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## Radiolysis effect on oxide film of 316L stainless steel formed in PWR primary water under irradiation

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FROM RESEARCH TO INDUSTRY



# RADIOLYSIS EFFECT ON OXIDE FILM OF 316L STAINLESS STEEL FORMED IN PWR PRIMARY WATER UNDER IRRADIATION

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11th specialist workshop on radiation chemistry and electrochemistry in the nuclear fuel cycle, Friday 7th October 2016, Brighton, UK

www.cea.fr



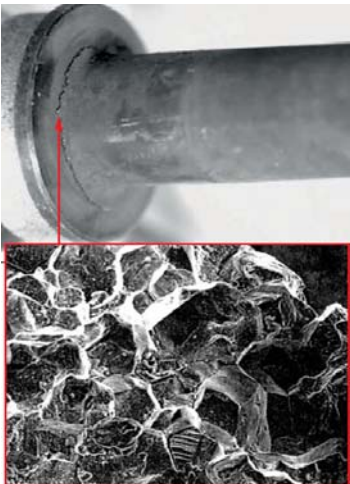
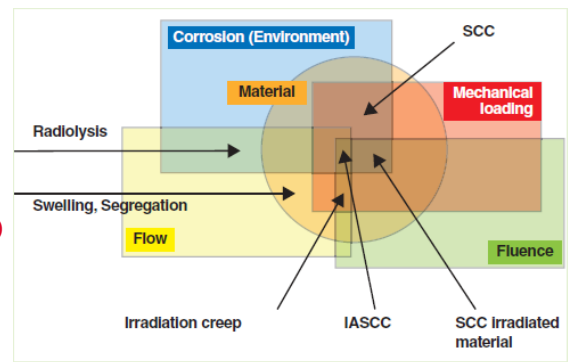
## CONTENT

Background

Experimental setup

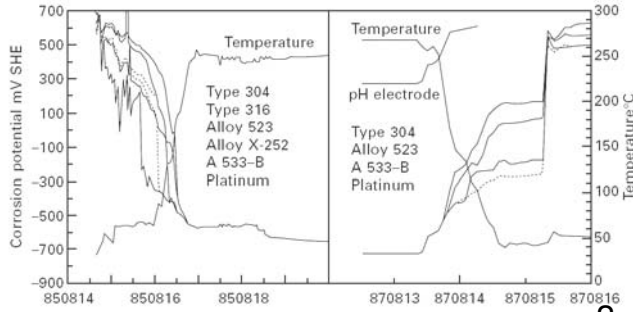
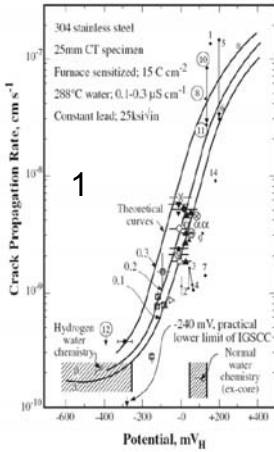
Results

Conclusive remarks



## Increase of SCC initiation and propagation with corrosion potential

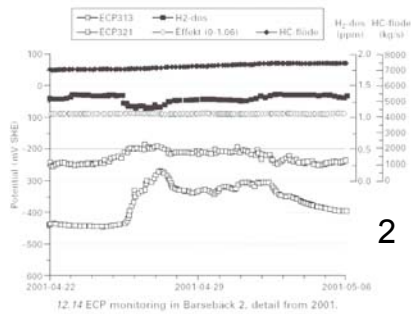
- High Temperature and High pressure



12.21 Examples of ECPs measured during start-up and shut-down in a PWR primary system.

## Increase of $E_{cor}$ under irradiation

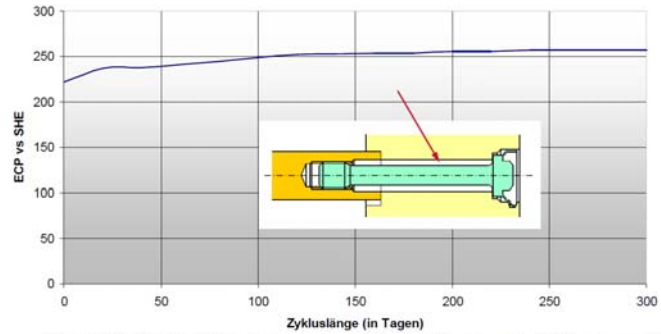
- Reported for BWRs (low hydrogen)
- PWRs (high hydrogen): low potentials
- Slight increases under irradiation (proton & electron) in PWR conditions



1 D.D. Macdonald, in Nuclear Corrosion Science and Engineering, Woodhead Pub., 2012  
2 A. Molander, in Nuclear Corrosion Science and Engineering, Woodhead Pub., 2012

## Increase of $E_{cor}$ under irradiation calculated in confined zones, like gaps between the bolt-shank and the former for PWR internals

- Radiolysis simulation is based on hydrogen addition following the primary chemistry guidelines, radiolysis dissociation and recombination under the influence of hydrogen and acceleration of radiolysis by the presence of oxygen



The REDOX-Potential is in the range of 220 to 260 mV<sub>SHE</sub> ("oxidizing" conditions) and increases along one fuel cycle.

Renate Kilian and al., Results from systematic compilation of barrel bolt findings in S/KWU type PWRs in the context of computational analysis, Fontevraud 8, 15-18 September 2014

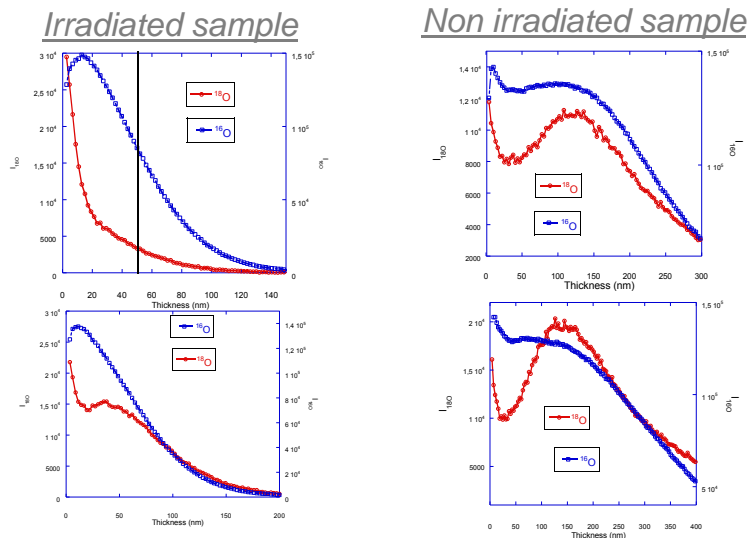
- Higher potentials than expected are calculated due to water radiolysis in PWRs primary environments

## Radiation and stainless steel corrosion

- Influence of irradiation on the growth of stainless steel oxide layer at 300°C ( $H_2^{18}O$  / PWR conditions)

Short term exposure

Long term exposure

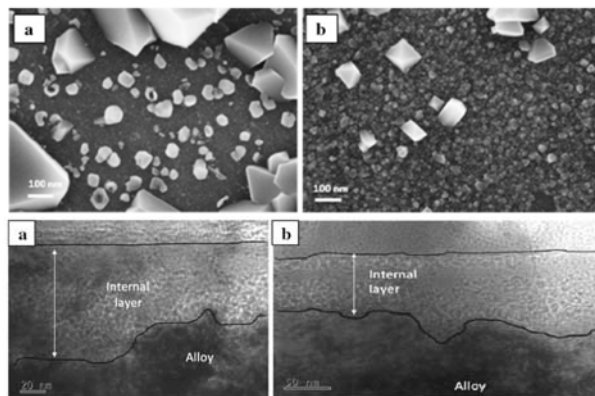


S. Perrin & al., Eurocorr 2011  
Dumervil & al., Corrosion Science, 2016

➔ Growth at external interface + internal interface  
Slower diffusion in the irradiated sample

## Radiation and stainless steel corrosion

- Oxide layers (proton irradiation / PWR chemistry)
  - Increase of the density of the crystallites of the external layer
  - Slower diffusion of oxygen in the internal layer ( $O^{18}$  experiments)

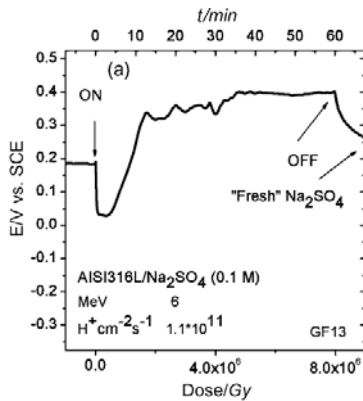


S. Perrin & al., Oxidation of metal, 2013, 80, pp 623-633

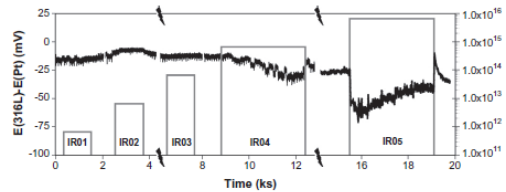
a Non-irradiated sample / b Irradiated sample

## Radiation and electrochemical behavior

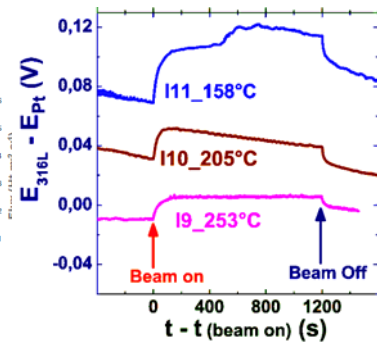
- Electrochemical behaviour (proton & electron irradiations)
  - Importance of radicals
  - Immediate oxidative response to electron and proton beams
  - Response ( $\Delta E$ ) decreases when temperature and hydrogen increase



E. Leoni & al., *Electrochimica acta*, 53 (2007) 495-510



B. Muzeau & al., *JNM*, 419 (2011) 241-247

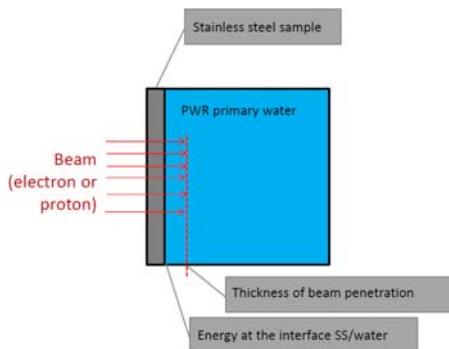


## Proton &amp; electron irradiation

- Defects in the materials
- Evolution of the oxide layer
- Radiolysis

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## Objective: radiolysis versus irradiation



- With proton beam: defects in the material, oxide film and radiolysis
- With electron beam: mainly radiolysis
- Similar penetration thickness in water
- Platinum electrodes and hydrogen sensor far from the beam penetration

- Conditions of e- beam
  - Energy 0.6 MeV at 316L/PWR water
  - Penetration 500  $\mu\text{m}$
  - Flux: varying or fixed
  - Duration: hours - days

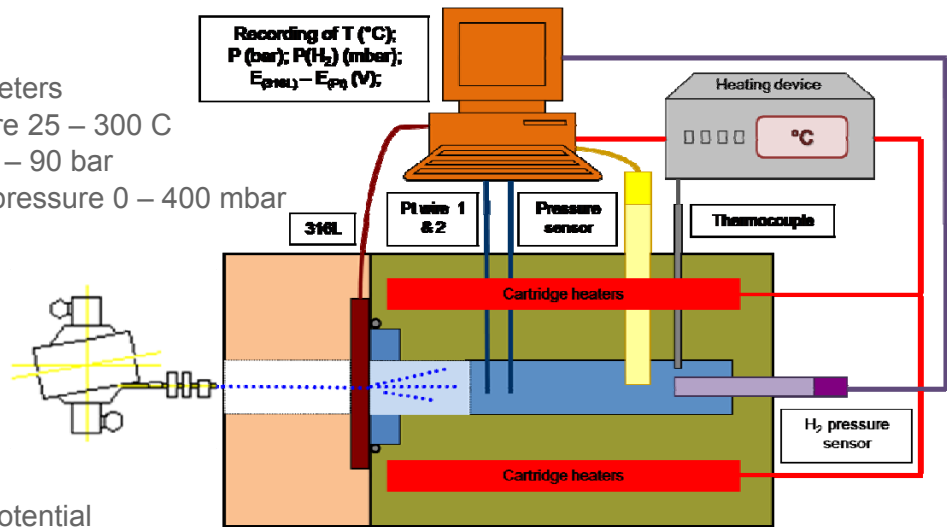
- Conditions of H+ beam
  - Energy 6 MeV at 316L / PWR water
  - Penetration 480  $\mu\text{m}$
  - Flux: varying or fixed; mostly 30 nA
  - Duration: 20 – 60 min

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## HTHP cell

- Designed to record the potential of a 316L / PWR water interface under irradiation at high temperature (HT) and high pressure (HP) and to monitor the hydrogen concentration

- Monitoring: parameters
  - Temperature 25 – 300 C
  - Pressure 0 – 90 bar
  - Hydrogen pressure 0 – 400 mbar



- Measuring: Free potential
  - Platinum wire electrodes
  - E316L – Ept accuracy ± 1 mV

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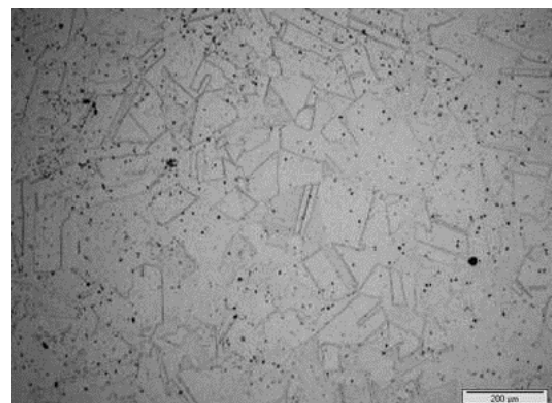
Sample material: 316L stainless steel

C	Mn	Si	P	S	Cr	Ni	Mo	Co	Cu	N	Fe
0.03	1.82	0.3	0.033	0.028	16.6	10.2	2.21	0.11	0.43	0.056	68.2

Surface finishing: bright  
electrochemical polishing

Thickness: 0,6 to 1,0 mm

Mean grain size: 20 μm



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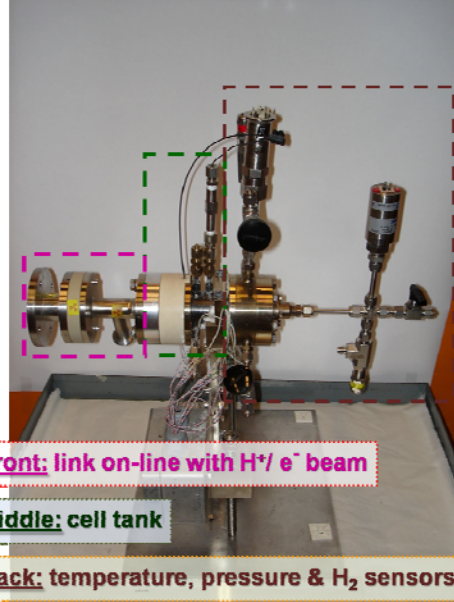
## HTHP cell

- Designed to record the free corrosion potential of a 316L / PWR water interface under irradiation at high temperature (HT) and high pressure (HP).

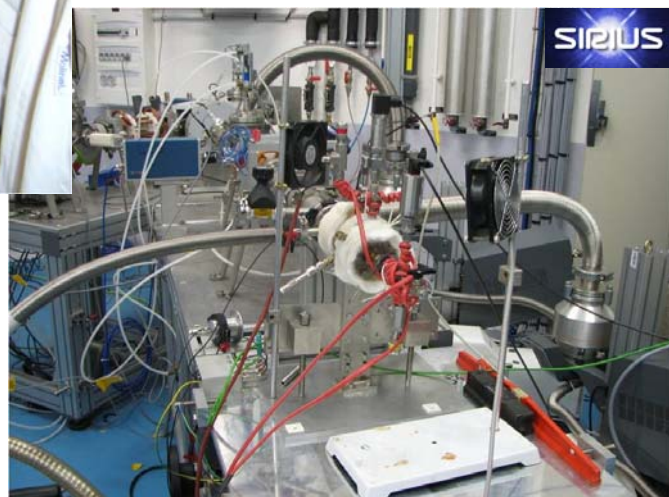
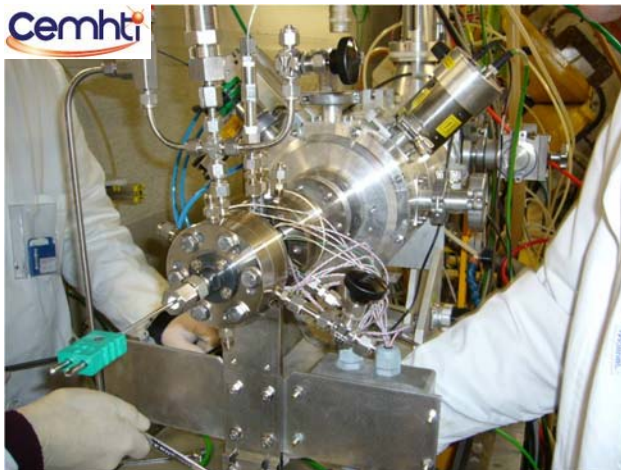
- Material: Stainless steel 316L
  - 17Cr/ 10Ni/ 3Mo
- Primary PWR water
  - 2 ppm [Li] + 1000 ppm [B]
  - Deaerated, H<sub>2</sub> addition
  - pH300C = 7
  - no flow, static water
- Radiation:
  - proton
  - electron

Cemhti

SIRIUS



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## Electrochemical behaviour under irradiation

- Results presented at the last workshop in Sapporo (2014)

## Characterisation of Oxide Film

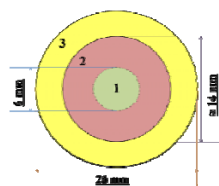
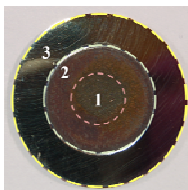
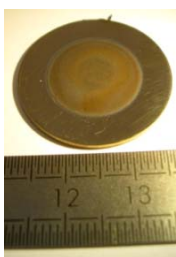
- Morphology – SEM Analysis
- Oxide Film – TEM Analysis

## Comments & Outlooks

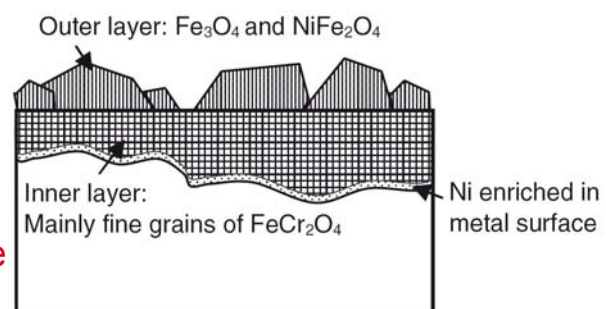
## CHARACTERISATION OF OXIDE FILM

Comparison → continuously e<sup>-</sup> irradiated 316L vs. unirradiated 316L

Sample	Duration (hr at 300C)	P(H <sub>2</sub> ) (mbar)	Energy (MeV)	Fluence (x10 <sup>18</sup> e <sup>-</sup> cm <sup>-2</sup> )
Non irradiated	72	133	No	No
Irradiated	65	29	1.8 / 0.6	4.736



Non irradiated 316L oxide film in PWRs



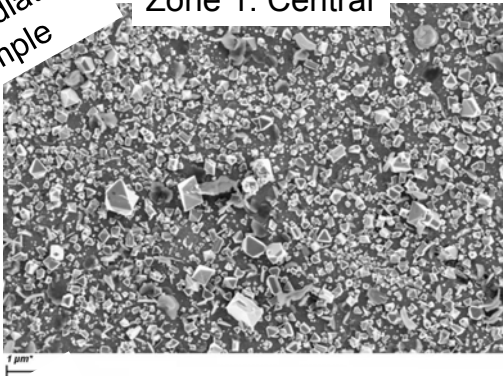
### Three zones on the irradiated sample

- Zone 1: irradiation & PWR water
- Zone 2: no irradiation & crevice PWR water
- Zone 3: no irradiation & no PWR water



Non irradiated  
sample

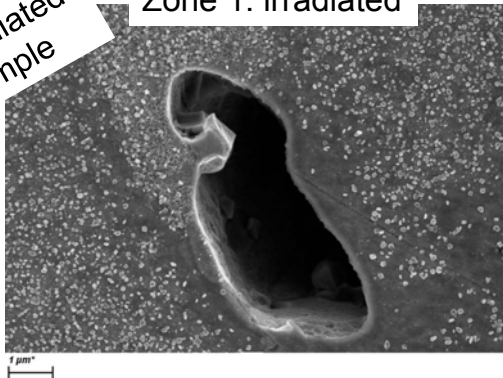
Zone 1: Central



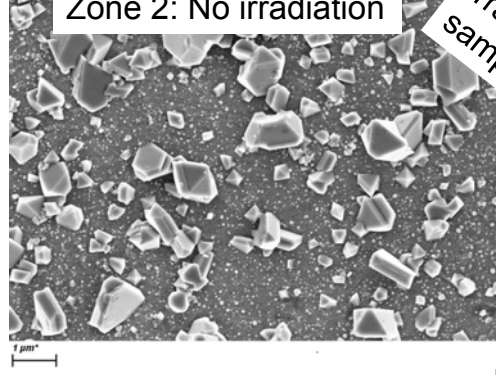
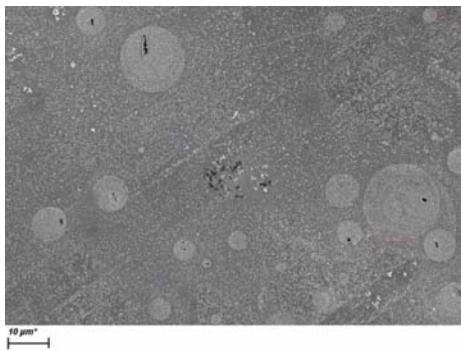
Zone 2: surrounding

Non irradiated  
sampleIrradiated  
sample

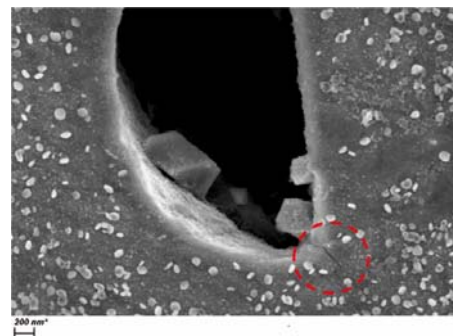
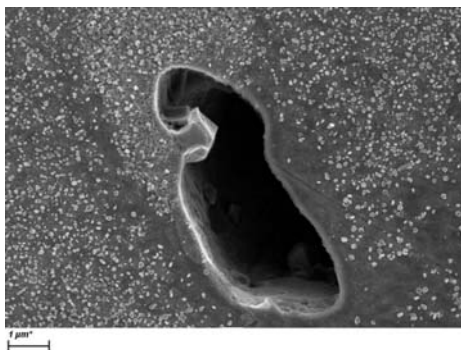
Zone 1: irradiated



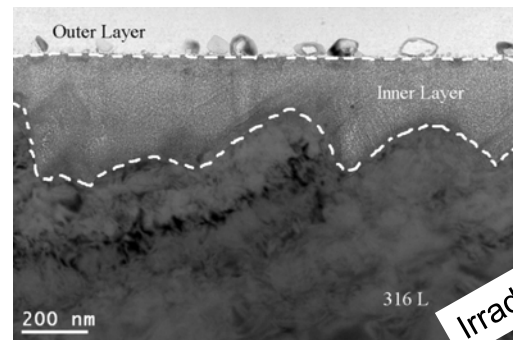
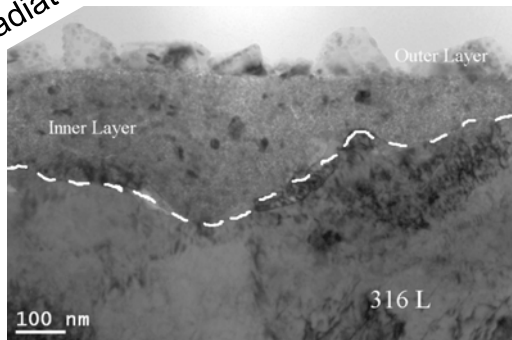
Zone 2: No irradiation

Irradiated  
sample

SEM micrographs of irradiated  
316L stainless steel in the  
irradiated zone (zone 1) at  
various magnifications  
Cavities with small crystals  
inside and some cracks



Unirradiated



Irradiated

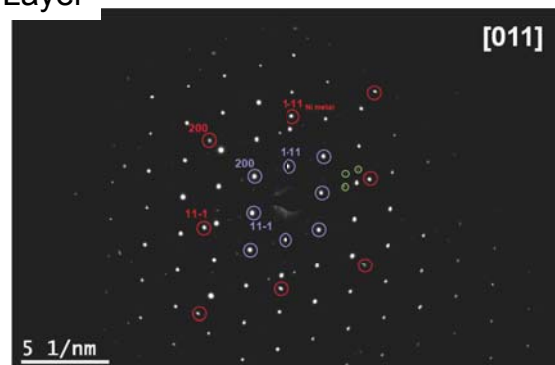
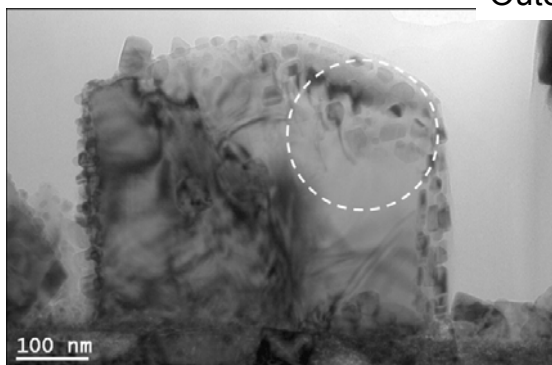
### Both unirradiated and irradiated oxide film

- Double-layer oxide with heterogeneous thickness
- No main difference between the thickness of the oxide layers with or without irradiation (electrons)

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Mi Wang &amp; al., Corrosion of 316L stainless steel under radiation and exposed to representative PWR chemistry, paper O-1030, EUROCORR2012, Estoril, Portugal, 2012

Outer Layer



### Unirradiated – Inner layer

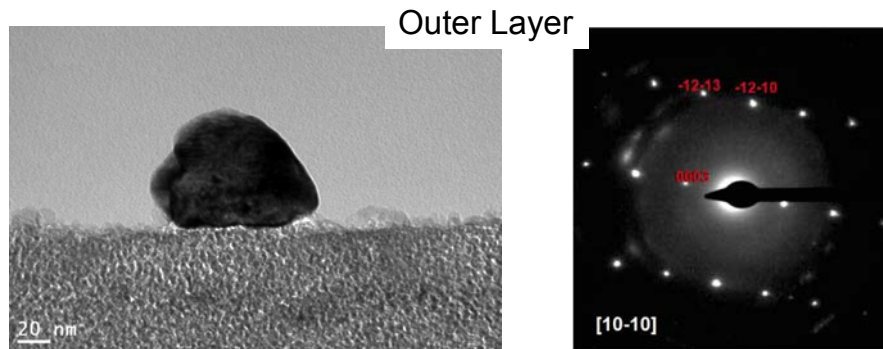
- Spinel oxide with polycrystalline structure  
(Ni,Fe)(Fe,Cr)<sub>2</sub>O<sub>4</sub>
- Red dots: metallic Nickel

### Unirradiated – Outer layer

- Spinel oxide structure
- Red dots: metallic Nickel

- Unirradiated oxide film is a spinel oxide with a metallic nickel second phase  
→ Reducing environment (around 30 mbar of hydrogen)

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### Irradiated – Inner layer

- Spinel oxide with polycrystalline structure  $(\text{Ni,Fe})(\text{Fe,Cr})_2\text{O}_4$
- Strong texture
- Epitaxial growth of the oxide

### Unirradiated – Outer layer

- Hematite structure probably  $(\text{Fe,Cr})_2\text{O}_3$

- No metallic nickel in the inner neither in the outer layers
- Presence of hematite (FeIII) in the outer layer

→ Oxidative environment

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## CORROSION UNDER IRRADIATION IN THE LITTERATURE

**Localised corrosion** observed also on copper alloys in granitic waters under **gamma irradiation** and stagnant conditions

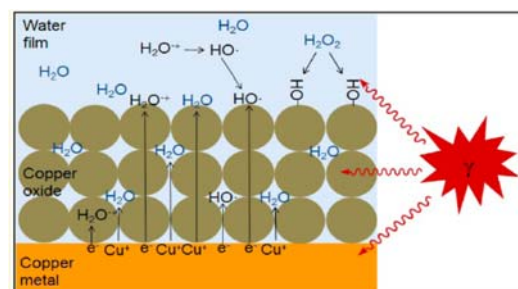
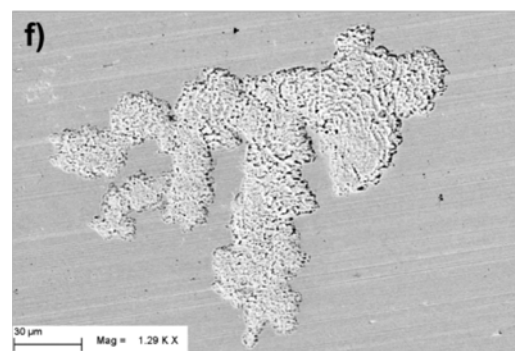
These degradation are attributed to:

- oxydants produced by radiolysis and mainly the hydroxyl radicals  $\text{HO}\cdot_{\text{aq}}$ ,
- the enhancement of the cathodic reaction,
- the possible heterogeneities in the solution (no circulation).

**In PWR conditions under electron irradiation, on stainless steel:**

- localised corrosion,
- high metallic cation concentrations,
- stagnant conditions

Radiolysis calculations under PWR conditions at 300°C lead to 3 main oxidants  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$  (in the order of  $10^{-6}$ ) and  $\text{HO}\cdot_{\text{aq}}$  (in the order of  $10^{-7}$ ) under our irradiation conditions.



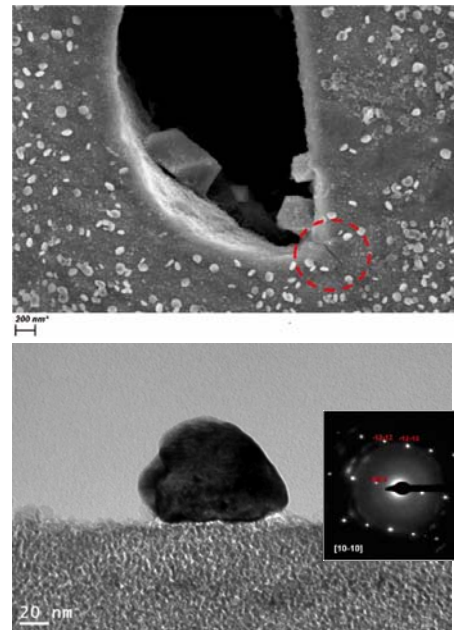
From Björbacka A. et al., J. Phys. Chem. C, 2016

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### In PWR conditions under electron irradiation, on stainless steel:

- localised corrosion,
- high metallic cation concentrations,
- stagnant conditions

Radiolysis calculations under PWR conditions at 300°C lead to 3 main oxidants  $O_2$ ,  $H_2O_2$  (in the order of  $10^{-6}$ ) and  $HO\cdot_{aq}$  (in the order of  $10^{-7}$ ) under our irradiation conditions.



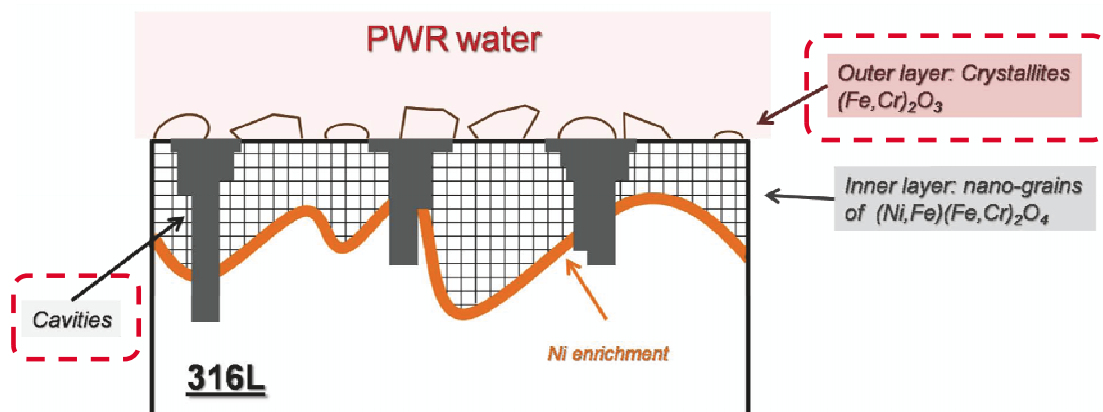
From Mi Wang, thesis, Ecole polytechnique, 2013

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### Chemical evolution of the solution under irradiation

- Lower pH after irradiation (from 6,2 down to 4,25 at 25°C )
- High cation concentrations after irradiation

### Evolution of the oxide film under electron irradiation



### Outlook

- Formation of cavities linked to the oxidative environment during and after irradiation in PWR conditions

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## Evolution of the oxide film under electron irradiation

- Very oxidative environment/oxide interface under irradiation, in agreement with
  - the electrochemical behavior
  - the oxides found in the oxide layer (reducing conditions without irradiation / oxidative conditions under irradiation)
  - the high concentration of cations
  - the simulation calculation of oxidative species linked to radiolysis
- Probably local electrochemical heterogeneities with high oxidative zones under irradiation with stagnant conditions (no flow)

Localised corrosion (pit and cracks)  
linked to the oxidative conditions

**Thank you for your attention**