U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
SOLAR ENERGY TECHNOLOGIES OFFICE

SETO CSP Program Summit 2019

Interfacial Studies of Performance of Protecting Layer for Corrosion Inhibition

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UIC

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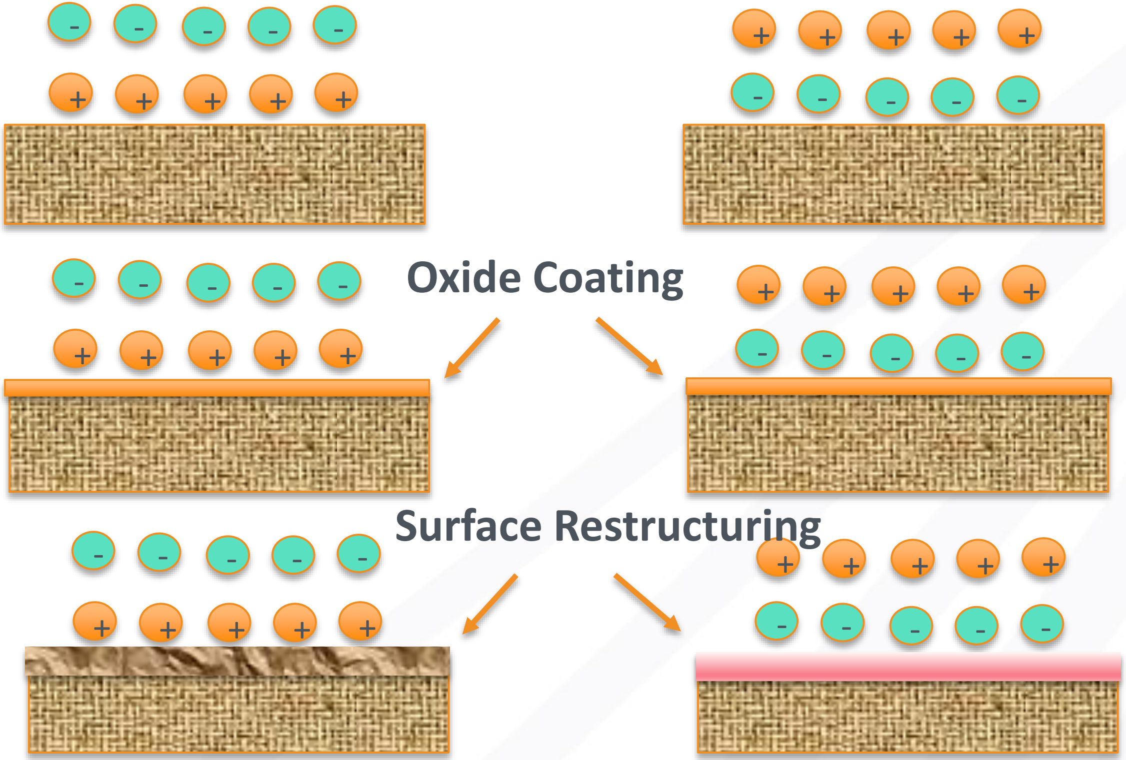
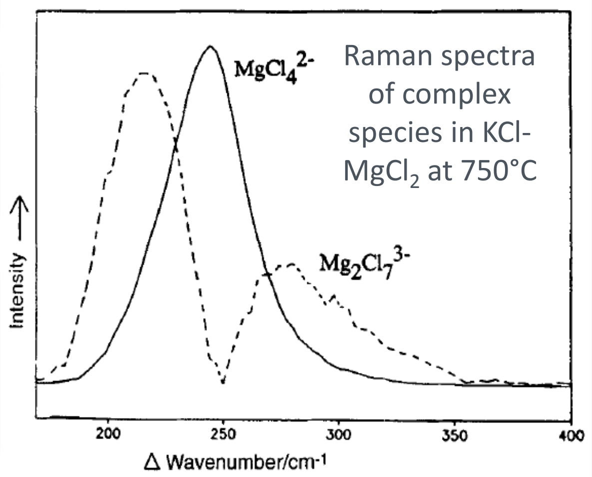
Knowledge Gap in Interfacial and Melt Structures

- Multicomponent species in equilibria
- Melts are not always ionic; can be molecular, network like



Complexity at interfaces

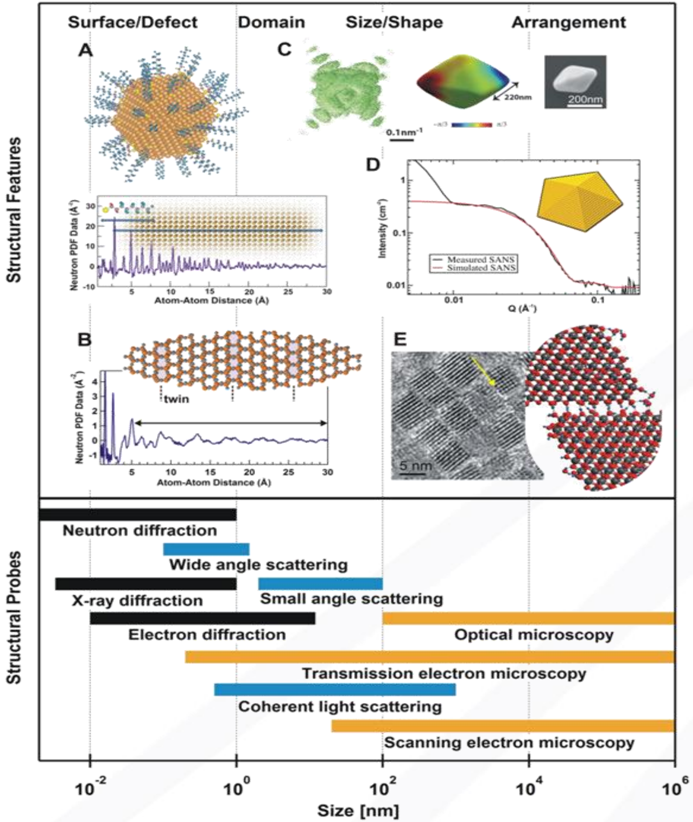


Raman spectra of complex species in KCl-$MgCl_2$ at 750°C

Dai, S., *et. al. J. Raman Spectr.* **1995**, *26*, 929-932

Complexity in melt structures

X-ray and neutron scattering are ideal to probe complex molten salt media in operando



Neutrons can help in many ways:

- Neutrons easily penetrate many vessel materials, enabling *in situ* measurements
- Probe speciation in complex multi-component melts and correlate atomistic structures to thermodynamic and corrosion properties of molten salt systems
- Characterize in-situ interfacial structures between metals and molten salts

Main challenges and goals

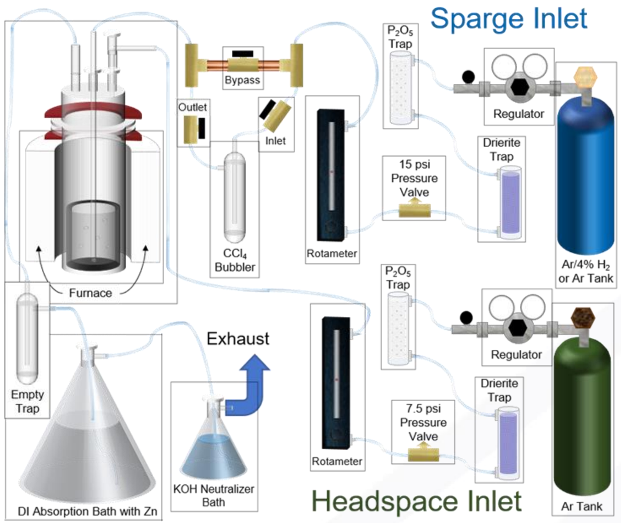
- The extreme corrosivity of chloride-based transfer fluids for concentrated solar power hinders the use of molten salts.

- Find the mechanism of the corrosion allowing us to make educated decision on how to proceed with salt implementation in existing setups or how to create new better ones
- Employ cutting edge spectroscopy techniques, such as grazing incidence X-ray absorption, scattering, and reflectometry, allowing us to approach corrosion on the interface and study it at the molecular level.
- Design a new cell enabling *in situ* studies to see the corrosion happening step-by-step.

Key activities

- Purification of the candidate salt for transfer fluid: $MgCl_2$ and KCl
- Film preparation by sputtering of the pure alloy and then the salt on a substrate
- Annealing of the films for *ex situ* studies
- Grazing Incidence X-ray spectroscopy and scattering measurements
- *In situ* measurements and *in situ* cell design

Salt purification



CSP Salt + NH_4Cl
(1:2 ratio)

5% water

Δ
450-750°C

Dry CSP Salt

~5000 μmolal oxide

750°C/40hrs
CCl_4/Ar

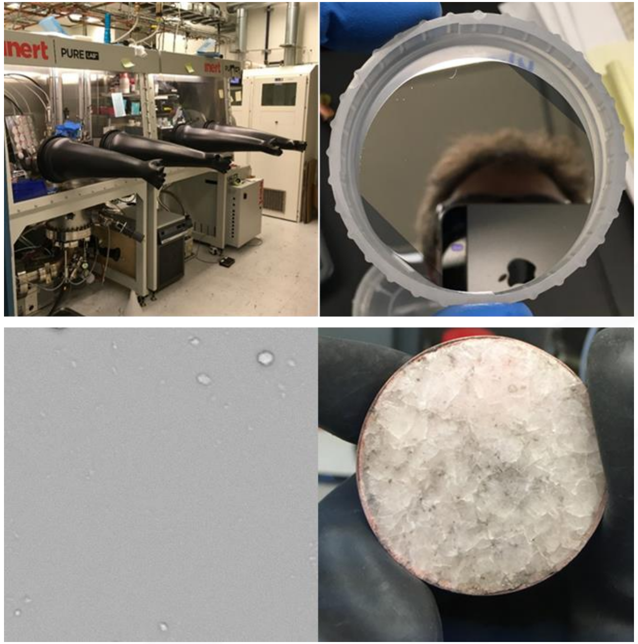
Low-Oxide CSP Salt

~150-250 μmolal oxide

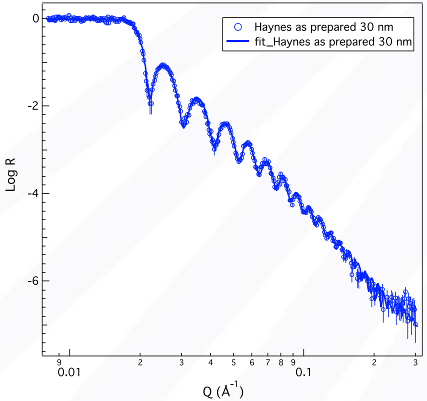
- Ultra High purity argon
- P_2O_5 filled traps to further dry gas
- Salt quantity dictates sparging time
- Final purge with H_2/Ar mixture to remove residual chlorination products

Oxide content measured via acid/base titration (~50ppm)

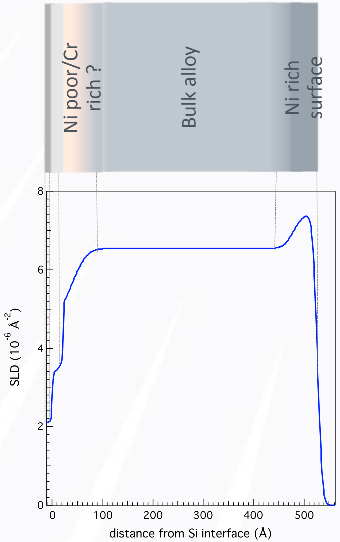
Alloy and salt deposition



Deposition of alloys and salt



Haynes "30 nm" Film			
	Thickness (Å)	SLD ($\times10^{-6}$ Å^{-2})	Roughness/Interfacial Width (Å)
Surface layer	47.5	7.42	7.6
Bulk layer	440.5	6.54	15.6
Interfacial layer	25.0	5.19	9.7
SiOx	21.7	3.25	1.2
Si Substrate	--	--	1.6



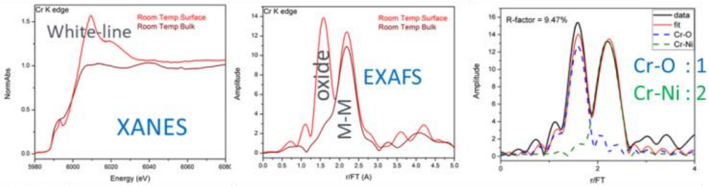
- As-deposited film thickness of 51.3 nm
- Film segregates into 3 regions
  - Ni rich surface
  - Bulk alloy
  - Ni poor or Cr rich substrate interface

Grazing Incidence X-ray Absorption measurements

Room temperature

Chromium

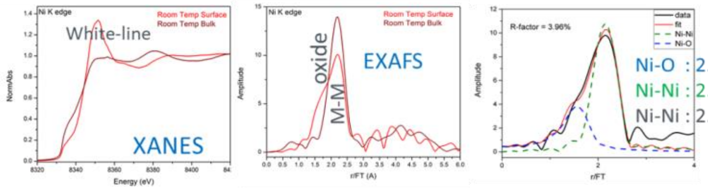
Surface at RT



Cr-O : 1.97(2) Å

Cr-Ni : 2.51(2) Å

Nickel



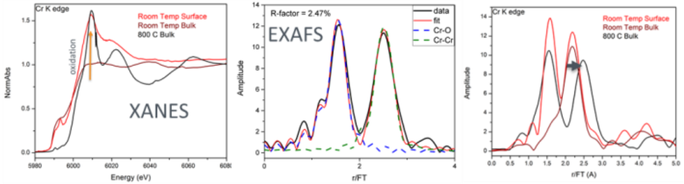
Ni-O : 2.01(3) Å

Ni-Ni : 2.48(2) Å

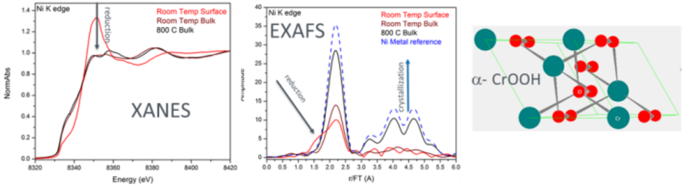
Ni-Ni : 2.49 Å (in metal)

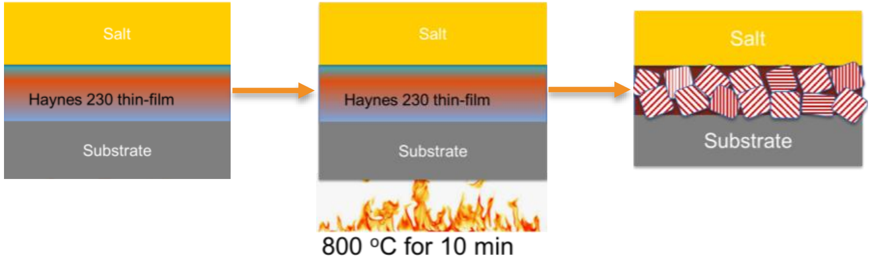
After annealing

Chromium



Nickel





800 °C for 10 min

- Loss of planar interface
- 111 Textured Haynes film transformed to grain-coarsened untextured FCC Ni
- Evidence for α-CrOOH and other phases

Summary

- Successfully purified $MgCl_2$ and KCl and lowered **oxide concentration down to 50 ppm**, which allows more systematic study of corrosion
- Deposited **smooth alloy and salt films**, which are necessary for grazing incidence studies
- Grazing incidence X-ray absorption shows **oxidation of Cr in the alloy to α-CrOOH** indicating pathway for the corrosion
- Grazing incidence diffraction also shows **texturing of Ni metal** after Cr leaves the alloy structure showing what happens to the corroded alloy
- Neutron and X-ray scattering can be done ***in situ* up to 600°C and 900°C**, respectively
- Neutron scattering cell for **higher temperatures is designed to allow *in situ* studies** at operating temperatures