Long-Term Passive Dissolution and Localized Corrosion of Alloy 22

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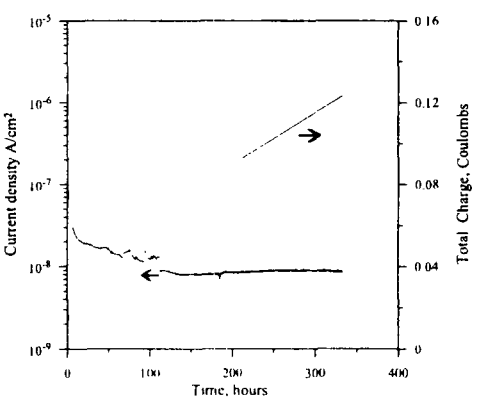
Uniform Passive Dissolution of Alloy 22

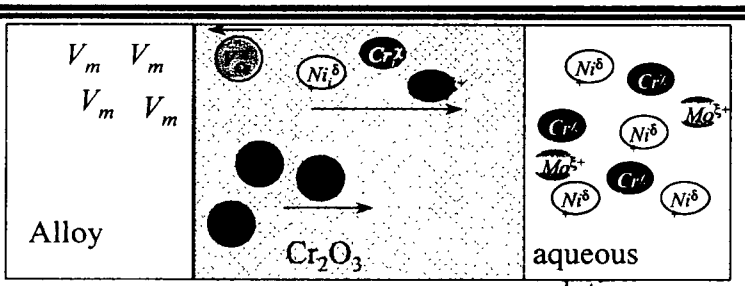


- A steady passive current density of ~10^{-8} A/cm^2, corresponding to a corrosion rate of ~0.1 μm/yr, was measured in 0.028 M Cl^- at 95 °C in a 15-day test at 0.1 V_{SCE}
- A container lifetime of ~100,000 yr can be estimated from this value by using Faraday's laws
- This estimate does not consider defect generation or the accumulation of metastable events that may lead to higher corrosion rates at longer times
- The effects of fabrication processes on long-term dissolution rates need to be considered

Long-Term Prediction of Uniform Passive Corrosion

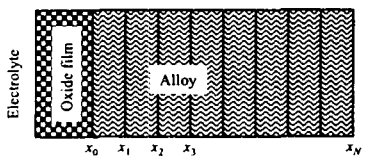
- Concerns about the validity of long-term (thousands of years) extrapolation of experimental (electrochemical or gravimetric) measurements of corrosion rates
- Need of critical assessment of mechanistic models to provide bases for new concepts, approaches, and methods to be used in experimental measurements
  - Modified Point Defect Model
  - Semiconductive oxide model
  - Passive film breakdown/repair models
- Validity of high temperature experiments as accelerated tests for extrapolations to low temperature conditions
- What other factors can be used to accelerate the occurrence of possible enhancement effects on corrosion rates?

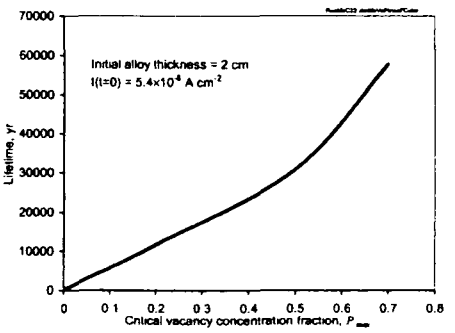
Modeling of Long-Term Passive Corrosion



- Modified Point Defect Model
- Conduction by interstitial cations or oxygen vacancies or both carriers
- Very low vacancy diffusivities in the metal lead to vacancy accumulation at the metal/film interface
- Film spalling at irregular locations caused by vacancy accumulation assuming no efficient sink exists
- Heuristic model proposed to account for film spalling
- As a result, steady state passive dissolution is stoichiometric

Estimation of Container Lifetime Considering Vacancy Generation





- Lifetime of container is a function of critical vacancy concentration fraction, P_{max}, at the metal-oxide interface
- Film spalling is assumed to occur when $P > P_{max}$ at position $x_0 \ldots x_i$

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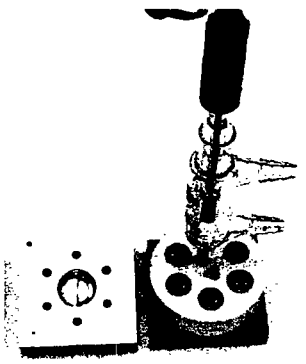
Uniform Passive Corrosion Experiments



- Measure solution composition using capillary electrophoresis to evaluate stoichiometric vs. preferential dissolution of alloying elements
- High resolution passive current density measurements over extended time periods
- Resistivity measurements of thin metal foils to evaluate possibility of metal vacancy accumulation

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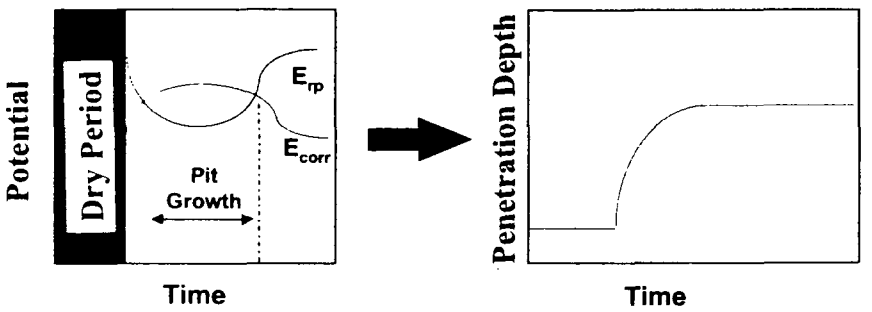
Additional Aspects to Consider on Passive Corrosion

- Other possible processes leading to small increases of passive current density
  - Cumulative metastable passive film breakdown and repassivation events
  - Modification of outer deposit layer creating a local, more aggressive environment with time
- Methodology to evaluate these processes
  - Enhanced resolution of long-term potentiostatic and zero resistance ammeter measurements
  - Appropriate consideration of naturally corroding conditions (role of cathodic area) compared to potentiostatic control

Semi-Empirical Model of Localized Corrosion



- Repassivation potential, $E_{rp} = f$ (T, [X^-], [Inh], metallurgical factors)
- Corrosion potential, $E_{corr} = f$ (T, [Ox], pH, i^0_{Ox}, surface state, metallurgical factors)
- Pit growth is affected mainly by dissolution kinetics and mass transport processes within pits
- If $E_{corr} < E_{rp}$ only passive dissolution occurs

Factors Affecting the Evolution of Corrosion and Repassivation Potentials

Environment or material factors	E_{corr}	E_{crit} (E_{rp})
T decrease	(+)	(+)
pH increase	(-)	(0)
$[Cl^-]$ increase	(-)	(-)
$[NO_3^-]$ or other inhibitor increase	0	(+)
$[HCO_3^-]$ increase	(-)	(0)
$[S_2O_3^{2-}]$ or other activator increase	(-)	(-)
E_h (from air and radiolytic species) decrease	(-)	(0)
Aging of passive film	(+)	(0)
Precipitation of intermetallic phases at g.b.	(0)	(-)
Segregation of impurities and depletion of alloying elements in welds	(0)	(-)

variability in composition of material

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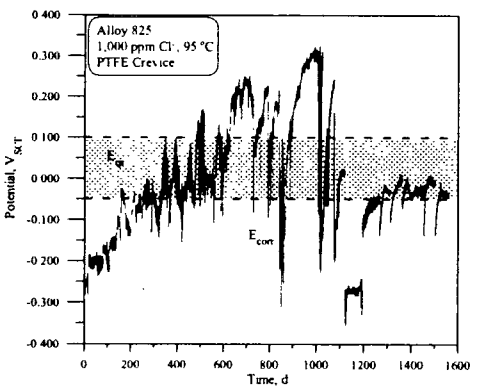
This presentation represents the position of his author and does not necessarily reflect the views or regulatory position of the NRC

Supplementary Slides

Evolution and Monitoring of Corrosion Potential



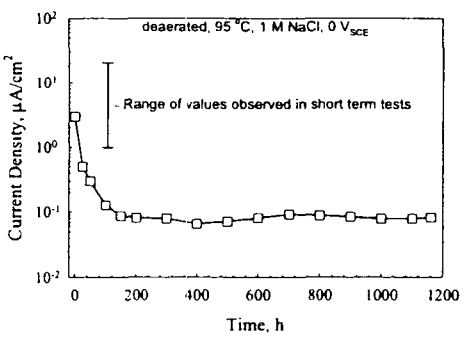
- The corrosion potential (E_{corr}) is the additional electrochemical parameter required to determine the occurrence of localized corrosion
- E_{corr} is calculated in TPA Code using the anodic passive current density and electrochemical kinetics expressions for the cathodic reduction of O_2 and H_2O/H^+
- E_{corr} is measured in an air-saturated 0.028 M Cl^- solution in prolonged tests (> 870 days) to verify model calculations and validity of the approach

Uniform Corrosion Rates of Alloy 22

Starting Condition of Alloy C-22	$[Cl^-]$, molar	pH	Temp, °C	Potential,m V_{SCE}	Anodic Current Density, A/cm^2	Corrosion Rate, mm/yr	Lifetime of 20 mm Thick WP Barrier, Years
As-received	0.028	8	20	200	2×10^{-9}	2×10^{-5}	~1,000,000
As-received	0.028	8	95	200	3×10^{-8}	3×10^{-4}	~70,000
As-received	0.028	0.7	95	200	7×10^{-8}	7×10^{-4}	~30,000
As-received	4	8	95	200	3×10^{-8}	3×10^{-4}	~70,000
As-received	4	8	95	400	4×10^{-8}	4×10^{-4}	~50,000
TPA 3.2 Calculation Low Dissolution Rate					6×10^{-8}	7×10^{-4}	~30,000
TPA 3.2 Calculation High Dissolution Rate					2×10^{-7}	2×10^{-3}	~10,000

These table summarizes data obtained in short-term (approximately 48hs) potentiostatic measurements

Uniform Passive Dissolution of Ti Grade 7

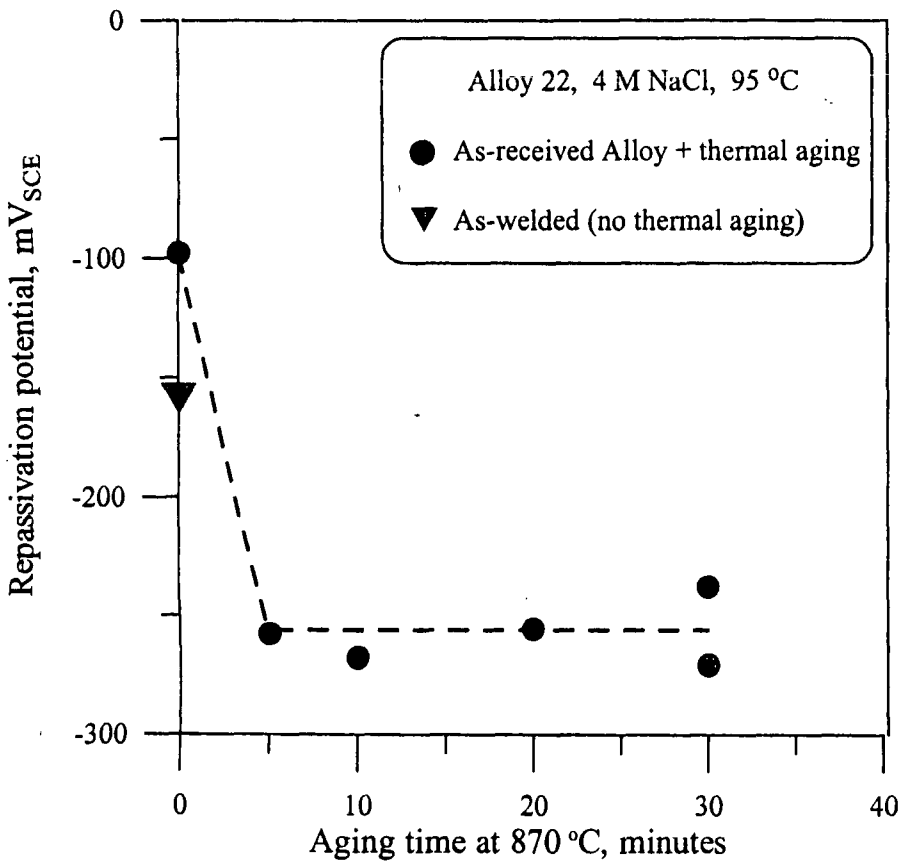


- A steady passive current density lower than 10^{-7} A/cm^2, corresponding to a corrosion rate of 0.9 μm/yr, was measured in a 50-day potentiostatic test
- A drip shield lifetime of approximately 17,000 yr can be estimated from this value
- In addition to other long-term aspects considered for alloy 22, values are only valid assuming that fluoride is not present in the aqueous environment

Engineered Barrier Alloys in DOE Program

- Type 316L SS: Fe-17%Cr-10%Ni-2.5% Mo
- Alloy 825: Fe-42%Ni-21.5%Cr-2%Cu-3%Mo
- Alloy 625: Ni-21.5%Cr-9%Mo-3.7%Nb
- Alloy 22: Ni-3%Fe-21.5%Cr-13.5%Mo-3%W
- Ti Grade 7: Ti-0.15%Pd

Effect of Fabrication Processes on Localized Corrosion of Alloy 22



- Very short heat treatment times (few minutes) at 870 °C decreases significantly E_{rcrev}
- The effect of welding on E_{rcrev} is less pronounced
- Additional data is need to evaluate the combined effect of welding plus thermal aging

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Effect of Thermal Treatment on Localized Corrosion of Alloy 22

- Thermally treated at 870 °C for 5 min and tested in 0.01 M NaCl at 95 °C
- E_{rcrev} is 350 mV_{SCE} and 3/24 crevice sites exhibited this grain boundary attack, accompanied by some attack at twin boundaries
- No attacks was observed in 0.001 M NaCl after 1 hr treatment at 870 °C