Evaluation of Environmentally-assisted Fatigue Behavior of Type 316L Stainless Steel in Simulated Small Modular Reactor Environments

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II. Experimental

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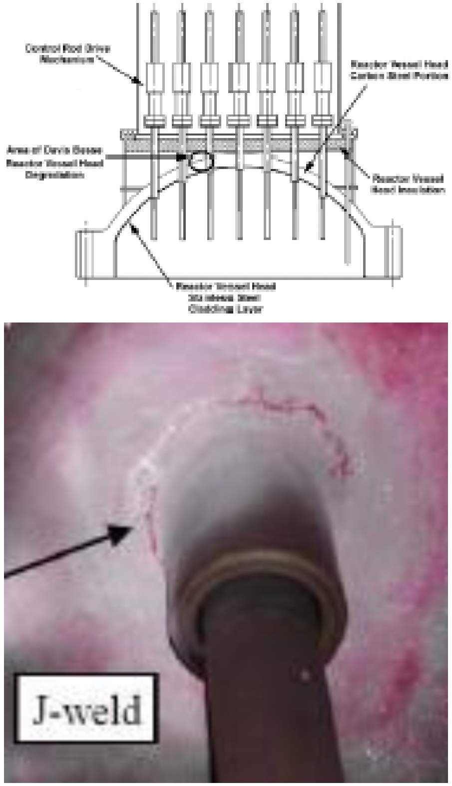
Introduction

❑ EAC (Environmentally Assisted Cracking)

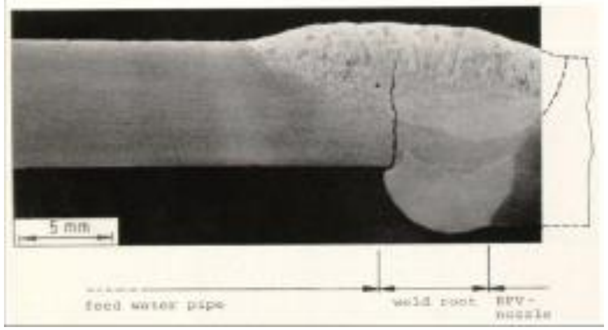
- Reactor internals, containment & reactor vessels, piping & tubing, turbine discs
- Carbon & low-alloy steels, stainless steels, Ni-alloys, brass, base metal, weld and weld heat-affected zone materials, dissimilar welds
- SCC (Stress Corrosion Cracking), IASCC (Irradiation Assisted Stress Corrosion Cracking), EAF (Environmentally Assisted Fatigue), SICC (Strain Induced Corrosion Cracking)

▼ SCC & IASCC in austenitic stainless steels (sensitized piping, high carbon SS)

▼ SCC in DMWs austenitic Ni-alloy welds



▼ SICC initiation in LAS FW nozzle from weld root defects as local stress raisers or crevices



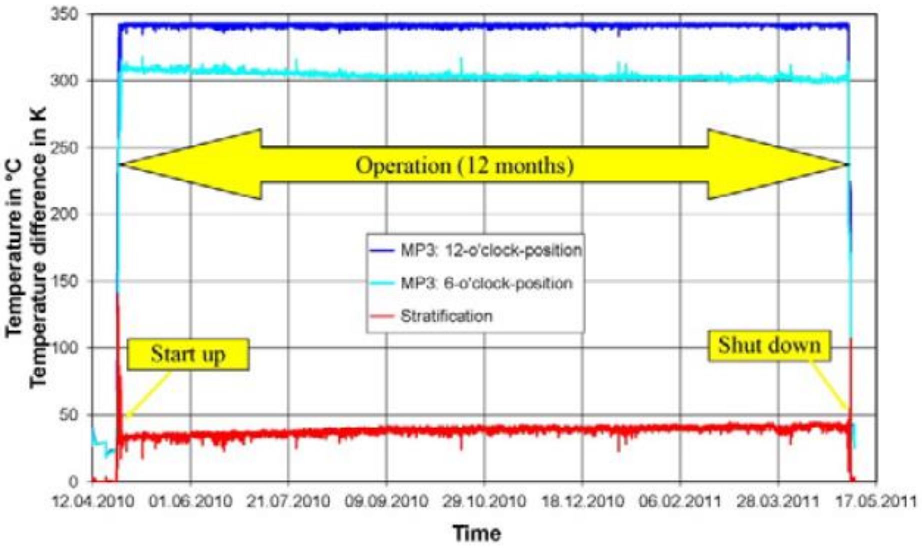
▼ SICC / EAF in LAS FW piping

Introduction

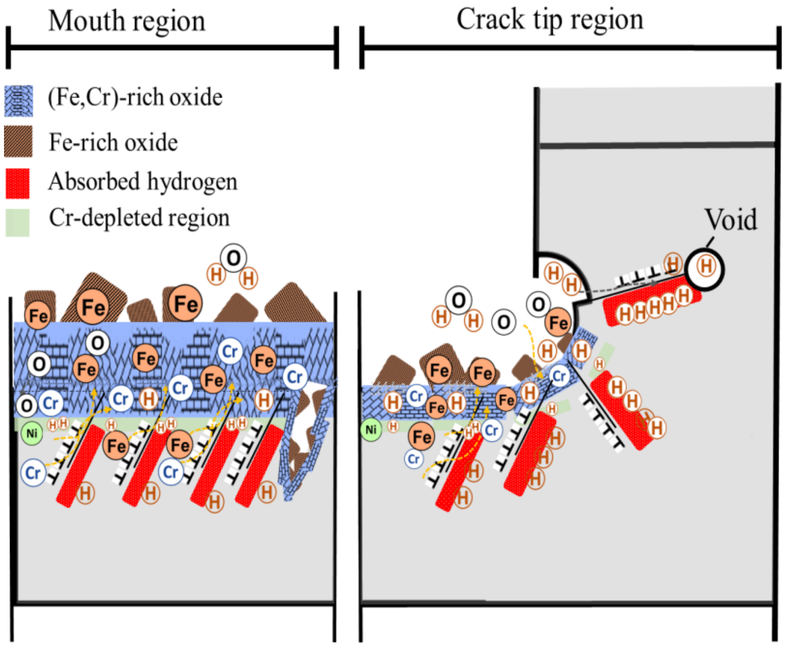
[1] S.H. Reese, PVP 2014-28191
[2] J. Chen, NE&T, 2019

❑ Environmentally-assisted fatigue (EAF)

- One of most significant degradation mechanisms in nuclear power plant
  - Caused by repeated cyclic stress (thermal & mechanical load) in LWR environment
  - Expression of environmental effect : environmental multiplier (F_{en})
    - ☐ $F_{en} = N_{air} / N_{water}$
- Hydrogen induced cracking (HIC)
  - Hydrogen produced by corrosion at the crack tip
  - Hydrogen absorbed into the stress concentrated localized region



▲ Elastic – Plastic stress field near the crack tip [1]



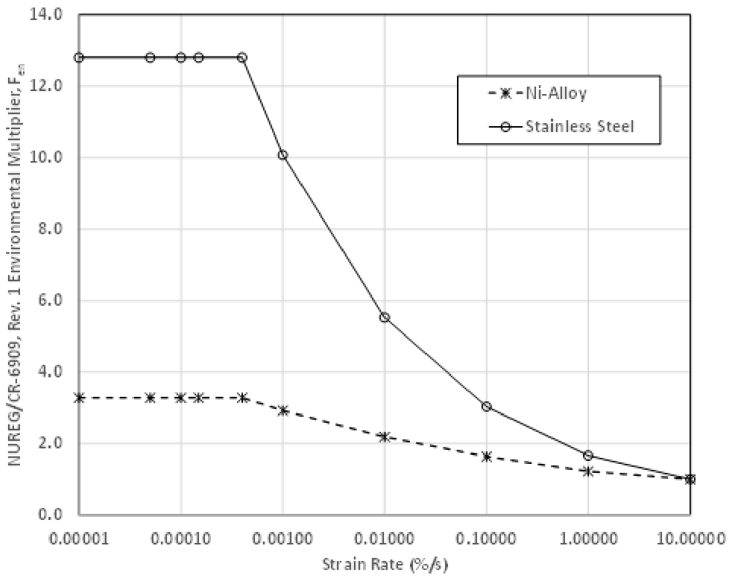
▲ Schematic diagram of corrosion mechanisms and fatigue behavior during LCF test in PWR environment [2]

Introduction

[3] EPRI, TR-3002020450, 2021

❑ Environmentally-assisted fatigue of austenitic stainless steels

- RG 1.207 & NUREG/CR-6909
  - Require to incorporate environmental effect of NPP in Design Fatigue Analysis of Class 1 components for new reactor and license renewal
  - Cumulative usage factor (CUF) X environmental multiplier (F_{en}) = $CUF_{en} < 1.0$
- Numerous studies have been performed to meet the requirements, but existing data are performed in LWR environments
- EAF test results in SMR environments are not available



▲ **Fen multiplier for stainless steel and Ni-base alloy vs. strain rate in 325 ℃ PWR water [3]**

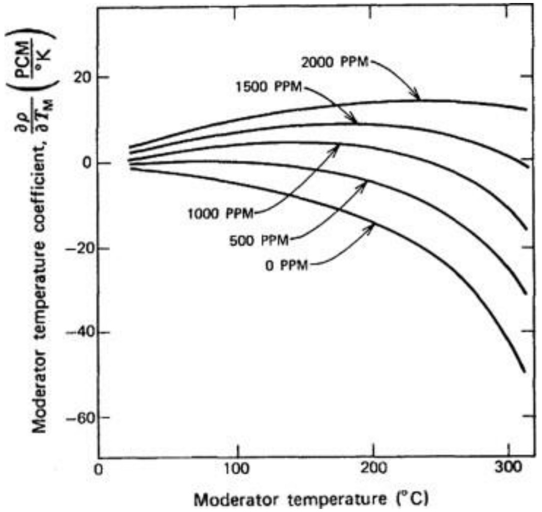
=> EAF behavior of ASSs should be evaluated in boron-free SMR environments for design and integrity analysis

Introduction

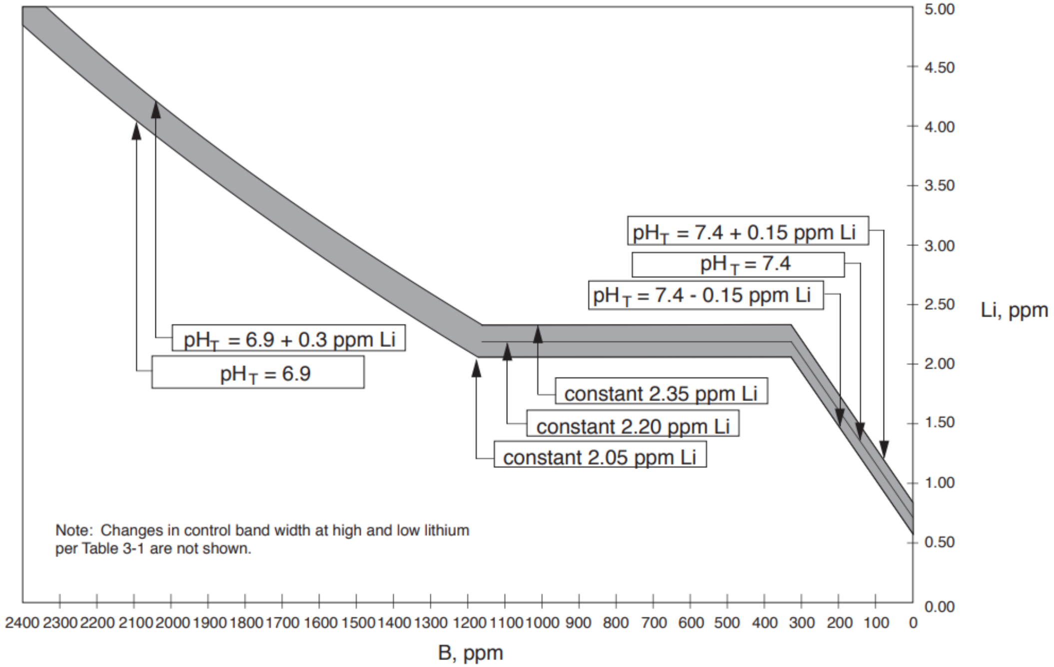
[5] EPRI, TR-105714-V1R4, 1999
[6] J.J. Duderstadt, Nuclear reactor analysis, 1976
[7] EPRI, TR-1008102, 2004

❑ Small Modular Reactor (SMR)

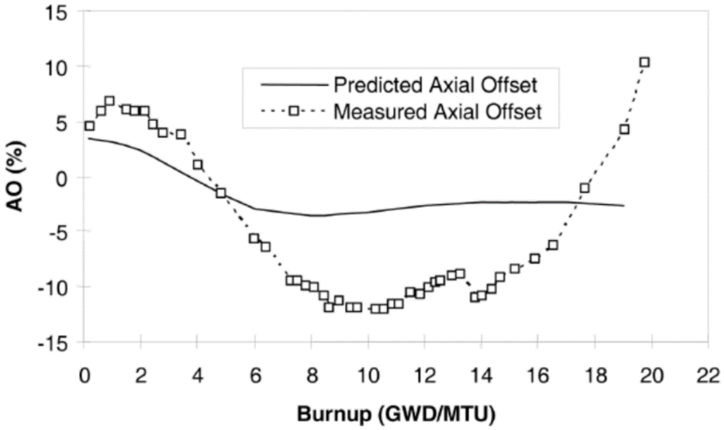
- NuScale (USA), CAREM (Argentina), i-SMR (Korea), etc
- Soluble boron free (SBF) environment
  - Boric acid (H_3BO_3) is dissolved up to 2500 ppm in PWRs
  - However, the use of boric acid has unfavorable safety features
    - ☐ Shifting of the moderator temperature coefficient positively at BOC
    - ☐ Occurrence of CRUD induced power shift (CIPS) due to boron accumulation
    - ☐ SBF is considered in an innovative-SMR (i-SMR) as well



▲ Effect of chemical shim on the MTC [6]



▲ Boron and lithium concentration in PWRs [5]



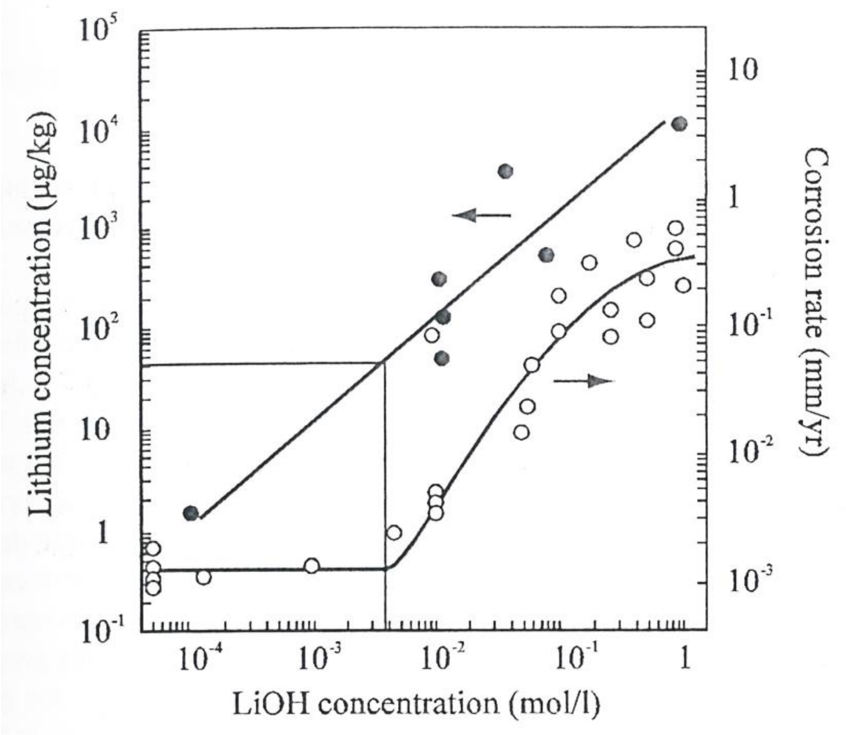
▲ CRUD induced power shift [7]

Introduction

[8] V.G. Kritsky, Water chemistry and corrosion of NPP structural materials, 1999

❑ Soluble boron free (SBF) environment

- Although the SBF does not contain the soluble boron, a pH control agent is still necessary due to mildly acidic at high pressure and temperature
  - LiOH has used as pH controller in PWRs
  - But, LiOH causes the fast corrosion rate of Zirconium alloy
- Consideration of new pH control agent such as KOH, NH_3, etc.



▲ Effect of LiOH concentration on the corrosion rate of Zircalloy-4 [8]

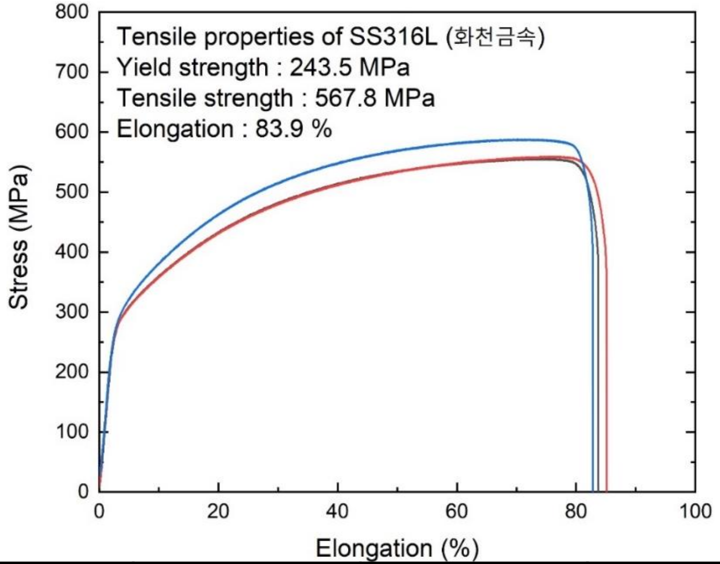
Experimental

❑ Materials (316L stainless steel)

- Chemical composition measurement

SS316L	Fe	Cr	Ni	C	Mn	Mo	Si	P	S	N
ASTM A240	Bal.	16.0-18.0	10.0-14.0	0.030	2.00	2.00-3.00	0.75	0.045	0.030	0.10
CMTR	Bal.	16.69	10.08	0.02	1.24	2.06	0.51	0.030	0.003	0.072
Measured	Bal.	16.82	10.01	0.027	1.28	2.04	0.53	0.032	0.001	0.067

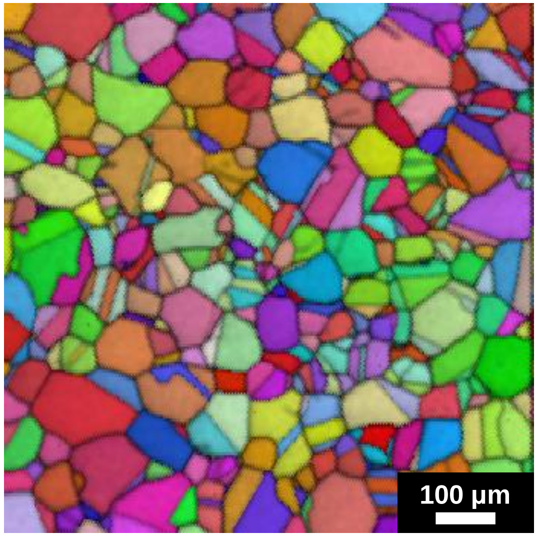
- Mechanical properties



Tensile properties of SS316L (화천금속)
Yield strength : 243.5 MPa
Tensile strength : 567.8 MPa
Elongation : 83.9 %

SS316L	Y.S (MPa)	T.S (MPa)	Elong. (%)
ASTM A240	170	485	40
CMTR	232	501	57.4

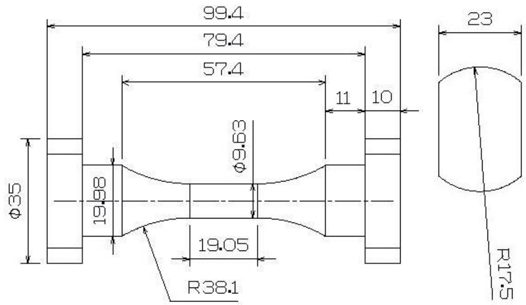
- Microstructure analysis
  - Grain size : 102 ± 44 μm



Experimental

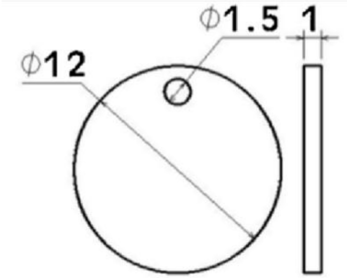
Environmentally-assisted fatigue equipment

- Recirculation loop usage for water chemistry control
  - Gas purging to achieve dissolved oxygen (DO) and dissolved hydrogen (DH) concentration
- Round bar shape of fatigue specimen used in this study
  - 9.6 mm of diameter and 19.05 mm of gauge length
- Coupon specimens were immersed simultaneously to evaluate corrosion behavior
  - 12 mm of diameter and 1 mm of thickness with a hole



▲ Schematic of round bar type specimen

▲ EAF test equipment



▲ Schematic of coupon specimen

Experimental

[9] ERPI, PWR Primary Water Chemistry Guidelines
[10] NIST, Thermophysical properites of Fluid Systems

Determination of pH controller concentration

- Based on criteria of PWR water chemistry guideline[9]
  - pH values at operating temperature should be 7.0 to 7.4
- Calculation of pH at operating temperature
  - Ionization constant of water at target pressure and temperature (150 bar and 325 °C)

$$pK_w = -2n\left[\log(1+Q) - \frac{Q}{Q+1}\rho(\beta_0 + \beta_1 T^{-1} + \beta_2\rho)\right] + pK_w^G + 2log\frac{m^0 M_w}{G}$$ [10]

  - Concentration of pH controller ($[pH^+]$ = mol/L of pH agent)

$$[pH^+] = \frac{K_w}{[H^+]} - [H^+]$$

$$pH = -log_{10}\left(\frac{-[pH^+] + \sqrt{[pH^+]^2 + 4K_w}}{2}\right)$$

  - Determination of pH controller concentration

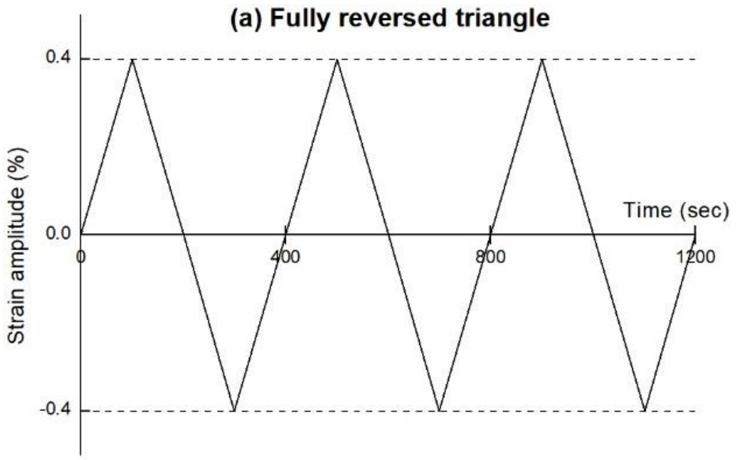
pH agent	Pressure(bar)	Temperature(°C)	pK_w	pH_T	mol/L	ppm
KOH	150	325	11.71	7.4	0.000048	2.75
NH_3						0.00082

Experimental

❑ Environmentally-assisted fatigue test condition

- EAF test performed according to ASTM E606
- EAF test in simulated SMR environments with 2 kinds of pH agent (KOH & NH_3)
- Simulated SMR water chemistry : 2.75 ppm KOH or 0.00082 ppm NH_3

Test condition		PWR
Control type		Strain control (ASTM E606)
Temperature		325 °C
Pressure		150 bar
Strain amplitude (%)		0.4
Strain rate (%/s)		0.004
Water Chemistry	DO	< 5 ppb
	DH (cc/kg)	25
	pH_T (325 °C)	7.4



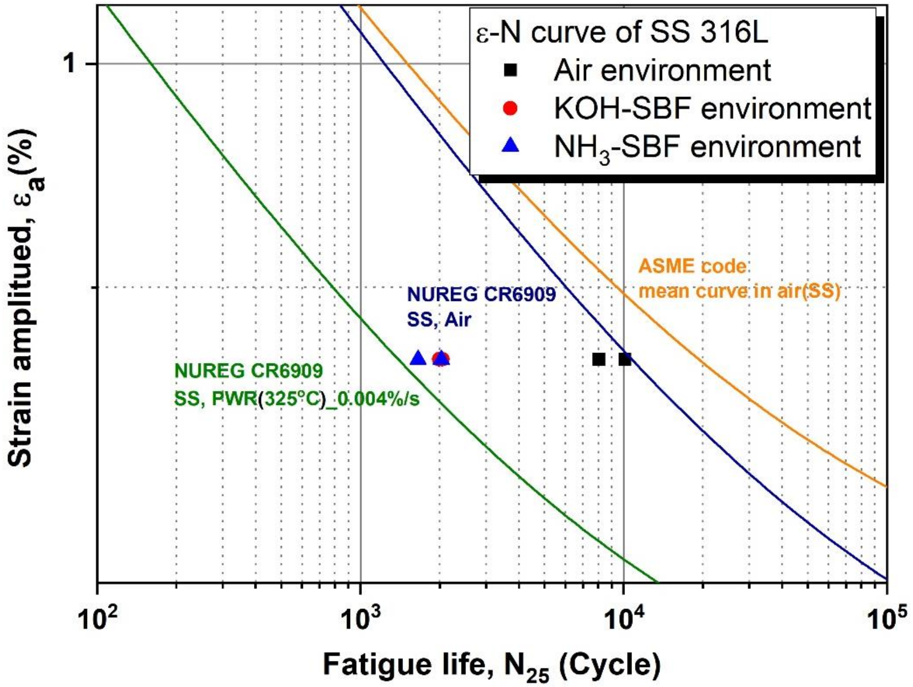
▲ Loading condition

Results - EAF

[11] NUREG/CR-6909

❑ Environmentally-assisted fatigue test results

- Fatigue life (N_{25}) : number of cycles for the tensile stress to drop 25 % from its peak value
- EAF life results
  - RT air : 10125, 8045 cycles
  - KOH-SBF SMR environment : 1991, 2053 cycles
  - NH_3-SBF SMR environment : 1657, 2030 cycles
- Estimated EAF life in PWR environment according to NUREG/CR6909[11] : 1533 cycles
- No significant change in fatigue lives in simulated SMR environment

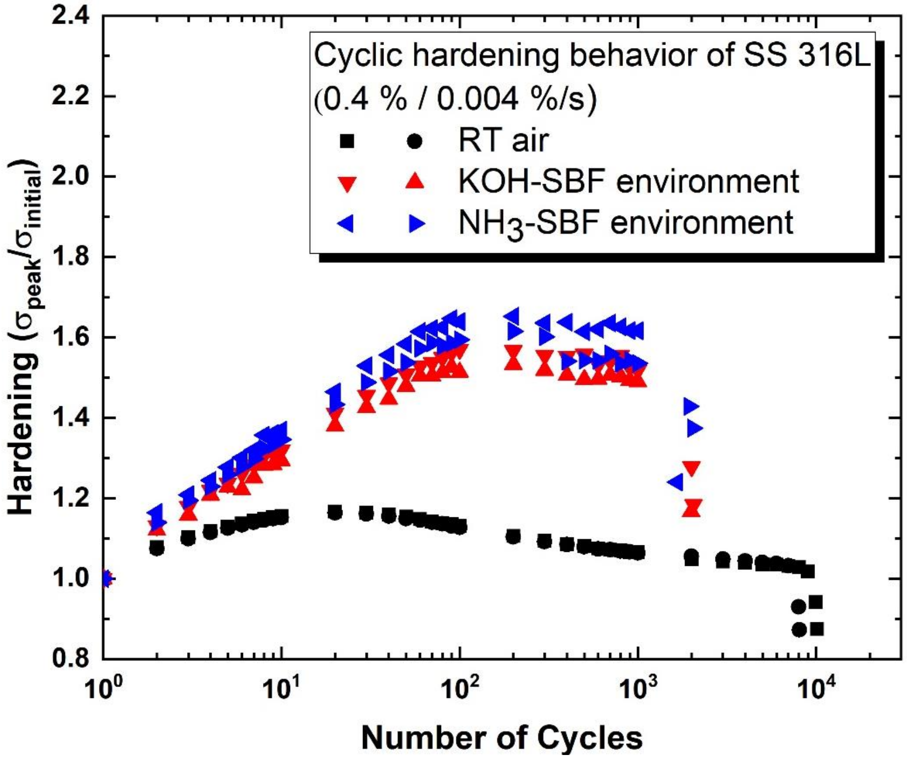


▲ ε-N curve

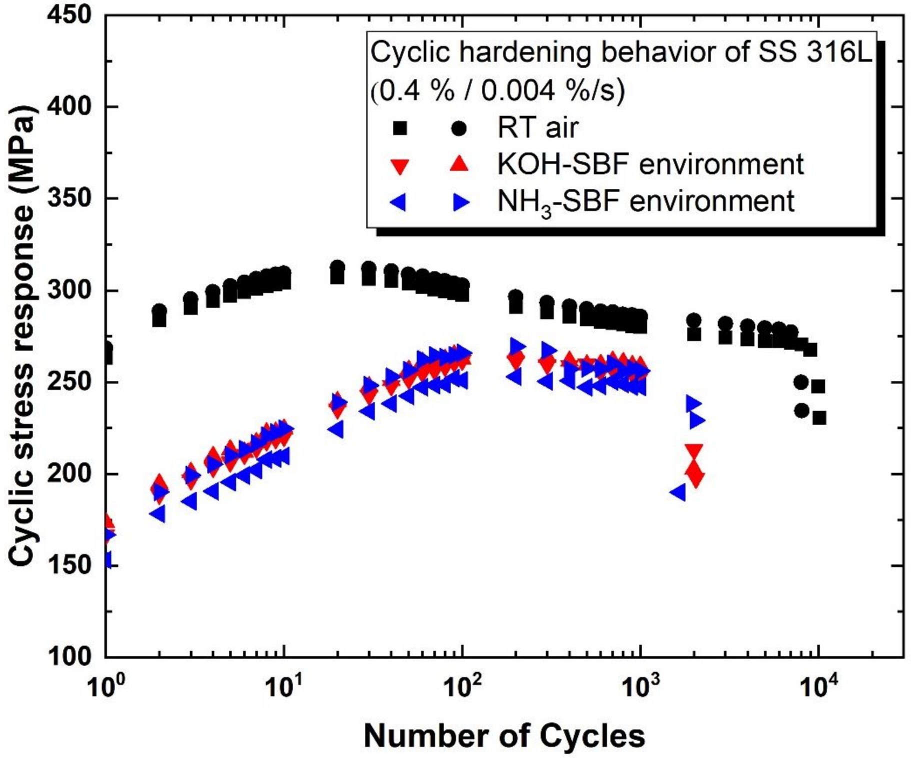
Results - EAF

❑ Environmentally-assisted fatigue test results

- Cyclic hardening response
  - RT air : primary hardening up to ~ 20 cycles / softening behavior until failure
  - SMR environment : primary hardening up to ~ 100 cycles / softening behavior until failure
- Primary hardening
  - Increase in bulk dislocations
  - Dynamic strain aging (DSA) occurrence in simulated SMR environment



▲ Cyclic hardening response



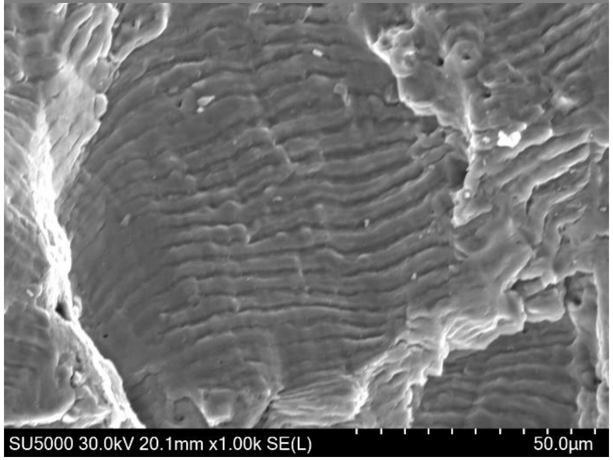
▲ Cyclic stress response

Results - EAF

❑ Fracture surface observation

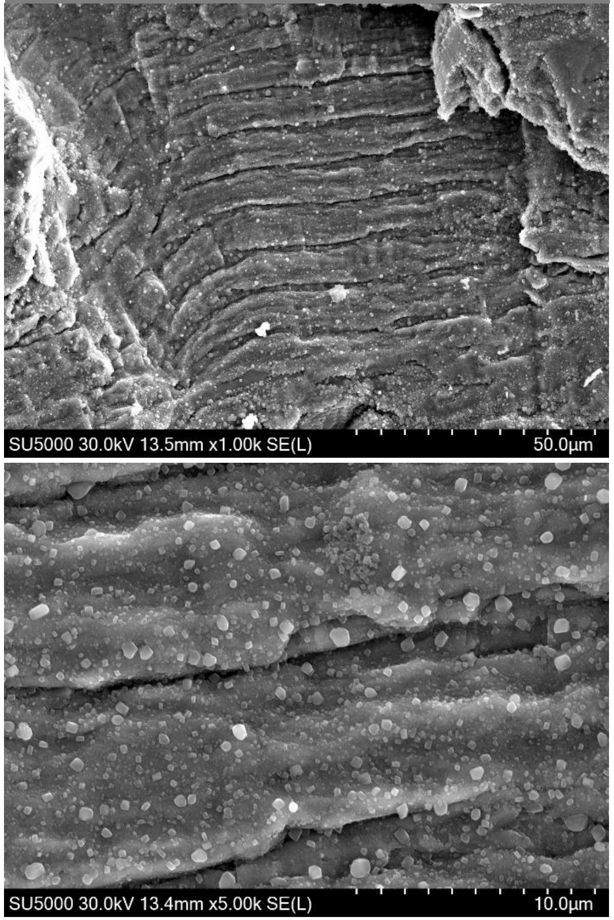
- 2.5 mm far from crack initiation point
- Well developed striation observed

RT air environment, 8045 cycles



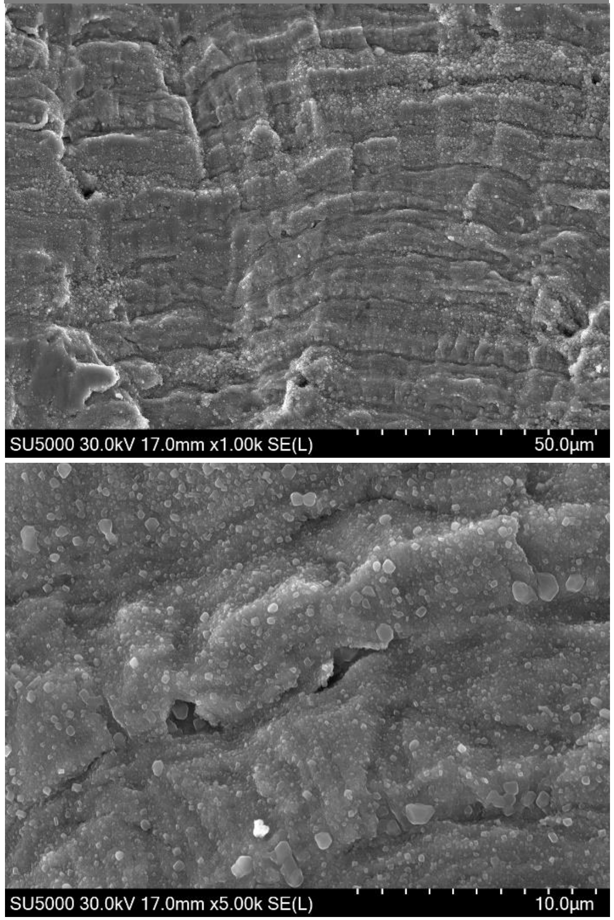
▲ Fracture surface tested in RT air environment

KOH-SMR environment, 1991 cycles



▲ Fracture surface tested in KOH-SMR environment

NH_3-SMR environment, 1657 cycles



▲ Fracture surface tested in NH_3-SMR environment

Results - Corrosion

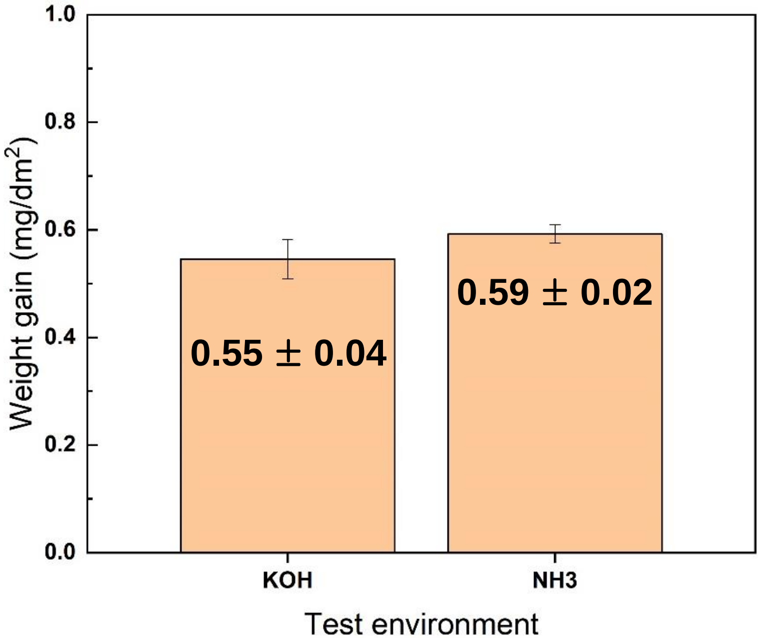
[12] H. Kim, JNM, 2018

❑ Weight change measurement

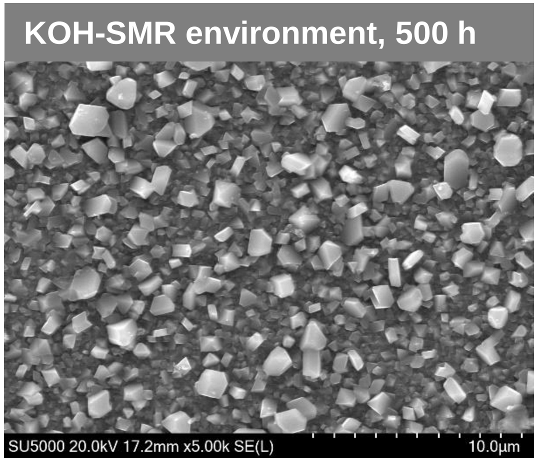
- 3 specimens were used for weight change measurement
  - Coupons were exposed to each test environments for 500 h
- Slightly higher weight gain behavior in NH_3-SMR environment
- Clear weight gain behavior compared to PWR environment
  - Kim et al.[12] reported negligible weight gain even exposure time was 30 days

❑ Surface observation

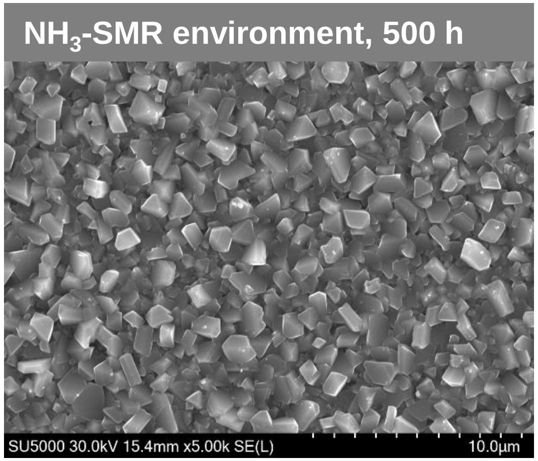
- Spinel type outer oxide particles on surface
- Number density of outer particles is high in NH_3-SMR environment



▲ Weight change of coupon specimens



▲ Surface oxide particles observation exposed in KOH-SMR environment

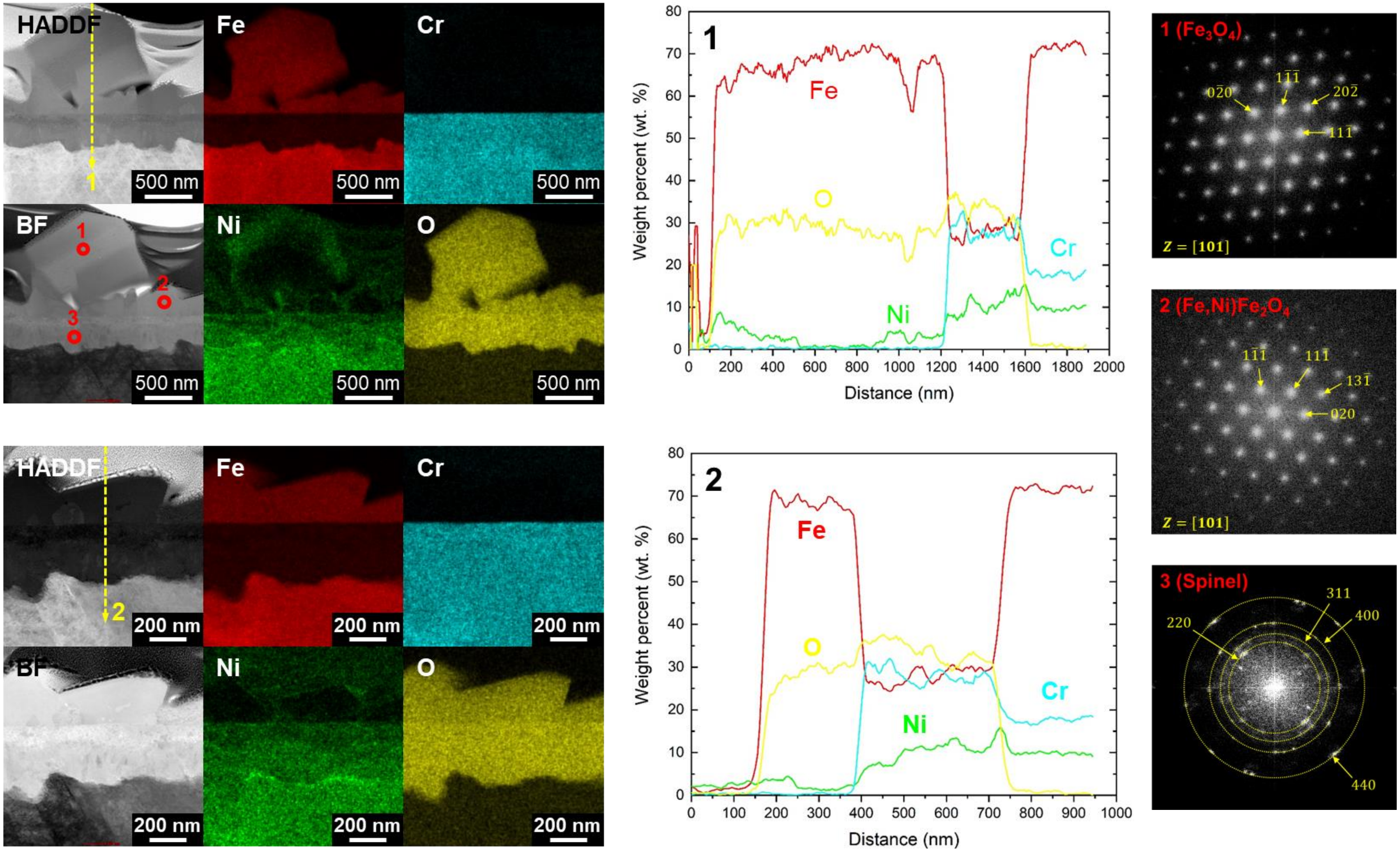


▲ Surface oxide particles observation exposed in NH_3-SMR environment

Results - Corrosion

❑ Oxide film observation

- KOH-SMR environment

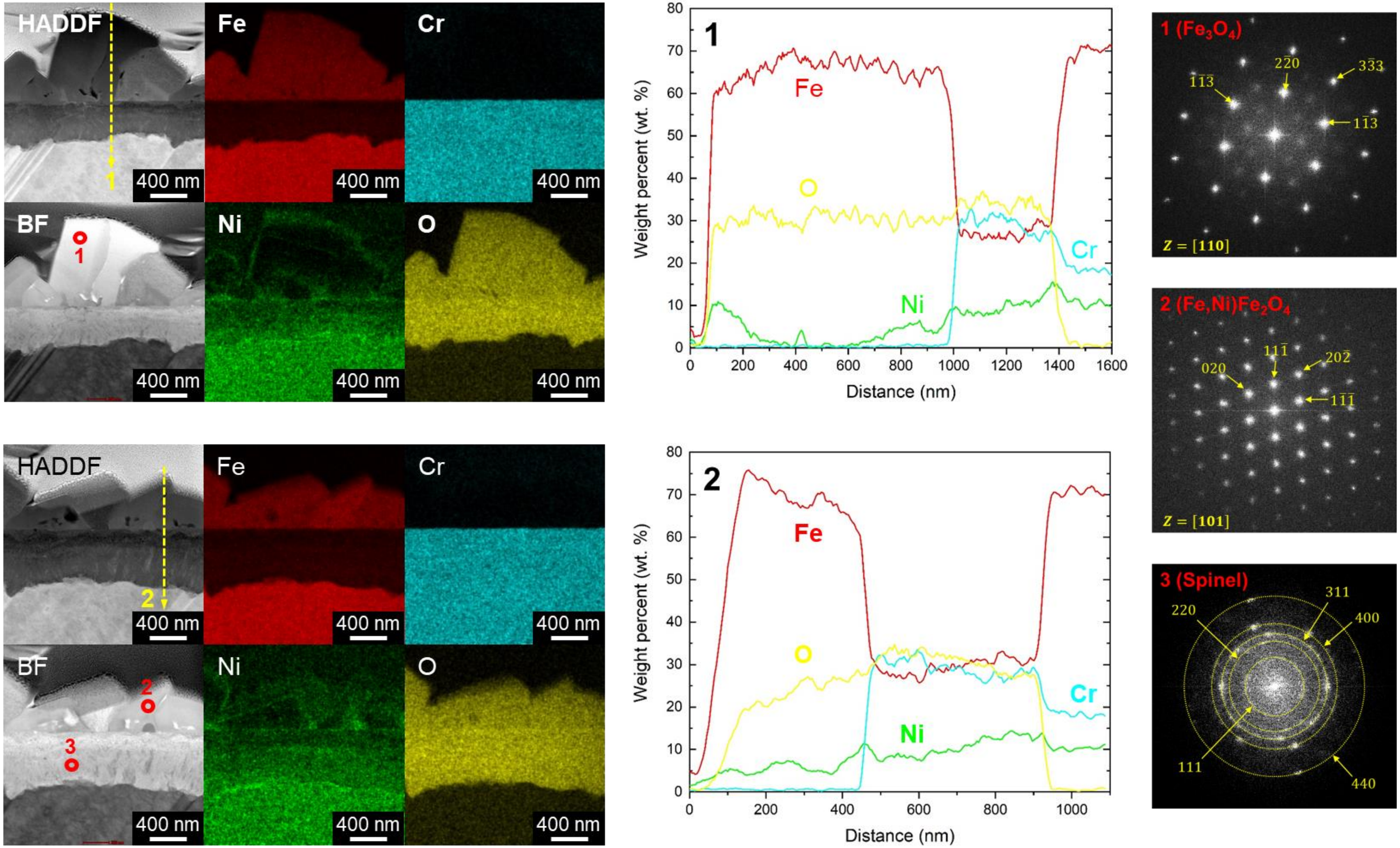


▲ Oxide film observation formed in KOH-SMR environment

Results - Corrosion

❑ Oxide film observation

- NH_3-SMR environment



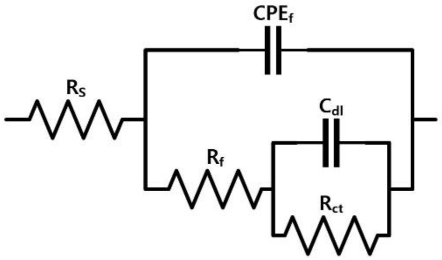
▲ Oxide film observation formed in NH_3-SMR environment

Results - Corrosion

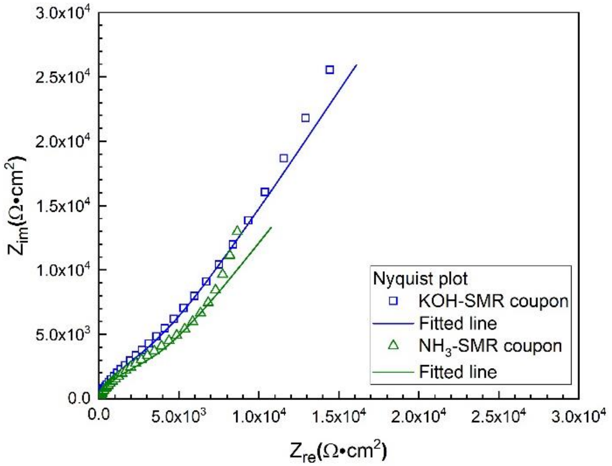
❑ Electrochemical impedance spectroscopy (EIS)

- Radius of capacitance loop : KOH > NH_3
- Impedance value at low frequency : KOH > NH_3
- Phase angle at low frequency : KOH < NH_3

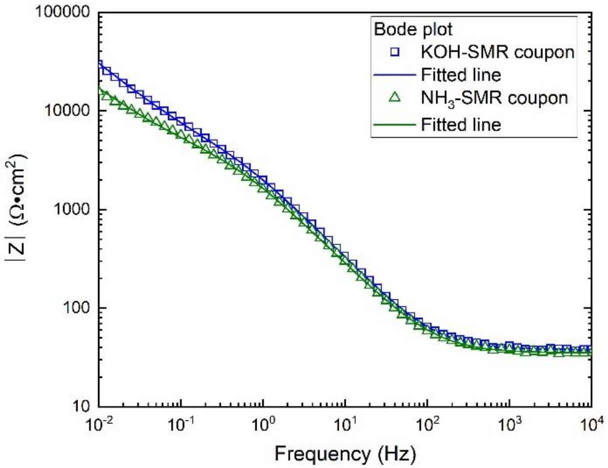
=> Higher reaction resistance in KOH-SMR environment



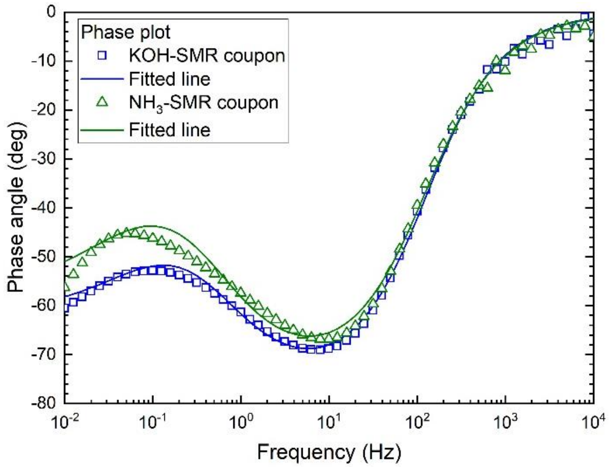
▲ Equivalent circuit used for fitting



▲ Nyquist plot



▲ Bode impedance plot



▲ Bode phase plot

Test cond.	Rs (Ω•cm^2)	Rf (kΩ•cm^2)	CPEf (μΩ•s^n•cm^{-2})	CPEf$_n$	Rct (GΩ•cm^2)	CPEdl (μΩ•s^n•cm^{-2})	CPEdl$_n$	χ^2 (10^{-4})
KOH	37.82	6.14	89.52	0.86	16.82	171.30	0.66	8.17
NH_3	34.89	4.81	112.40	0.84	9.39	329.50	0.63	19.77

Results - Corrosion

[13] M.E. Curley-Fiorino, Corros. Sci., 1980

❑ Mott-Schottky (M-S) for defect density calculation

- Semiconducting properties of the oxide layer measurement method
  - By measuring capacitance in the space charge or depletion region through application of a specific potential range to oxide layer

$$\frac{1}{C_{SC}^2} = \left(\frac{2}{\varepsilon\varepsilon_0 e N_D}\right)\left(U - UFB - \frac{kT}{e}\right)$$ for the n-type semiconductor

$$\frac{1}{C_{SC}^2} = -\left(\frac{2}{\varepsilon\varepsilon_0 e N_A}\right)\left(U - UFB + \frac{kT}{e}\right)$$ for the p-type semiconductor

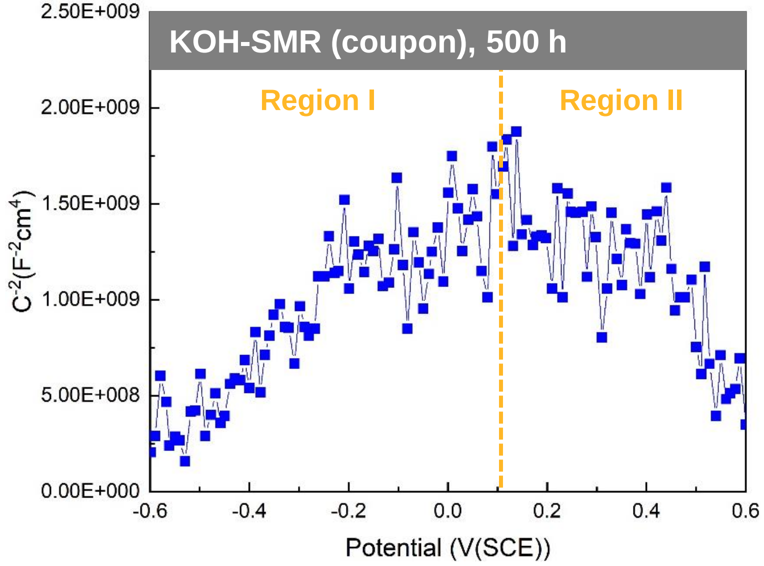
  - N_A, N_D = The density of the charge carrier (acceptor N_A, donor N_D)
  - ε = dielectric constant of oxide (assumed to 15.6 for stainless steels[13])
  - ε_0 = dielectric permittivity of vacuum = 8.85×10^{-14} F/cm
  - e = electron charge = 1.60×10^{-19} C
  - k = Boltzmann constant (1.381×10^{-23} J/K)
  - T = absolute temperature (K)
  - U = applied potential
  - U_{FB} = flat band potential

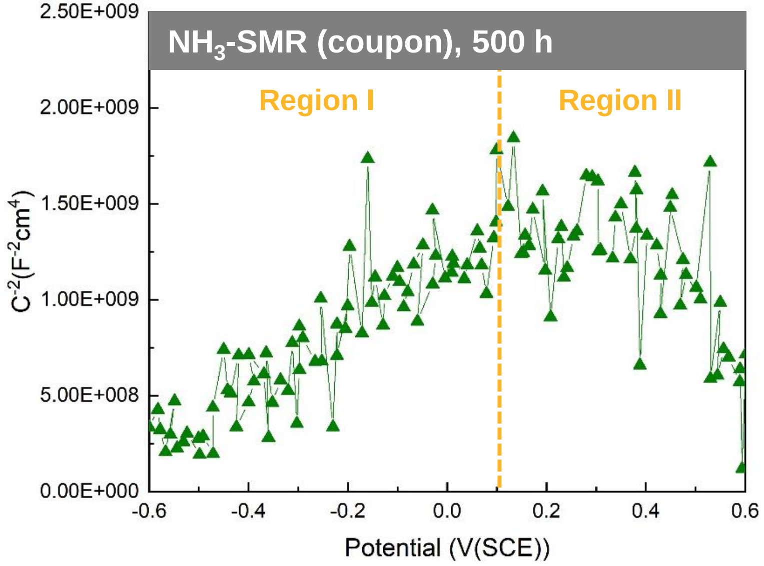
Results - Corrosion

[13] M.E. Curley-Fiorino, Corros. Sci., 1980

❑ Mott-Schottky (M-S) for defect density calculation

- No significant difference in defect density





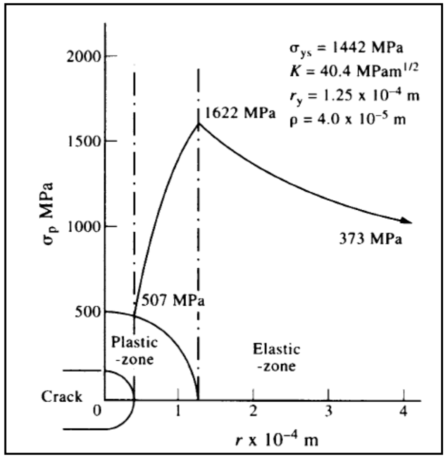
KOH-SMR			NH_3-SMR	
N_D (10^{20} cm^{-3})	N_A (10^{20} cm^{-3})		N_D (10^{20} cm^{-3})	N_A (10^{20} cm^{-3})
Region I	Region II		Region I	Region II
49.3	32.4		55.5	29.4
81.7			84.9	

Discussion

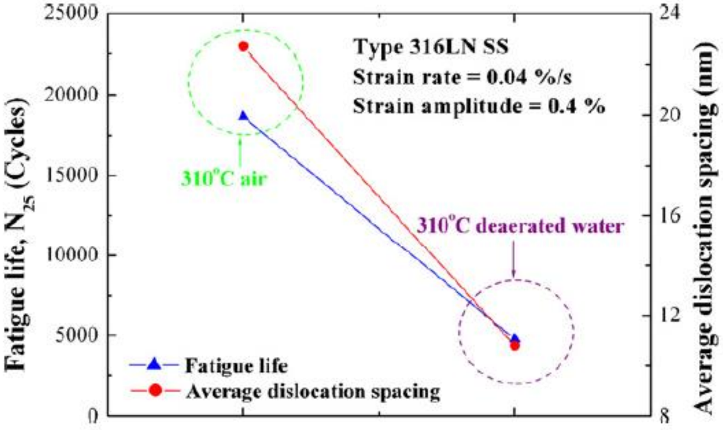
[13] A.T. Yokobori, Int'l J. of Frac., 2004
[14] H. Cho, MSEA, 2008
[15] N.K Das, Int'l J. of Hydrogen Energy, 2013
[16] H.J. Grabke, Mater. Tehno., 2000

❑ Role of Cr-rich oxide as a diffusion barrier of hydrogen absorption

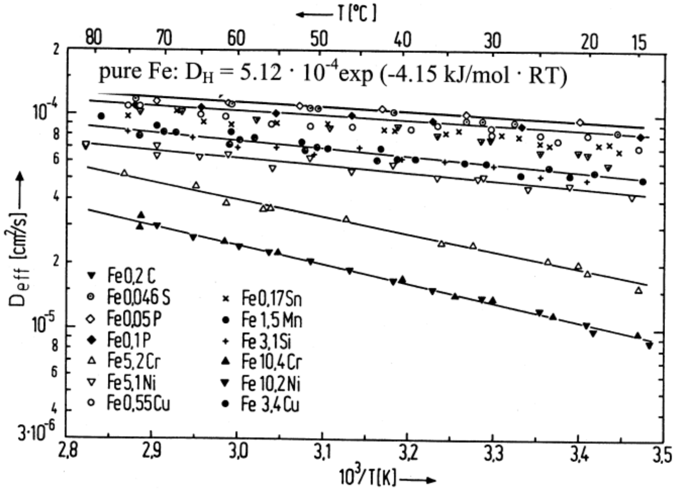
- Hydrogen induced cracking (HIC)
  - Dominant cracking mechanism of EAF of austenitic alloys
  - Corrosion produced hydrogen absorption into stress concentrated localized region
  - Decrease spacing & repulsive force between dislocations, increase dislocation density
- Hydrogen trapping by Cr-rich oxide
  - Hydrogen adsorption energy decreased on Cr-doped metal surface[15]
  - Diffusivity of hydrogen is lowered in Fe-Cr binary alloys[16]
  - Delaying occurrence of HIC by hydrogen trapping



▲ Elastic – Plastic stress field near the crack tip [13]



▲ Relationship between fatigue life and dislocation spacing [14]



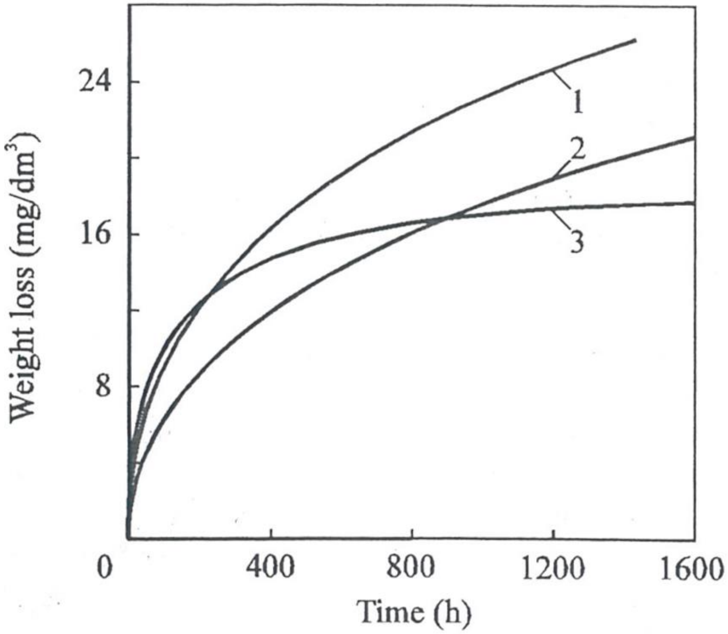
▲ Hydrogen diffusivity in binary Fe alloys [16]

Discussion

[8] V.G. Kritsky, Water chemistry and corrosion of NPP structural materials, 1999

❑ Corrosion rate in simulated SMR environments

- Clear weight gain behavior compared to PWR environment
  - Weight gain of NH_3-SMR environment was somewhat higher than KOH-SMR environment
- Parabolic kinetics of oxidation in KOH- and NH_3-SMR environment
  - Fast corrosion rate in KOH solution and fast saturation
  - Fast corrosion rate in NH3 solution and slow saturation
- Prolonged corrosion evaluation is considered



▲ Zirconium alloy (Zr-1% Nb) corrosion in water solutions at 310 ℃; 1 – NH_3, 2 – LiOH, 3 – KOH [8]

Summary & Further works

☐ Summary

- **EAF tests of 316L SS were performed in simulated SMR environment**
  - No significant change in EAF lives was observed
  - Cyclic tendency shows similar tendency
  - Distinct striations observed with oxide film formed on fracture surface

- **Oxide film characterization**
  - Thick oxide layer observation formed in both KOH- and NH_3-SMR environment compared to PWR environment
  - Higher reaction resistance was observed in KOH-SMR environment than NH_3-SMR environment
  - No significant difference in defect density measurement

☐ Further works

- Oxide film observation at the crack tip region
- Comparison of characteristics of oxide film formed on coupon and fatigue crack tip region
- Figure out the relationship between corrosion behavior and EAF behavior
- Identifying the mechanism of EAF in SMR environment that which mechanism is dominant whether HIC or metal dissolution

Energy for Earth !!

Thank you