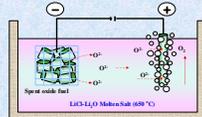


Structural Materials Development for the Electrochemical Reduction of Spent Oxide Nuclear Fuel in Molten Salt Electrolyte

C. T. Snyder, J. Figueroa, L. E. Putty, L. Leibowitz,
 J. E. Indacochea,^a A. Polar,^a F. Rumiche,^a and S. M. McDevitt
 Chemical Engineering Division and University of Illinois at Chicago^a

Introduction

Argonne National Laboratory has developed an electrometallurgical treatment technique that can be used to convert the current Department of Energy (DOE) inventory of mixed-oxide spent nuclear fuel types into three uniform product streams. The process involves the liberation of oxygen in a molten lithium chloride (LiCl) electrolyte too corrosive for typical structural materials; however, process components must withstand this chemically aggressive environment and remain resilient during operations at 650°C.



^aGraphic by Soony Won Park

Objective

- Develop Advanced Structural Materials for Electrochemical Reduction Technology
 - Assess and select candidate materials for service in the electrolytic reduction process vessel.
 - Develop new candidate material systems (e.g., functional barrier coatings) for service in the electrochemical reduction process.

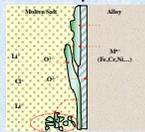
Factors Controlling Corrosion Rate

Kinetic Considerations

- Diffusion of oxygen through the corrosion layer to the metal-oxide interface.
- Oxidation reaction at the oxide-metal interface.
- Diffusion of chlorine through the corrosion layer to metal-oxide interface.
- Chlorine reaction at the oxide-metal interface.
 - The diffusion of oxygen and/or chlorine to the oxide-metal interface is the dominant step.

Fick's First Law applies

$$J_o = -D \frac{dC}{dx}$$



^aGraphic by Soony Won Park

The integration of dC is given between the limits of C_o (concentration of O at the metal-oxide equilibrium) and C_b (concentration of O in the bulk), and x is the thickness of the scale.

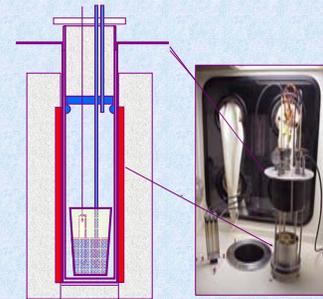
Method

- Corrosion-test commercially available alloys
- Design and build testing apparatus
- Test metal alloy coupons under simulated conditions:

Temperature:	625°C 675°C 725°C
Oxygen concentration in argon gas:	5%, 10%, 15%, 20%
Time intervals:	3 and 6 days

Continuing Corrosion Studies

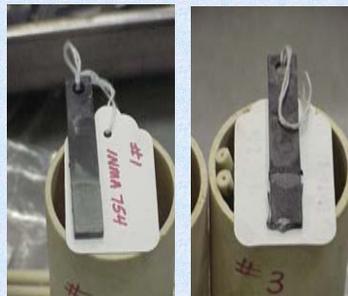
- Metal, metal alloy, and ceramic-based coatings
- Cathodic protection of base metal



CORROSION TESTING APPARATUS

Best and Worst Sample Coupons

9 days @ 625 °C in 6% Li₂O in LiCl and 10% O₂ in Argon



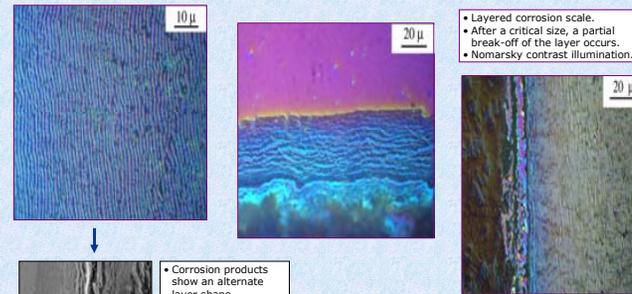
Inconel MA754

Inconel 600

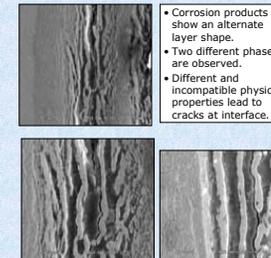
The Best Performer Was INMA 754

Ni 77.8, Cr 20.21, Fe 0.27, Al 0.32, C 0.05, O 0.32, Ti 0.44, S 0.002,
 Y203 0.59

After 9 Days of Exposure at 725°C Li₂O 6% in LiCl



- Layered corrosion scale.
- After a critical size, a partial break-off of the layer occurs.
- Nomarsky contrast illumination.



- Corrosion products show an alternate layer shape.
- Two different phases are observed.
- Different and incompatible physical properties lead to cracks at interface.

Conclusions

C_b is proportional to $\sqrt{P_{O_2}}$

C_o is equal to $\frac{1}{a_M K_h}$

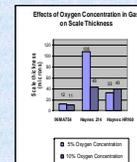
Hence,

$$J_o = D \frac{1}{a_M K_h} \frac{\sqrt{P_{O_2}}}{dx}$$

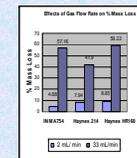
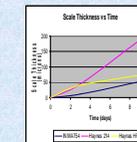
The diffusion coefficient D depends on temperature and the media in which the diffusion occurs.

Rate of Corrosion Depends On Several Factors

- Diffusion Coefficient (D) related to
 - Type of layer: porous, compact, unilayer, etc.
 - Temperature
 - Element
- Diffusion distance (dx) related to thickness of layer
 - Influenced by the type of corrosion layer
 - Effect of gas flow turbulence
- Driving force for diffusion: $(\sqrt{P_{O_2}})$
 - Oxygen in flow gas



Conditions
 3 days at 675 °C, Ar-10% O₂ at 2 mL/min in 3% Li₂O in LiCl
 3 days at 675 °C, Ar-5% O₂ at 2 mL/min in 3% Li₂O in LiCl



Conditions
 9 days at 675 °C, Ar-10% O₂ in 3% Li₂O in LiCl

