Interfacial Studies of Performance of Protecting Layer for Corrosion Inhibition

Sheng Dai, ORNL
Knowledge Gap in Interfacial and Melt Structures

- Oxide Coating
- Surface Restructuring

Complexity at interfaces

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

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

Complexity in melt structures

Raman spectra of complex species in KCl-MgCl$_2$ at 750°C
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

- Ultra High purity argon
- P$_2$O$_5$ 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)

CSP Salt + NH$_4$Cl (1:2 ratio)

$\Delta$
450-750°C

Dry CSP Salt

750°C/40hrs CCl$_4$/Ar

Low-Oxide CSP Salt

5% water

~5000 µmolal oxide

~150-250 µmolal oxide

SETO CSP Program Summit 2019
Alloy and salt deposition

Deposition of alloys and salt

- 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

White-line

XANES

Surface at RT

Cr-O : 1.97(2) Å
Cr-Ni : 2.51(2) Å

Nickel

White-line

XANES

Surface at RT

Ni-O : 2.01(3) Å
Ni-Ni : 2.48(2) Å
Ni-Ni : 2.49 Å (in metal)

After annealing

Chromium

Ni-OH

EXAFS

Nickel

Ni-OH

EXAFS

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

Salt

Haynes 230 thin-film

Substrate

800 °C for 10 min

Salt

Haynes 230 thin-film

Substrate

Salt

Substrate
Summary

• Successfully purified MgCl₂ 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.