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Effect of thermal aging on the corrosion behaviors of ER316L stainless steel welds in simulated PWR environments

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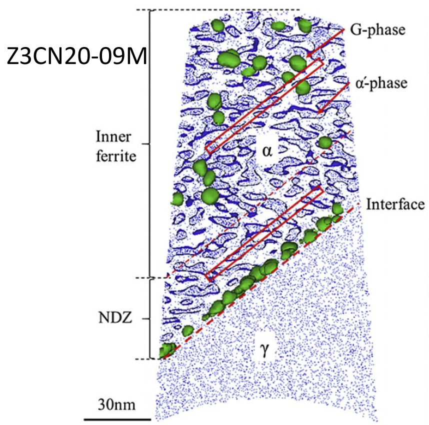
Contents

Introduction

❑ Thermal aging in LWRs systems

- Austenitic stainless steel (SS) welds and duplex stainless steel (DSS) in LWRs
  - cast primary coolant circuit pipes, safety-ends of the pressure vessels, cases of main pumps, weld joints and weld overlays
  - 5-20% δ ferrite for preventing hot cracking
- Thermal aging effect
  - Developed under 450 °C during long-term service
  - Microstructure evolution: spinodal decomposition, G-phase, Ni-depletion, etc.
  - Degradation of materials properties: corrosion resistance, mechanical properties, etc.



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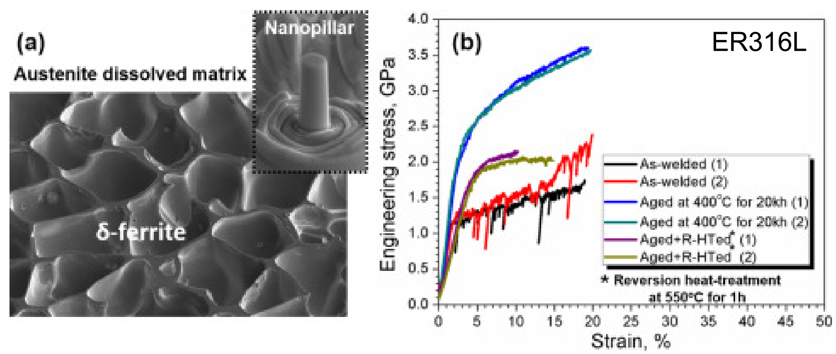

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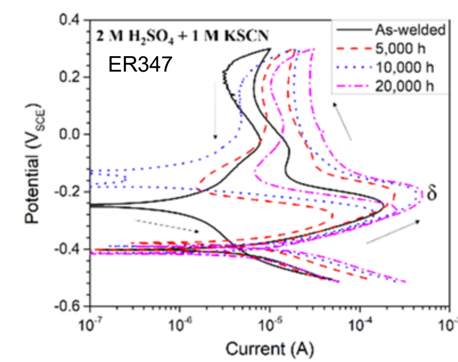


SCI REP-UK, 15091(2018)

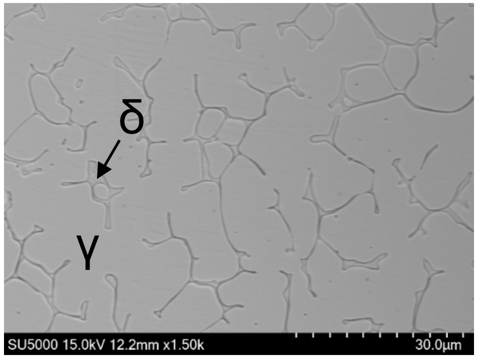
❑ Objective

- Corrosion behaviors of as-welded and thermal aged ER316L SS welds in simulated PWR primary water environment

Experimental

❑ Materials

- As-welded ER316L SS weld metal (GTAW)
- Thermal aged 10 kh @ 400 °C ER316L SS weld metal
- Composition (wt%):
  - Bulk: Fe Bal., Cr 18.4, Ni 11.0, Mo 2.6, Mn 1.7, Si 0.4, C 0.008
  - γ austenite phase : Fe 70.2, Cr 18.5, Ni 10.0 (TEM)
  - δ ferrite phase: Fe 68.1, Cr 28.4, Ni 2.4 (TEM)
  - Ferrite content (vol.%): 12.3 ± 1.3
- Pre-exposure preparation
  - 600# to 7000# SiC grinding → 1μm diamond paste polishing → 0.06 μm Alumina suspension polishing



❑ Simulated PWR primary water exposure

- B: 1200 ppm (H_3BO_3), Li: 2.2 ppm (LiOH), flow rate: ~3 L/h, pressure: 13 MPa, T@325 °C
- DO < 5 ppb, DH = 30 ml/kg water STP
- Exposure time: 500 h

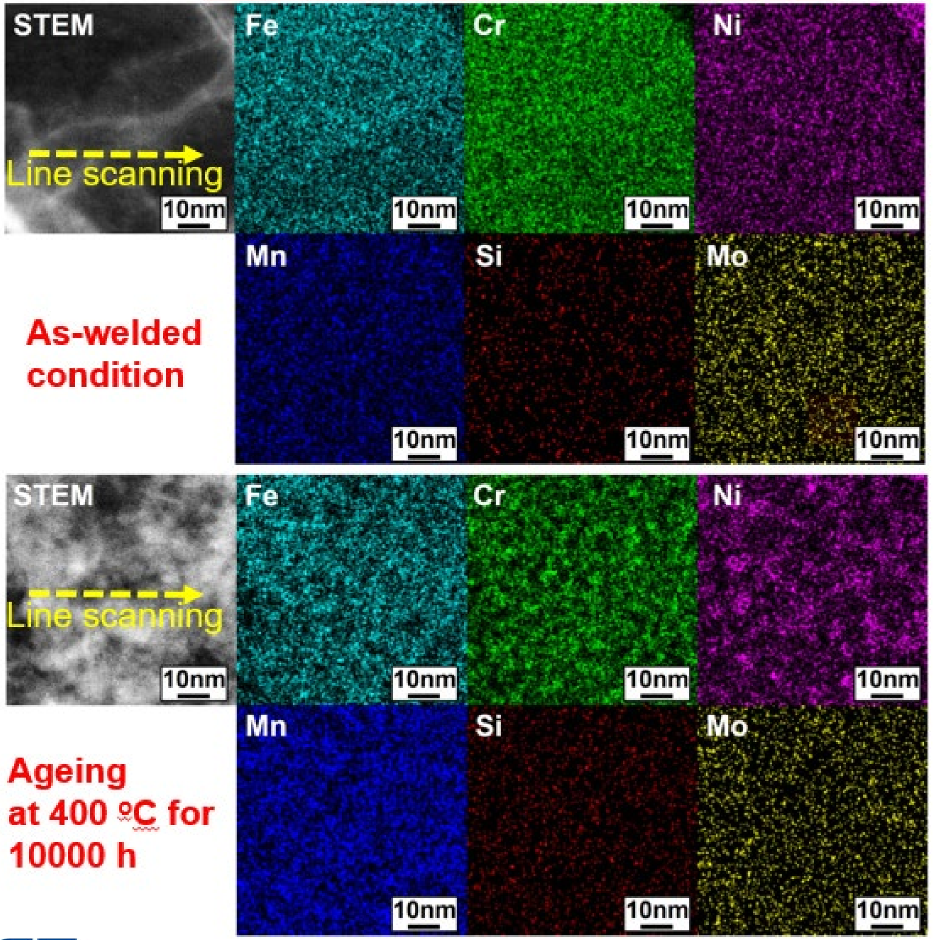
❑ Microstructure analysis

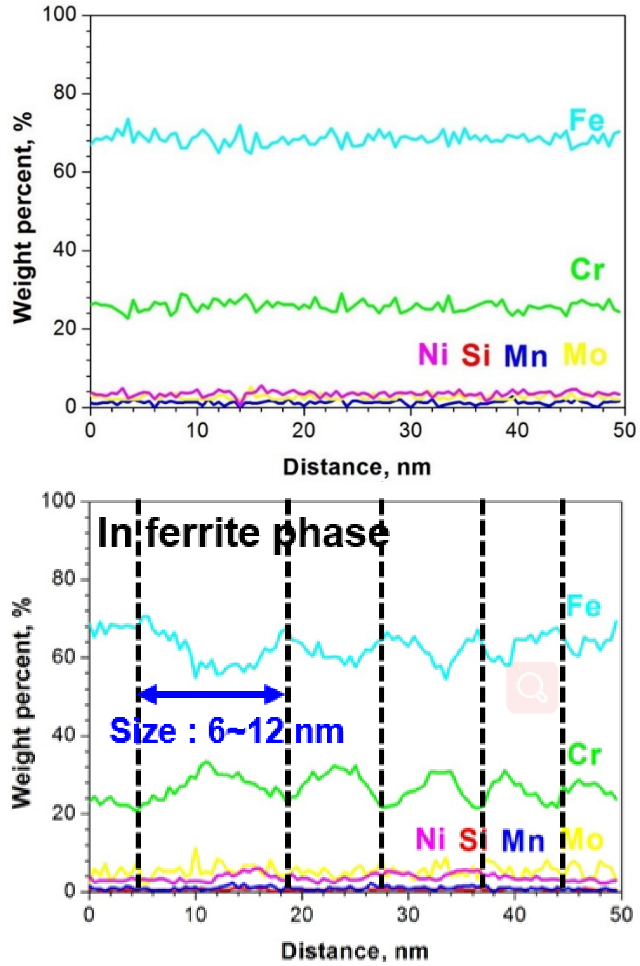
- SEM: Hitachi SU5000
- FIB: FEI Helios G4 UX
- TEM: FEI Talos F200X
- Mott-Schottky: -0.6 V(SCE) to 0.6V(SCE), @RT, buffer solution

Results

❑ Microstructure before exposure (δ ferrite)——TEM-EDS

- As-welded: no obvious element fluctuation and G phase
- Thermal aged 10 kh @ 400 °C :
  - Significant element fluctuation—— spinodal decomposition
  - No significant G phase

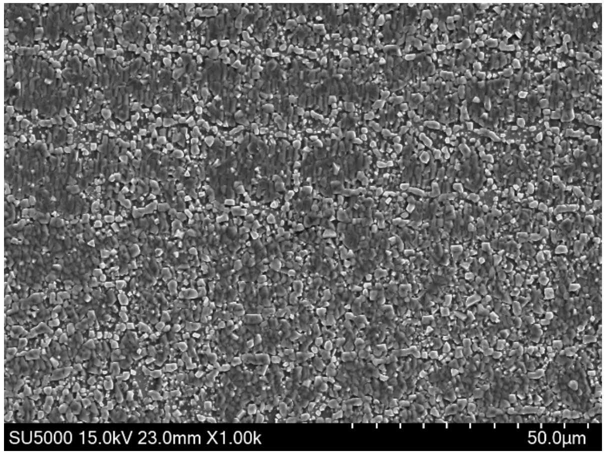


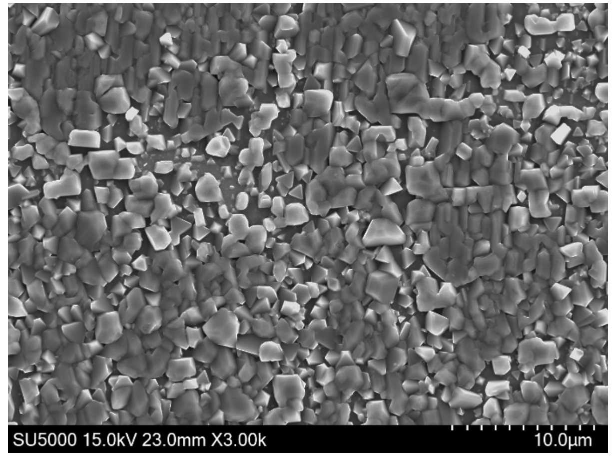


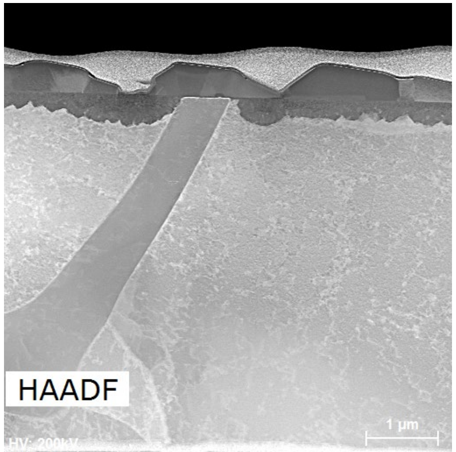
Results

❑ Oxide films analysis after exposure——SEM/TEM

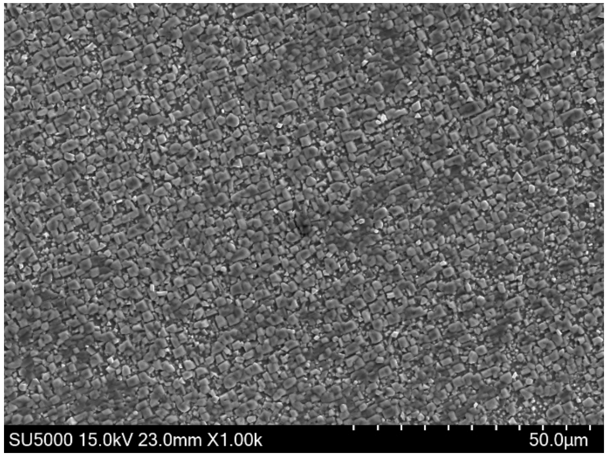
- Duplex structural oxide films

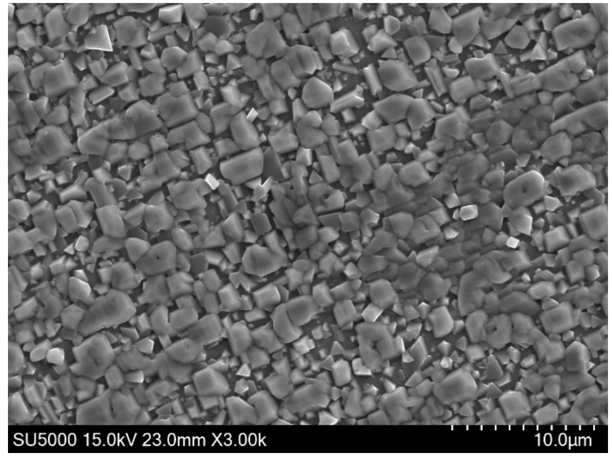


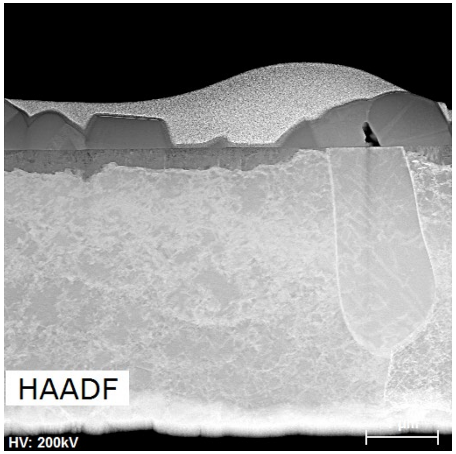




As-welded ER 316L





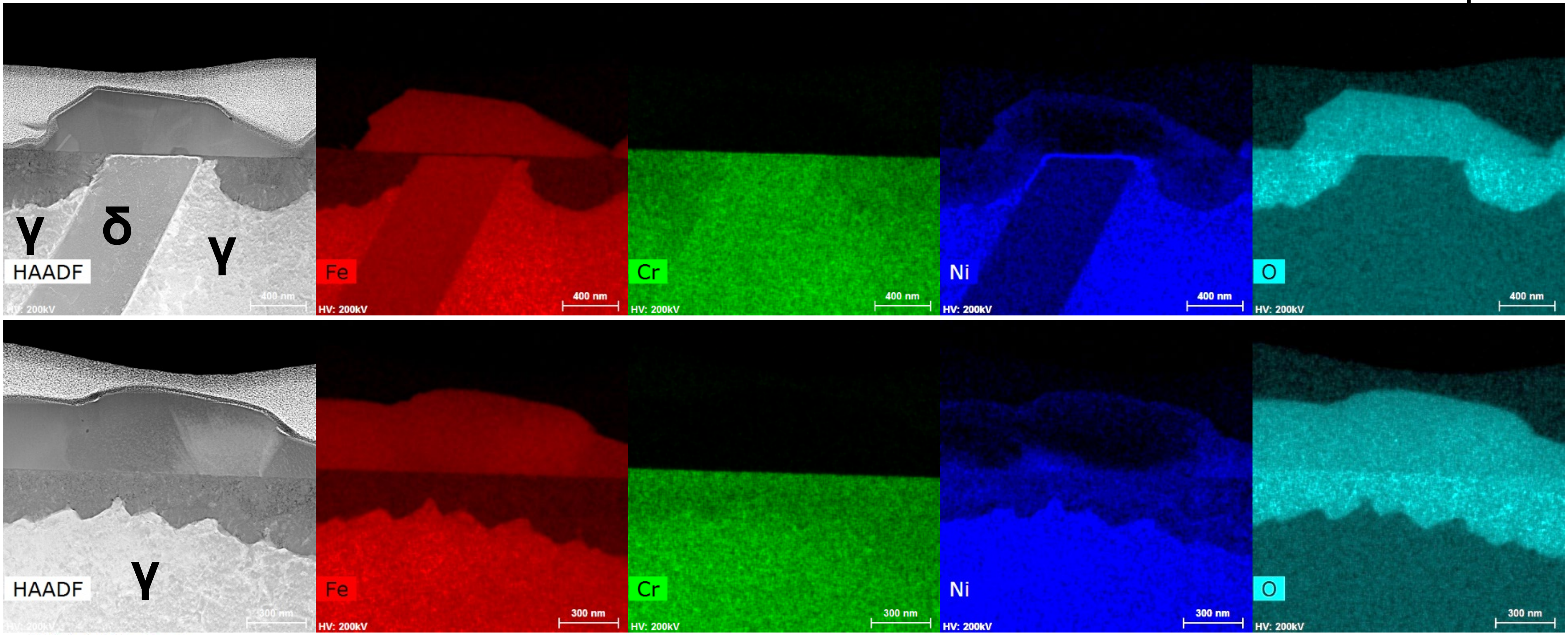


Thermal aged 10 kh ER 316L

Results

❑ Oxide films on as-welded ER316L——TEM-EDS

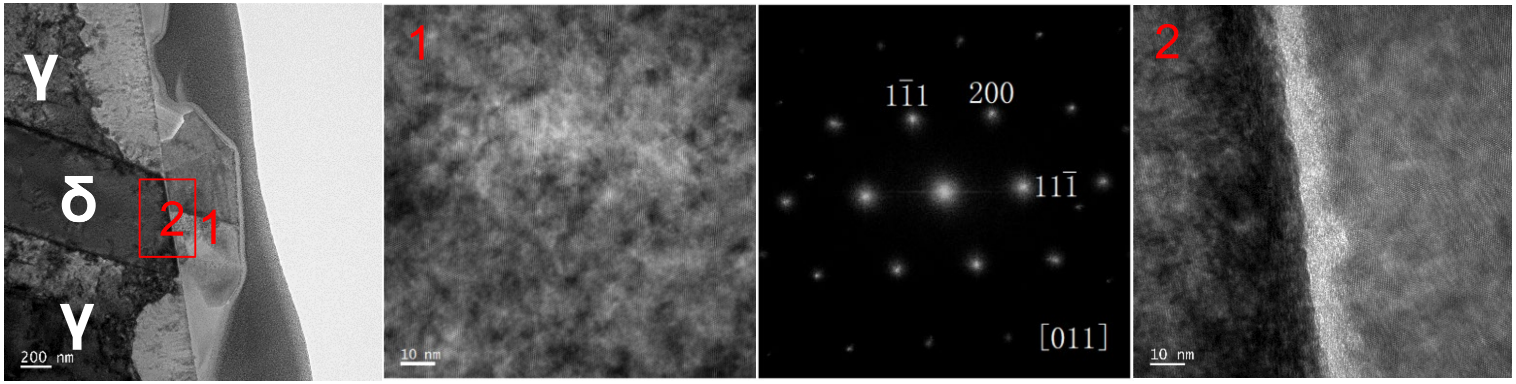
- Duplex structural oxide film
  - Outer big oxide particles on δ & γ phases: Fe-rich
  - Inner oxide films on δ phase: Cr-rich
  - Inner oxide films on γ phase: Fe, Cr, Ni
  - Ni enrichment in δ matrix beneath the δ/inner film interface
  - Ni enrichment in δ matrix close to the interface of δ/inner film on γ

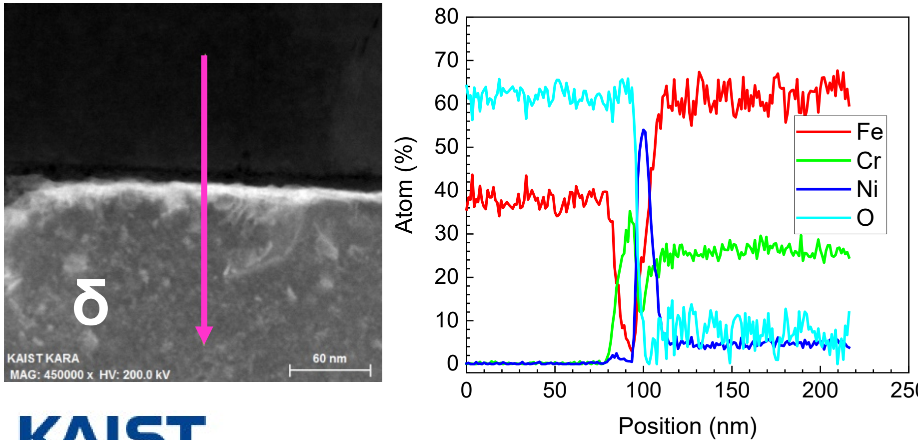


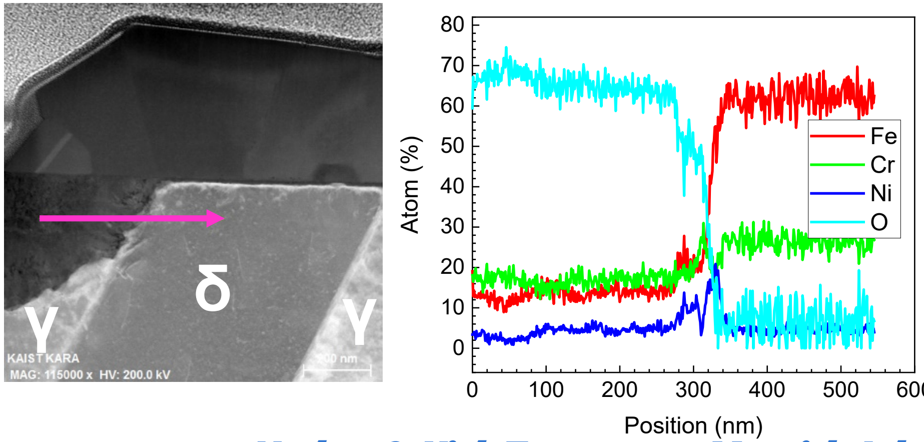
Results

❑ Oxide films on as-welded ER316L——TEM-EDS

- Duplex structural oxide film on δ phase
  - Outer spinel-type Fe-rich oxide particle
  - Inner Cr-rich amorphous thin oxide film
  - Ni enrichment in δ matrix beneath the δ/inner film interface
  - Ni enrichment in δ matrix close to the interface of δ/inner film on γ



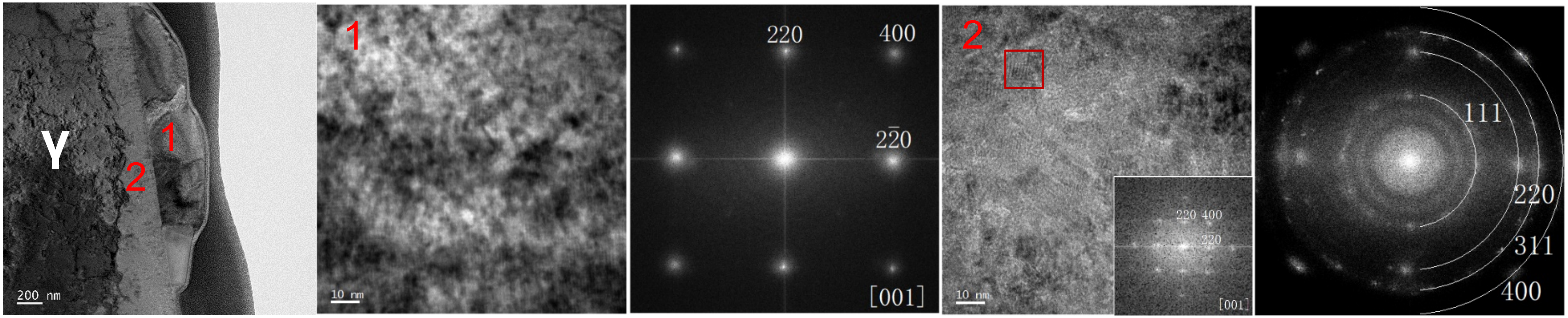


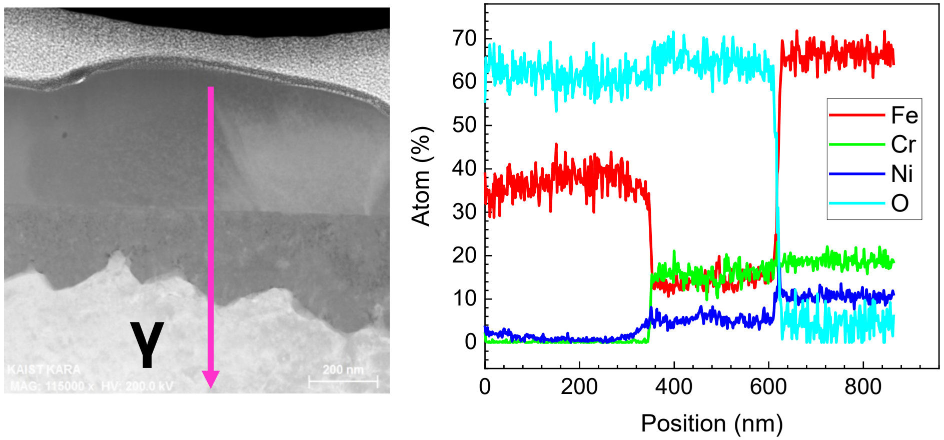


Results

❑ Oxide films on as-welded ER316L——TEM-EDS

- Duplex structural oxide film on γ phase
  - Outer spinel-type Fe-rich oxide particle
  - Inner Fe & Cr-rich spinel-type nanocrystalline/amorphous oxide film





Results

❑ Oxide films on thermal aged 10 kh ER316L——TEM-EDS

- Duplex structural oxide film
  - Outer big oxide particles on δ & γ phases: Fe-rich
  - Inner oxide films on δ phase: Cr-rich
  - Inner oxide films on γ phase: Fe, Cr, Ni
  - Ni enrichment in δ matrix beneath the δ/inner film interface
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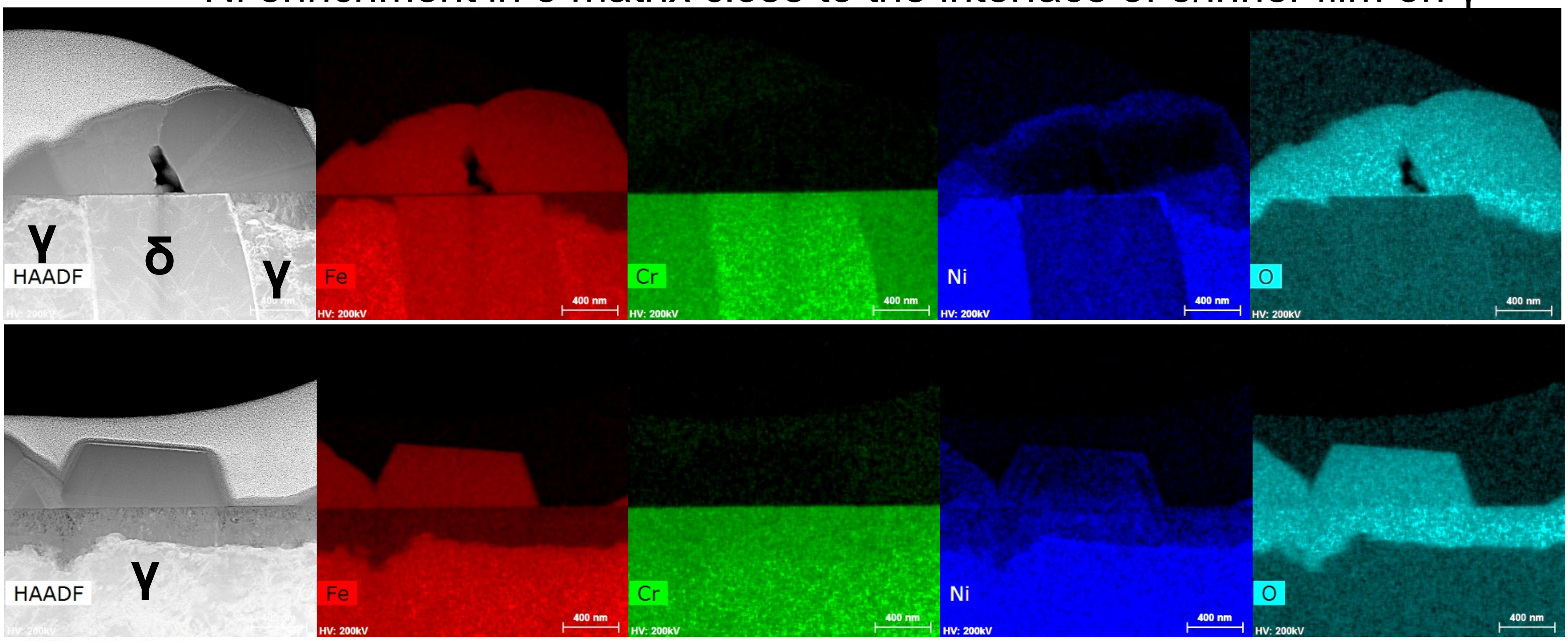
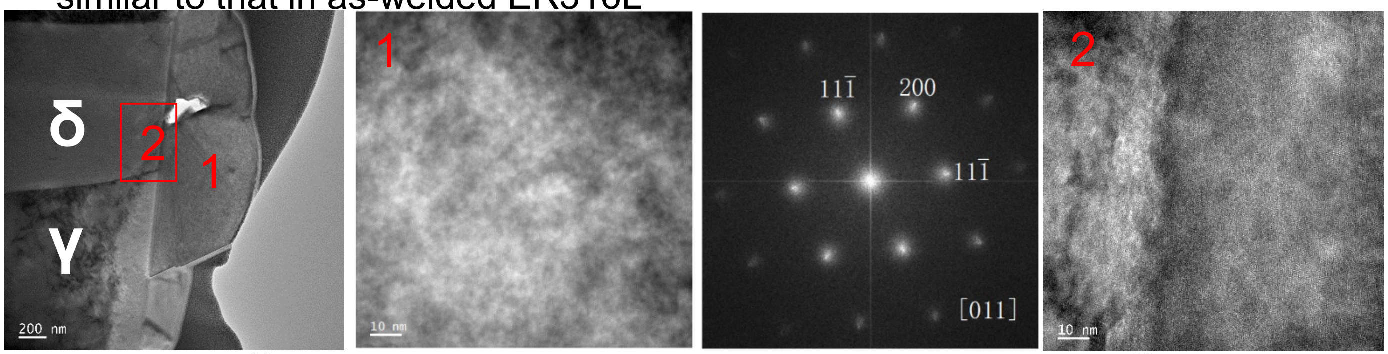
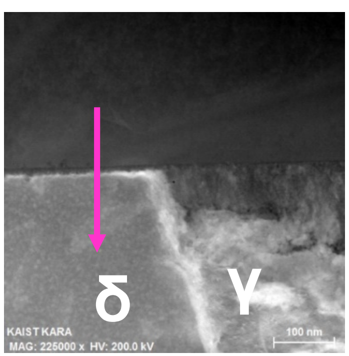


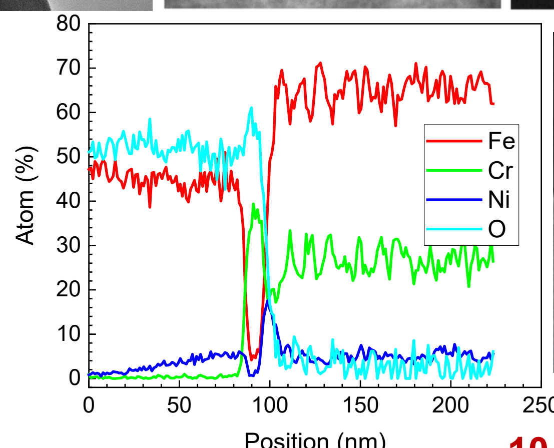
Results

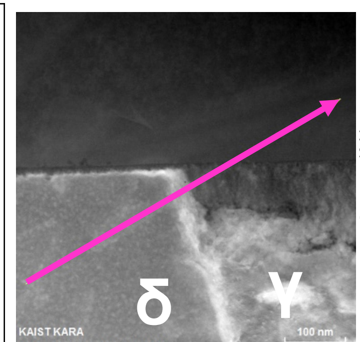
❑ Oxide films on thermal aged 10 kh ER316L——TEM-EDS

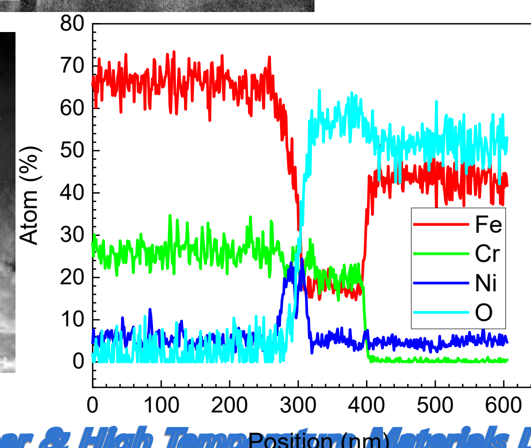
- Duplex structural oxide film on δ phase
  - Outer spinel-type Fe-rich oxide particle
    - slightly higher Ni content than as-welded ER316L
  - Inner Cr-rich amorphous thin oxide film
  - Ni enrichment in δ matrix beneath the δ/inner film interface
    - less than that in as-welded ER316L
  - Ni enrichment in δ matrix close to the interface of δ/inner film on γ
    - similar to that in as-welded ER316L







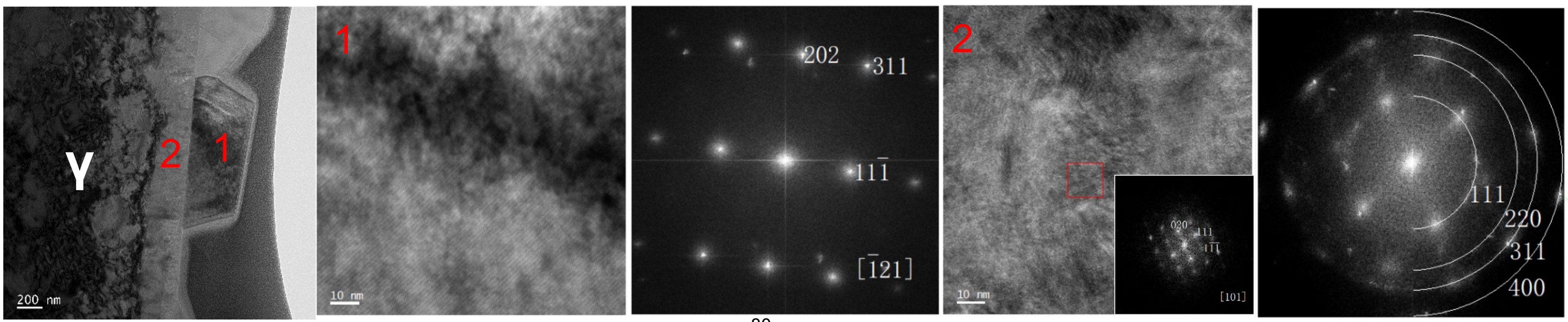


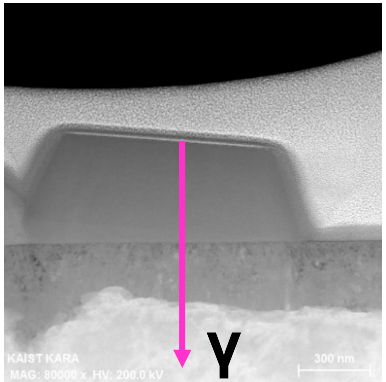


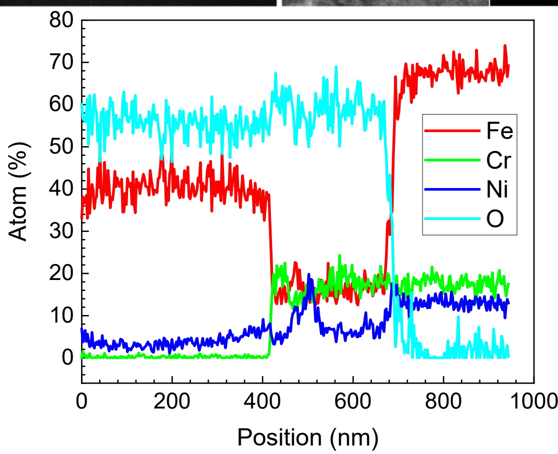
Results

❑ Oxide films on thermal aged 10 kh ER316L——TEM-EDS

- Duplex structural oxide film on γ phase
  - Outer spinel-type Fe-rich oxide particle
    - slightly higher Ni content than as-welded ER 316L
  - Inner Fe & Cr-rich spinel-type nanocrystalline/amorphous oxide film



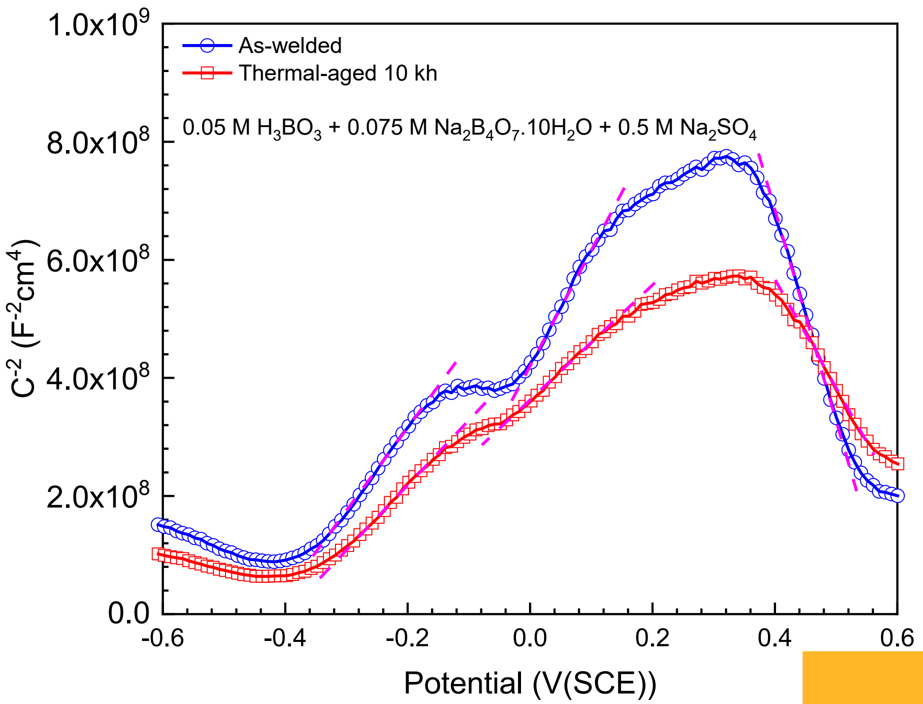




Results

Mott-Schottky analysis—— point defect density in oxides

- Higher point defect (donor or acceptor) densities in oxides on thermal aged 10 kh ER316L
  - p-type oxides: chromia, n-type oxides: spinel
  - In matrix: $D_{Cr} > D_{Fe} > D_{ni}$
  - In oxides (D): $Fe^{2+} > Ni^{2+} \gg Cr^{3+}$



For the n-type semiconductor

$$\frac{1}{C_{SC}^2} = \left(\frac{2}{\varepsilon\varepsilon_0 e N_D}\right)\left(U - U_{FB} - \frac{kT}{e}\right)$$

For the p-type semiconductor

$$\frac{1}{C_{SC}^2} = -\left(\frac{2}{\varepsilon\varepsilon_0 e N_A}\right)\left(U - U_{FB} + \frac{kT}{e}\right)$$

N_A Acceptor density
N_D Donor density
ε Dielectric constant of oxides
ε_0 Vacuum permittivity
E Electron charge
K Boltzmann constant
T Absolute temperature
U Applied potential
U_{FB} Flat band potential

	Region I N_D (10^{20} cm^{-3})	Region II N_D (10^{20} cm^{-3})	Region III N_A (10^{20} cm^{-3})
As-welded	47.5	33.4	30.9
Thermal aged	68.9	73.4	57.9

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Summary

- Microstructure after thermal ageing
  - As-welded ER316L: no obvious element fluctuation and G phase
  - Thermal aged 10 kh @ 400 °C ER316L:
    - Significant element fluctuation—— spinodal decomposition
    - No significant G phase
- Corrosion behaviors in PWR environment
  - Duplex structural oxide films formed on as-welded and thermal aged ER316L:
    - Outer spinel-type oxide particles
      -as-welded: Fe-rich, Ni & Cr-depleted
      -thermal-aged: Fe-rich, with slightly higher Ni content
    - Inter oxide film on γ austenite phase
      - nanocrystalline/amorphous spinel-type oxide film
    - Inter oxide film on δ ferrite phase
      - Cr-rich amorphous thin oxide film
    - Higher point defect densities in oxide films of thermal aged ER316L
      - as-welded: higher Ni enrichment in δ matrix beneath the δ/inner film interface
      - thermal-aged: slightly higher Ni content in the outer oxide films
- Future work
  - High resolution observation of oxide film/matrix interface on δ ferrite
  - Water chemistry effect

Energy for Earth !!

Thank you!