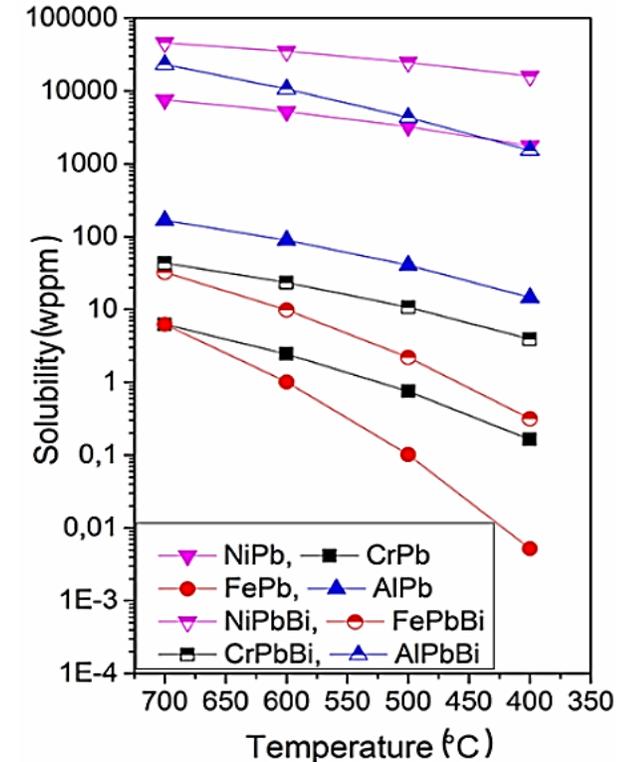
Corrosion in molten Pb \rightarrow selective dissolution attack



Severe dissolution of alloying elements (Ni)
Dissolution rate up to $1 \mu\text{m/h}$

Mitigation strategies

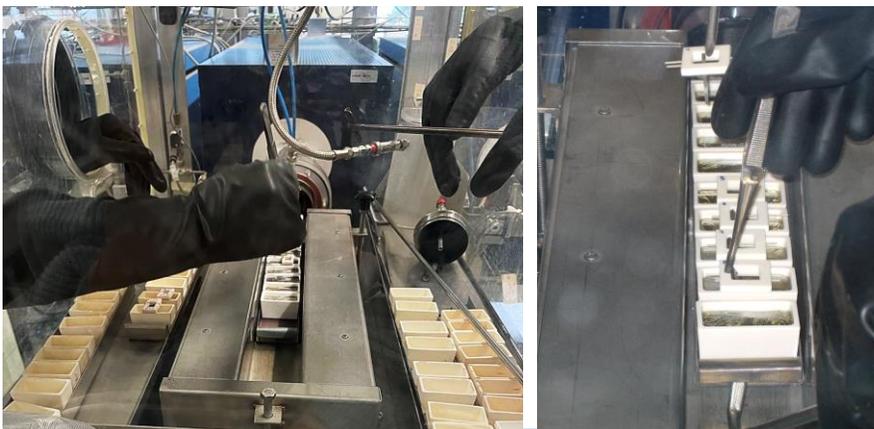
- Utilization of W, Mo \rightarrow Oxidation
- Tolerable corrosion rate
- Ni-free materials \rightarrow Mechanical considerations
- Alumina formers



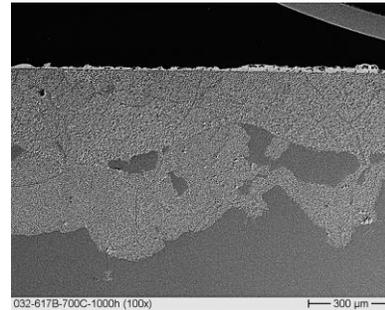
Solubility of alloying element in molten Pb:
Ni > Al > Cr > Fe

Corrosion behavior in liquid Pb

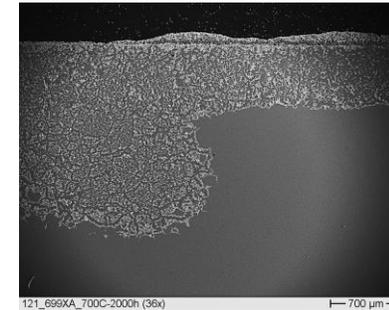
*COSTA Testing Facility at the IHM Institute,
KIT → Stagnant Pb containing 2×10^{-7} wt.% O_2
at 600°C and 700°C for up to 5000 h*



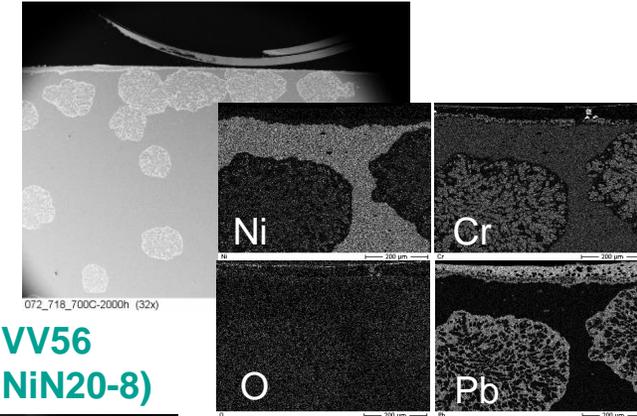
**Alloy 617B
(NiCr23Co12Mo)**



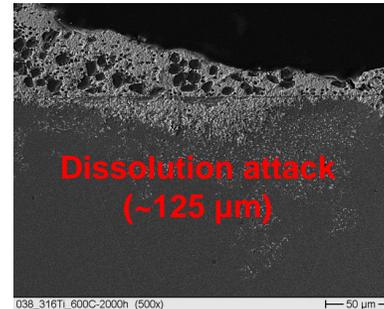
**Alloy 699XA
(NiCr30Al)**



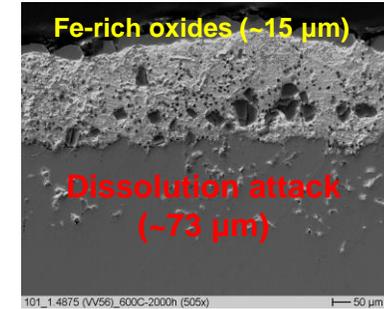
**Alloy 718
(NiCr19Fe19Nb5Mo3)**



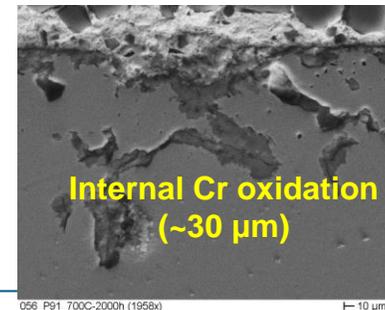
**1.4571 316Ti
(X6CrNiMoTi17-12-2)**



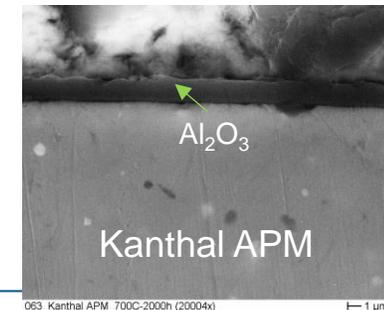
**1.4875 VV56
(X55CrMnNiN20-8)**



P91 (10CrMoVNb9-1)

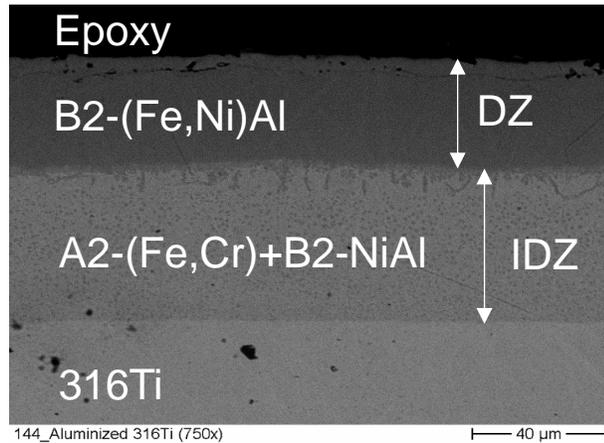


Kanthal APM (Fe22Cr6Al)

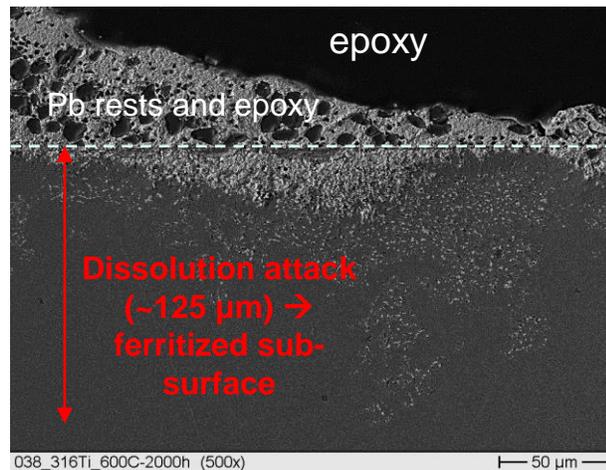


Corrosion mitigation strategies for liquid Pb

As-aluminized 316Ti



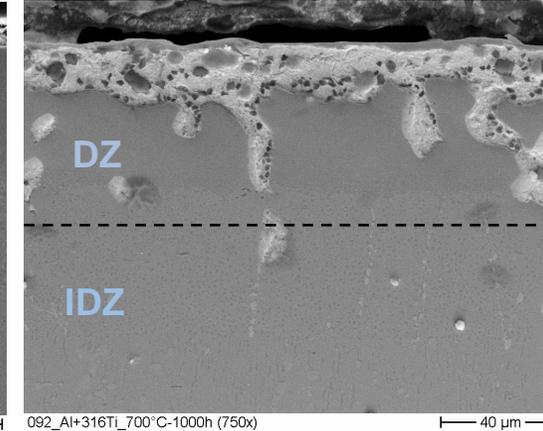
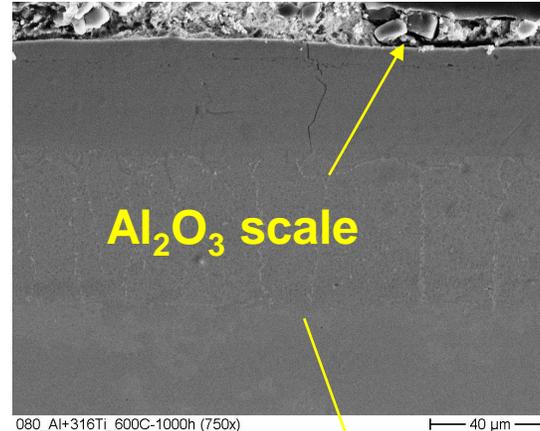
Uncoated 316Ti after 2000h in liquid Pb at 600°C



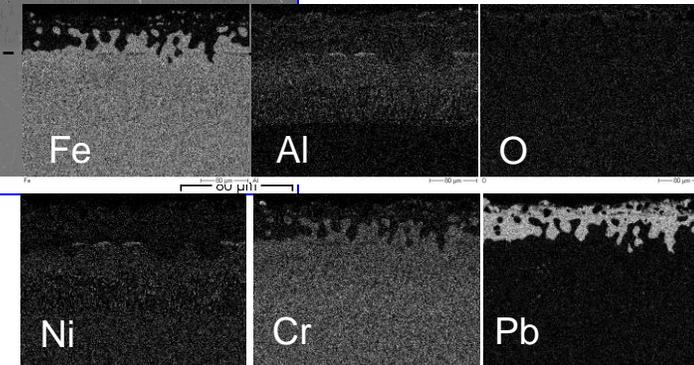
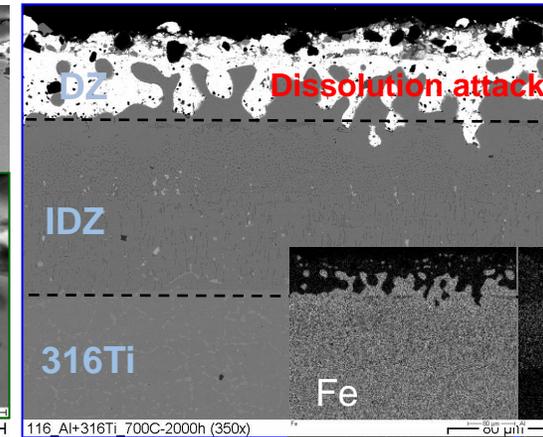
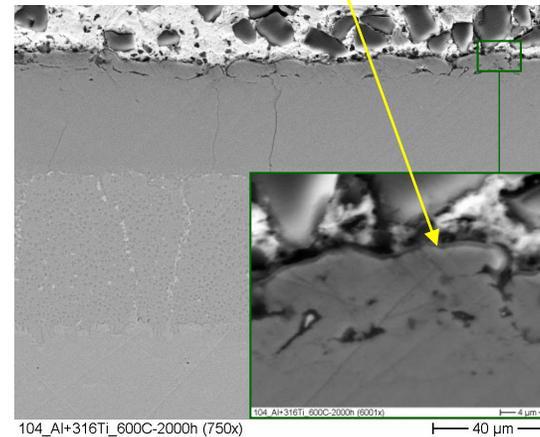
600 °C

700 °C

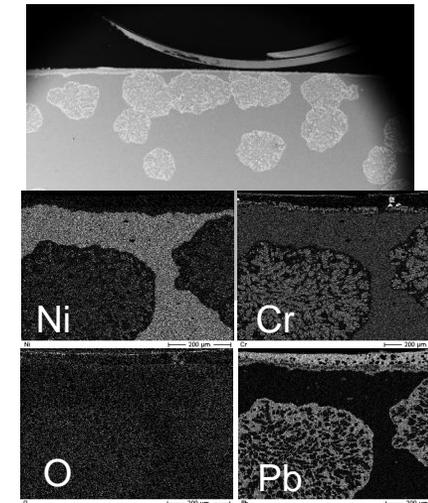
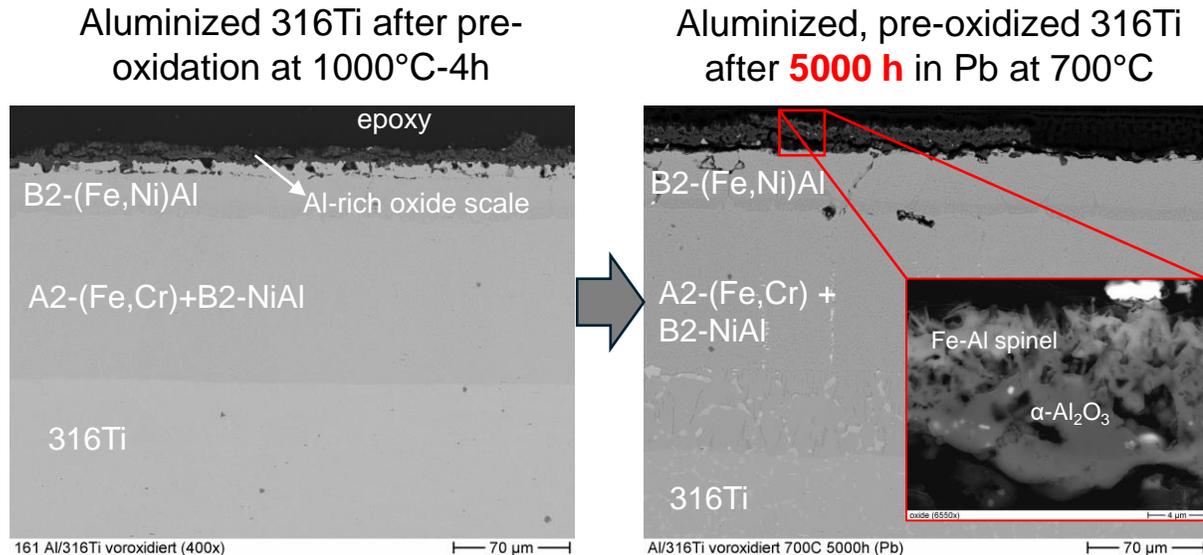
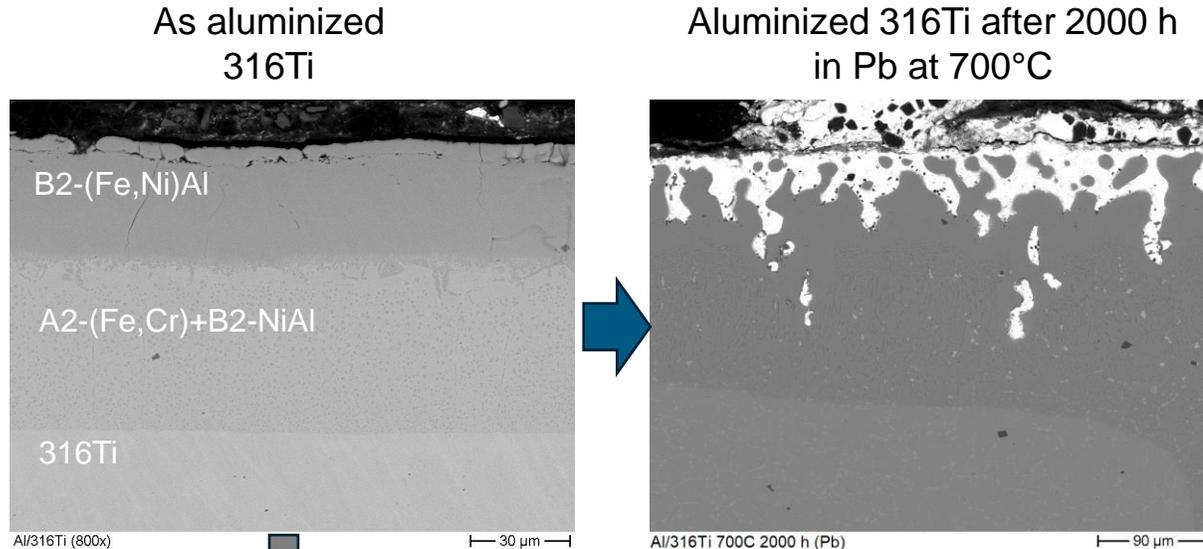
1000 h



2000 h



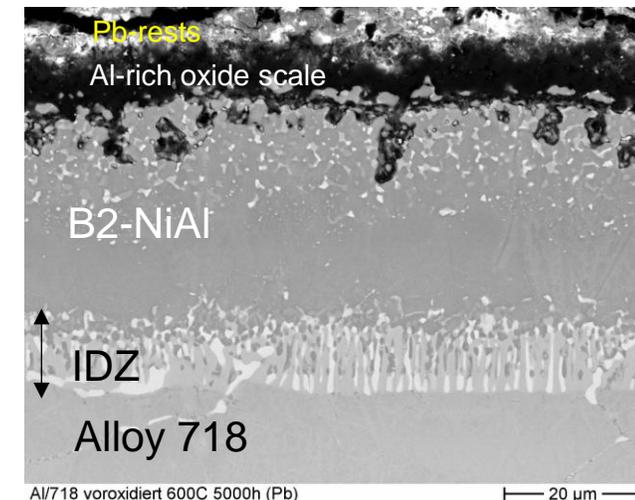
Corrosion mitigation strategies for liquid Pb



Uncoated Alloy 718 after 2000 h in Pb

Aluminized, pre-oxidized Alloy 718 after 5000 h in Pb at 600°C

Ni-based alloys?



Molten salt based TES

Corrosion in molten nitrates

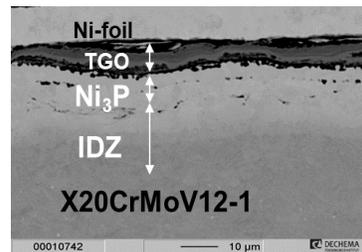
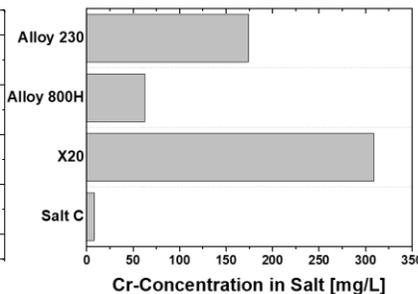
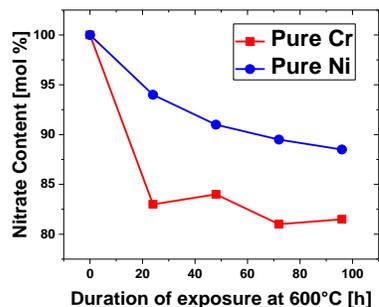
- Thermal decomposition reactions
- Cr-Dissolution into the salt melt

Corrosion behavior of commercial alloys

- Martensitic alloys → early onset of breakaway
- Austenitic alloys → higher resistance, but Cr-dissolution is evident

Mitigation strategies

- ✓ Alloys/coatings forming Al-rich scales
- ✓ Ni-P coatings



Liquid metal based TES

Corrosion in liquid Pb

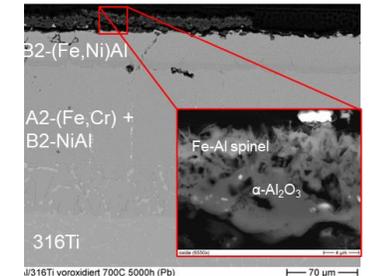
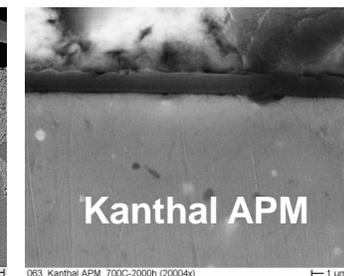
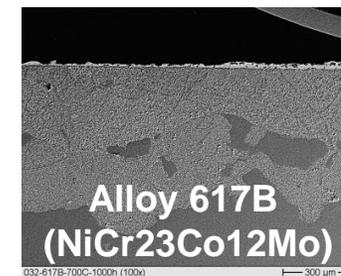
- Selective dissolution of alloying elements

Corrosion behavior of commercial alloys

- Martensitic and ferritic alloys → higher resistance, but mechanical behavior?
- Austenitic steels → ferritization of the sub-surface
- Ni-based alloys → catastrophic behavior

Mitigation strategies

- ✓ Alloys/coatings forming Al-rich scales
- ✓ Aluminization + pre-oxidation → possible utilization of austenitic alloys





Thank you for your attention!

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