

# MICROSTRUCTURAL INVESTIGATION OF OXIDE FILMS OF ALLOY 182 WELD METAL FORMED UNDER BWR ZINC WATER CHEMISTRY

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## 1. Background story

Radioactive build-up in oxide films of light water reactors (oxide films with radioactive isotope <sup>60</sup>Co).

**+ ZN INJECTION**

Zn ion diffusion into the Cr-rich passive layer; release of (active) <sup>60</sup>Co.  
 $FeCr_2O_4 + Zn^{2+} \rightarrow ZnCr_2O_4 + Fe^{2+}$   
 $NiCr_2O_4 + Zn^{2+} \rightarrow ZnCr_2O_4 + Ni^{2+}$

Reduction of radioactivity by Zn-injection (5-10 ppb in plants).

Potential side effect: Zn decreases susceptibility to stress corrosion cracking (SCC).

[1]

**HWC & PWR**

<sup>60</sup>Co  
Zn

Direct oxidation  
Dissolution  
Precipitation

**PRECIPITATED Fe-RICH OUTER LAYER ZnFe<sub>2</sub>O<sub>4</sub>**

**COMPACT PROTECTIVE Cr-RICH INNER LAYER OF SPINELS ZnCr<sub>2</sub>O<sub>4</sub>**

## 2. Objectives & environment

| Water chemistry | Temp. [°C] | Pressure [bar] | Dissolved H <sub>2</sub> [ppb] | pH <sub>T</sub> | Zn injection [ppb] | ECP conditions          |
|-----------------|------------|----------------|--------------------------------|-----------------|--------------------|-------------------------|
| BWR             | 274        | 90             | 253                            | 5.6             | 0                  | Ni/NiO phase transition |
|                 |            |                |                                |                 | 40                 |                         |
|                 |            |                |                                |                 | 0 + 40             |                         |
|                 |            |                |                                |                 | 40 + 40            |                         |

- To identify Zinc (Zn) in the oxide layers.
- To reveal the impact of Zn on SCC mitigation and to identify the underlying mechanism.
- The dependence of stress threshold, oxide film thickness and film microstructure on the Zn injection.

## 3. Methodology

Material & specimens:  
Coupons & flat tapered tensile specimens of Alloy 182 weld metal.

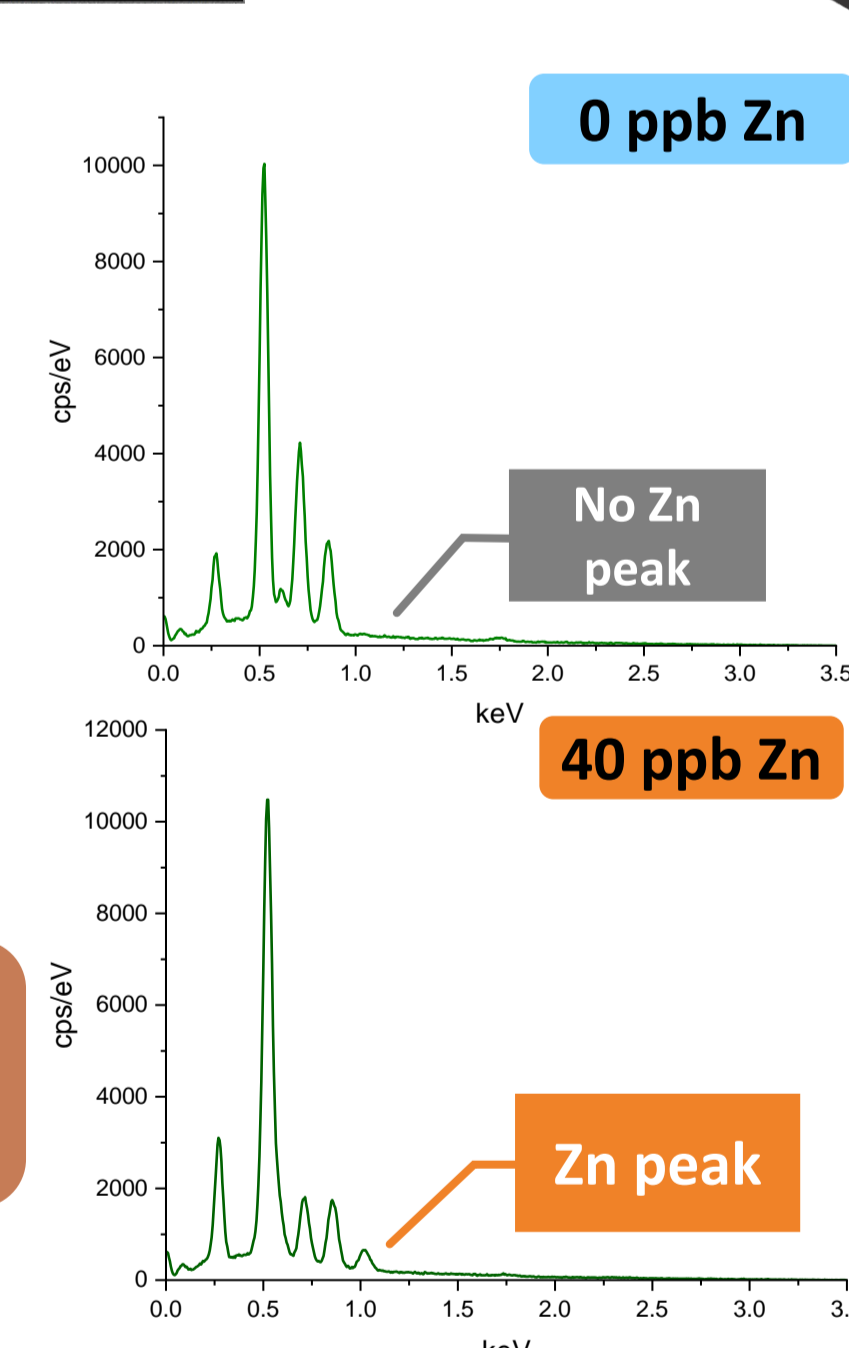
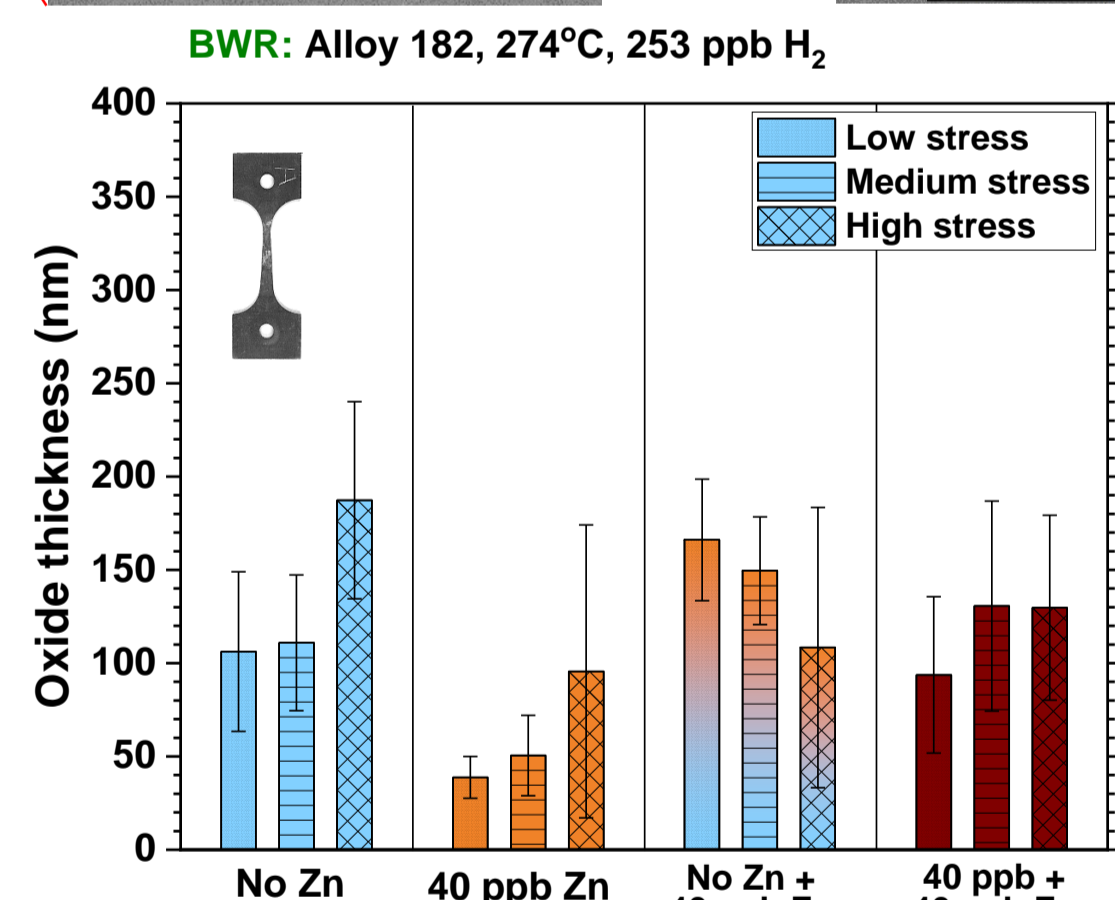
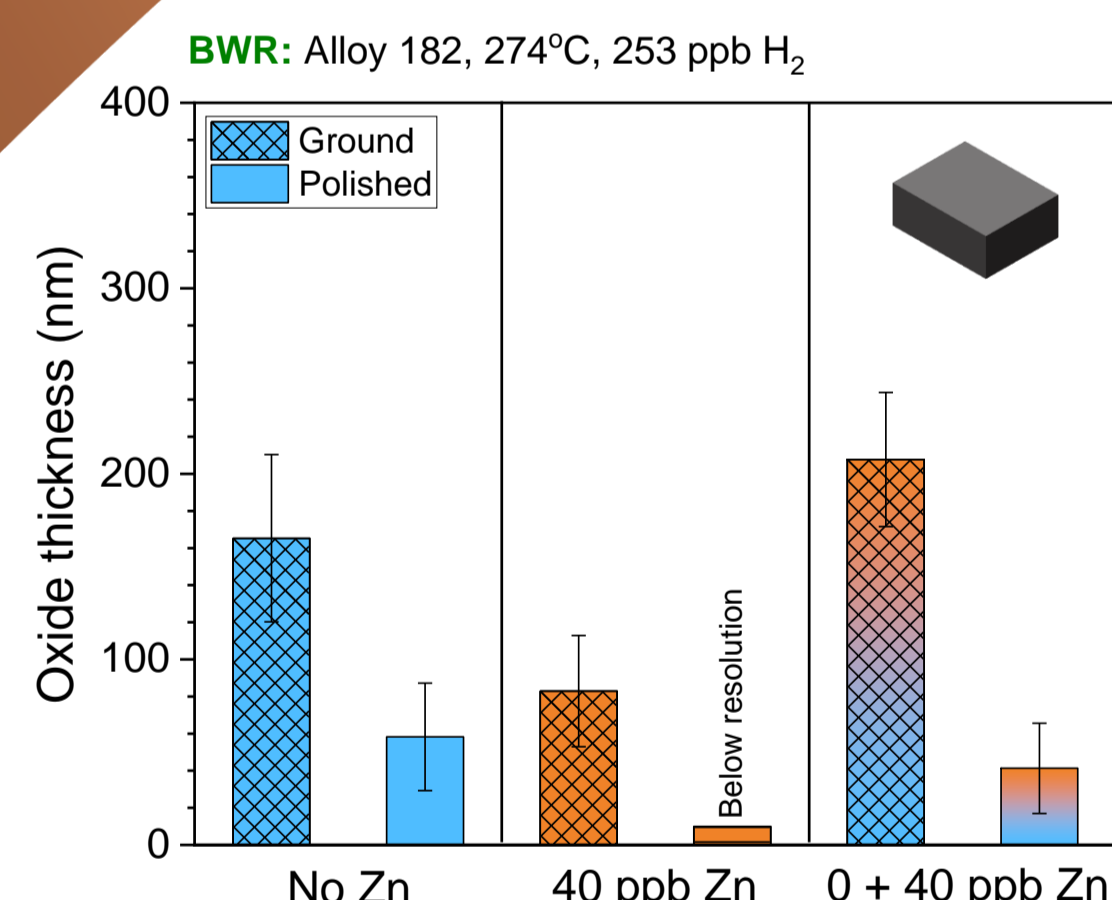
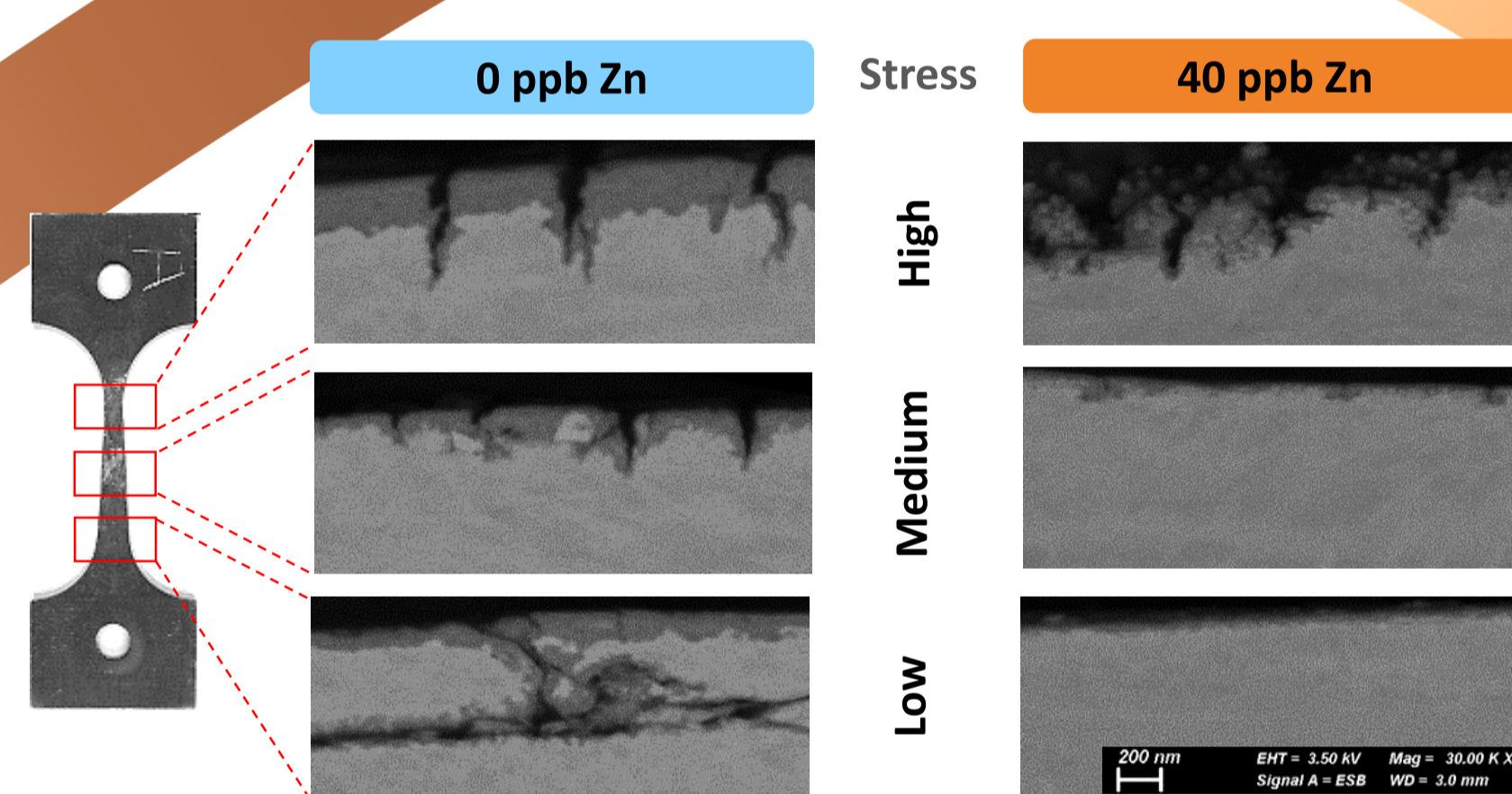
Testing procedure:

- Exposure tests for ~350 h per test.
- Constant extension rate tensile (CERT) testing with strain rate  $(d\epsilon/dt) = 5 \times 10^{-7} s^{-1}$ .

Microstructural characterization:

- Field emission gun SEM (Zeiss ULTRA™ 55)
- EDS windowless detector (Oxford Ultim Extreme)

## 4. SCC initiation (CERT tests)



Compare ground surfaces!

SEM  
Acc = 3.5 kV  
WD = 5 mm +/- 0.1 mm  
Aperture D = 60 μm  
Tilt: 0 deg  
Magnification: 2000 X

SEM-EDS  
Process time: 6 (dead time >38%, output counts 8000)  
Channels: 2048 (high resolution)  
Data collection with pick normalization  
Map resolution: 2048  
Dwell time 5 μs  
Autolock (drift correction for 5 μs)

1. A SCC mitigation effect by Zn was observed for accelerated CERT tests under BWR conditions.

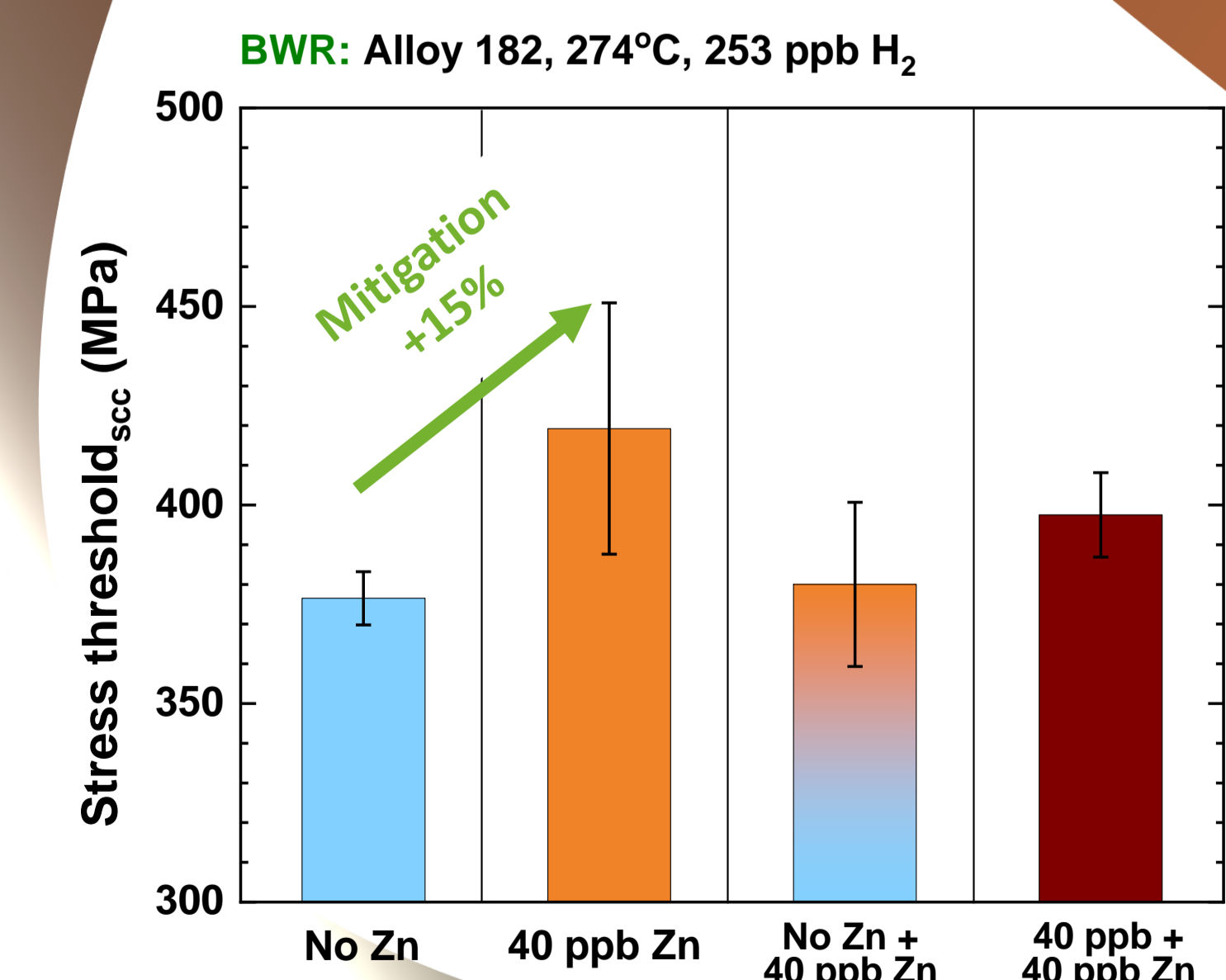
2. Zn is incorporated into the inner oxide layers and uniformly distributed.

3. The oxide layer is significantly thinner and seems to be more compact with Zn injection than without.

4. There is no clear evidence of neither SCC mitigation, nor oxide thickness reduction when short-term (~350 h) Zn injection is applied after pre-oxidation in Zn-free environment.

5. There is no influence of low and medium stress on the oxide layer thickness (for ground surface).

## 6. TAKEAWAYS



## 7. Outlook

Further microstructural and electrochemical characterization of the oxide film and SCC cracks are ongoing and planned. Tests with lower Zn contents (15 ppb) are ongoing.