



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

M. Wang, S. Perrin, C. Corbel, D. Feron

► To cite this version:

M. Wang, S. Perrin, C. Corbel, D. Feron. Radiolysis effect on oxide film of 316L stainless steel formed in PWR primary water under irradiation. NPC 2016 - Nuclear Plant Chemistry Conference - 11th specialist workshop on radiation chemistry and electrochemistry in the nuclear fuel cycle, Oct 2016, Brighton, United Kingdom. cea-02442342

HAL Id: cea-02442342

<https://cea.hal.science/cea-02442342>

Submitted on 16 Jan 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

FROM RESEARCH TO INDUSTRY



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

Mi Wang^{1,2}, Stéphane Perrin², Catherine Corbel¹ and Damien Féron²

1 – Laboratoire des Solides Irradiés, Ecole Polytechnique, Palaiseau, France

2- Den-Serve de la Corrosion et du Comportement des Matériaux dans leur Environnement (SCCME), CEA, Université Paris-Saclay, Gif-sur-Yvette, France

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

www.cea.fr



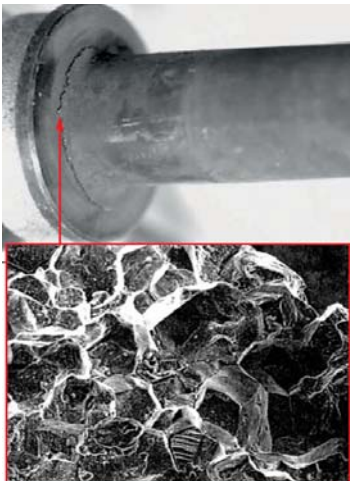
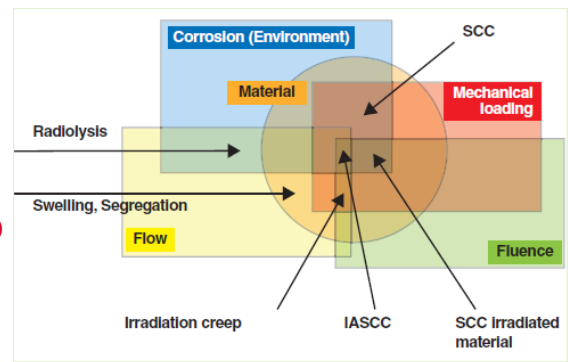
CONTENT

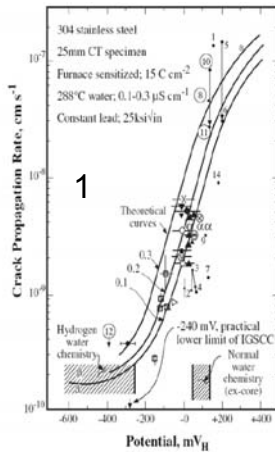
Background

Experimental setup

Results

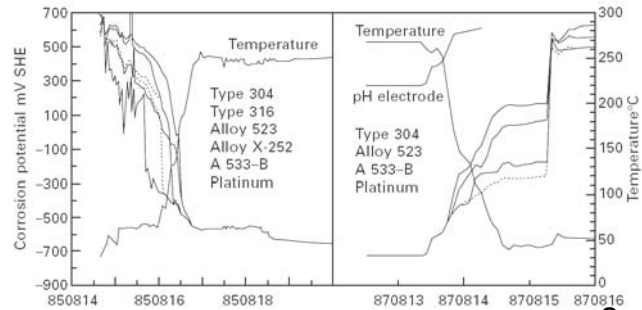
Conclusive remarks





Increase of SCC initiation and propagation with corrosion potential

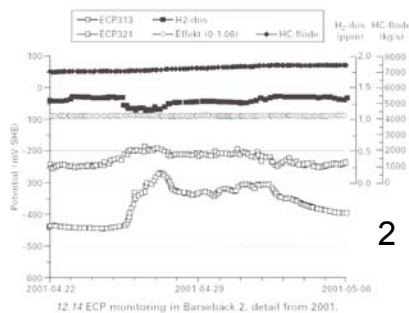
- High Temperature and High pressure



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

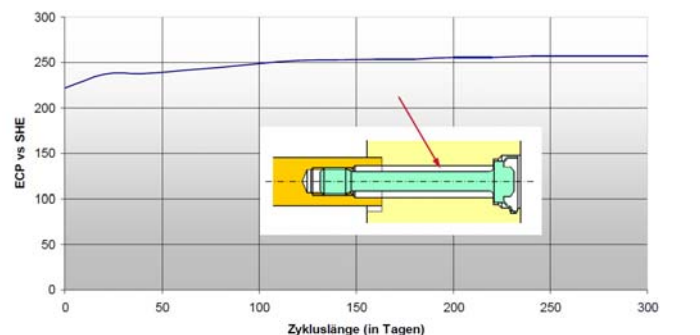


1 D.D. Macdonald, in Nuclear Corrosion Science and Engineering, Woodhead Pub., 2012
2 A. Molander, in Nuclear Corrosion Science and Engineering, Woodhead Pub., 2012

| PAGE 3

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_{SHE} ("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

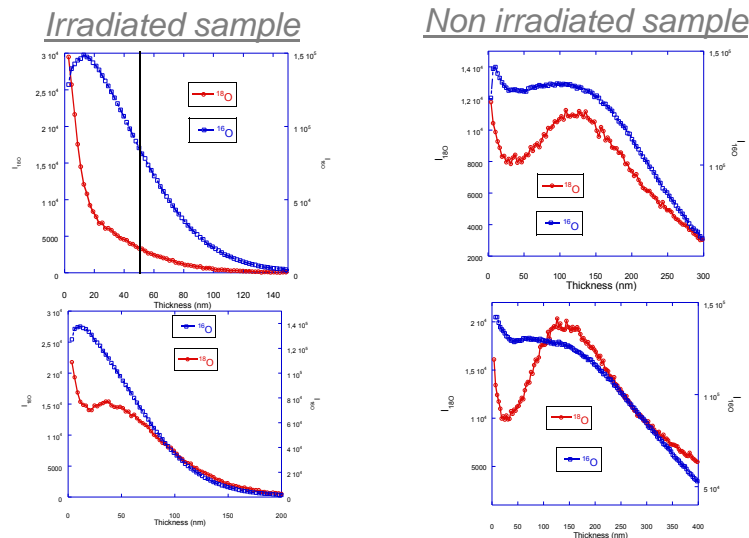
| PAGE 4

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



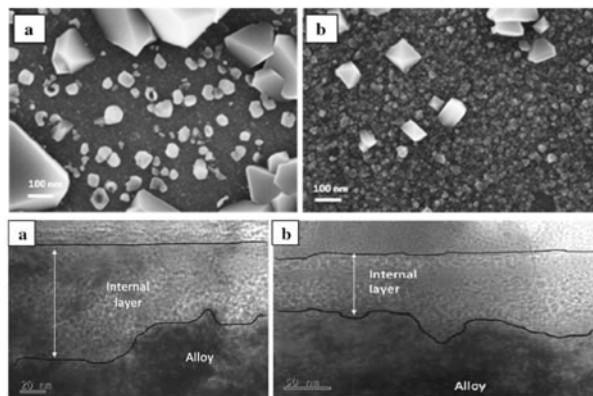
S. Perrin & al., Eurocorr 2011
Dumervil & al., Corrosion Science, 2016

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

| PAGE 5

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)



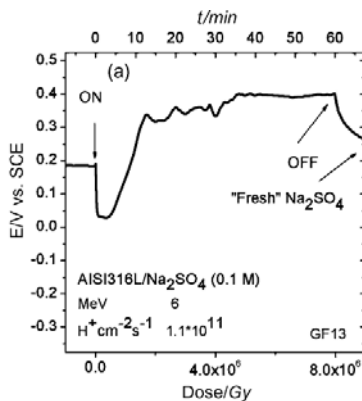
S. Perrin & al., Oxidation of metal, 2013, 80, pp 623-633

a Non-irradiated sample / b Irradiated sample

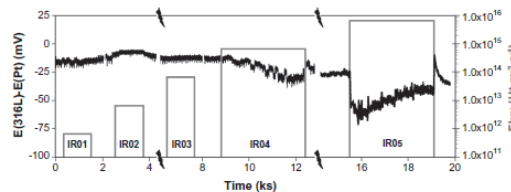
| PAGE 6

Radiation and electrochemical behavior

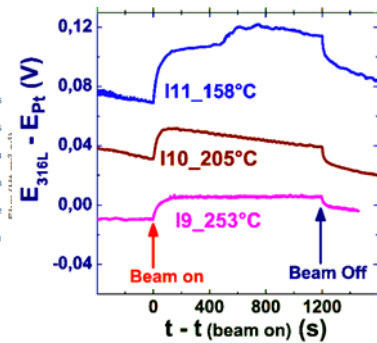
- Electrochemical behaviour (proton & electron irradiations)
 - Importance of radicals
 - Immediate oxidative response to electron and proton beams
 - Response (ΔE) decreases when temperature and hydrogen increase



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



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

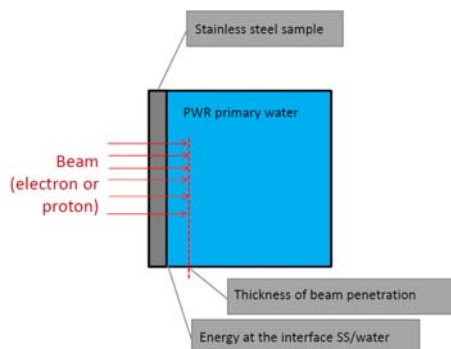


Proton & electron irradiation

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

| PAGE 7

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 μm
 - Flux: varying or fixed
 - Duration: hours - days

- Conditions of H+ beam
 - Energy 6 MeV at 316L / PWR water
 - Penetration 480 μm
 - Flux: varying or fixed; mostly 30 nA
 - Duration: 20 – 60 min

| PAGE 8

HTHP cell

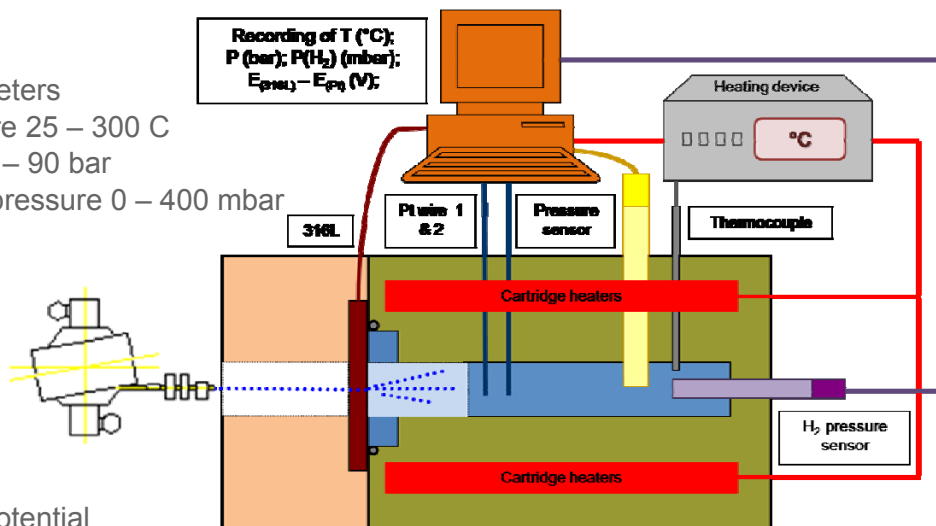
- Designed to record the potential of a 316L / PWR water interface under irradiation at high temperature (HT) and high pressure (HP) and to monitor the hydrogen concentration

- 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



| PAGE 9

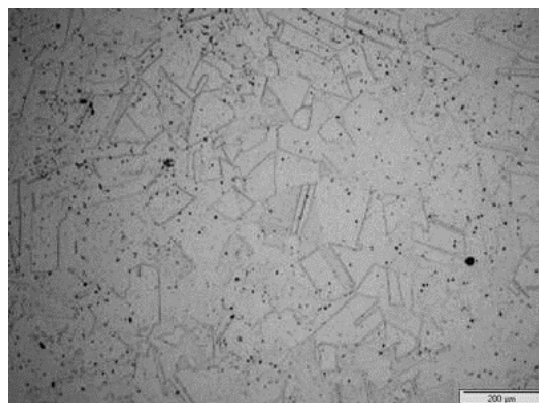
Sample material: 316L stainless steel

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 μ m

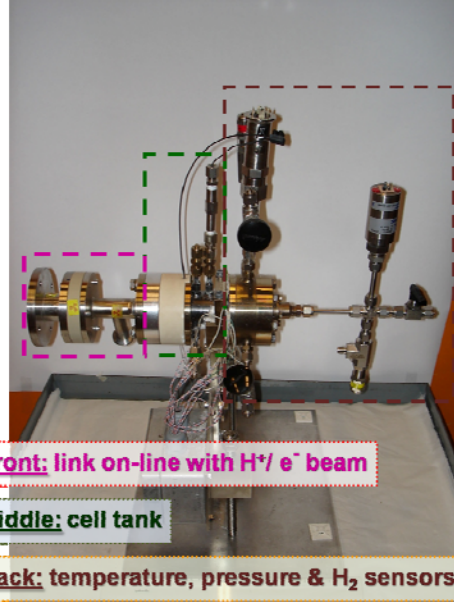


| PAGE 10

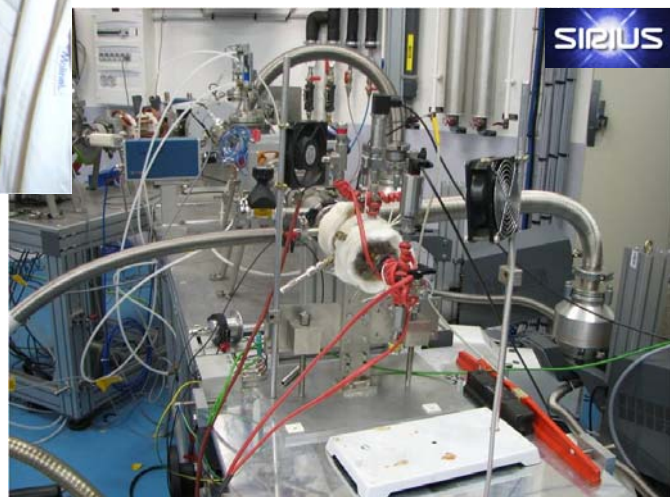
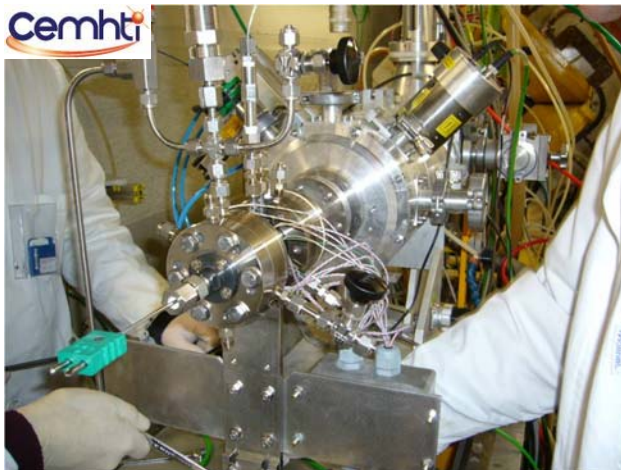
HTHP cell

- 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, H₂ addition
 - pH300C = 7
 - no flow, static water
- Radiation:
 - proton
 - electron



| PAGE 11



| PAGE 12

Electrochemical behaviour under irradiation

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

Characterisation of Oxide Film

- Morphology – SEM Analysis
- Oxide Film – TEM Analysis

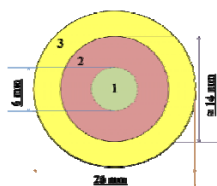
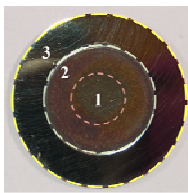
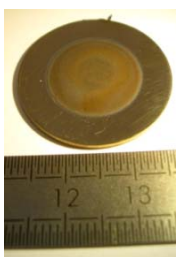
Comments & Outlooks

| PAGE 13

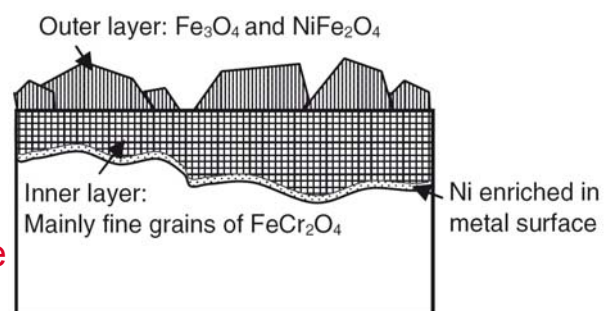
CHARACTERISATION OF OXIDE FILM

Comparison → continuously e⁻ irradiated 316L vs. unirradiated 316L

Sample	Duration (hr at 300C)	P(H ₂) (mbar)	Energy (MeV)	Fluence (x10 ¹⁸ e ⁻ cm ⁻²)
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

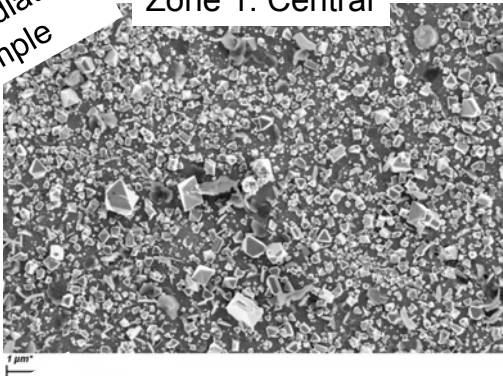
- Zone 1: irradiation & PWR water
- Zone 2: no irradiation & crevice PWR water
- Zone 3: no irradiation & no PWR water

Terachi T. et al. Microstructural characterisation of SCC crack tip and oxide film for UNSS 316 stainless steel in simulated PWR primary water at 320C.

| PAGE 14

Non irradiated sample

Zone 1: Central



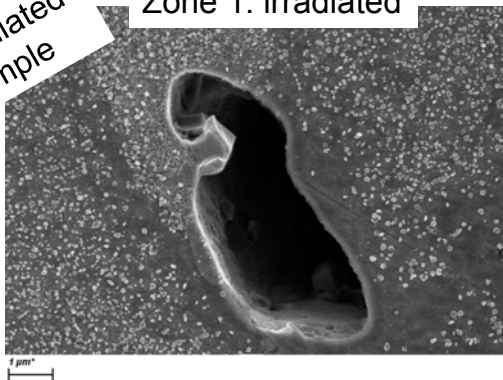
Zone 2: surrounding

Non irradiated sample



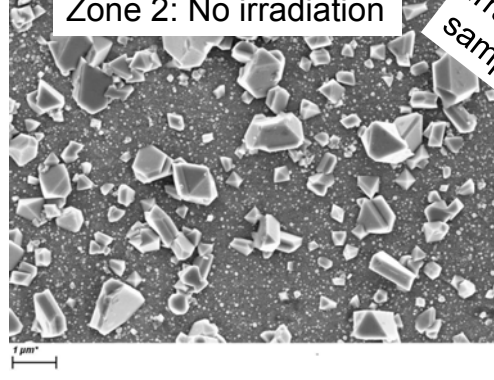
Irradiated sample

Zone 1: irradiated

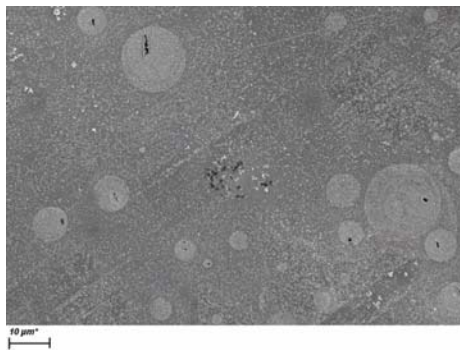


Zone 2: No irradiation

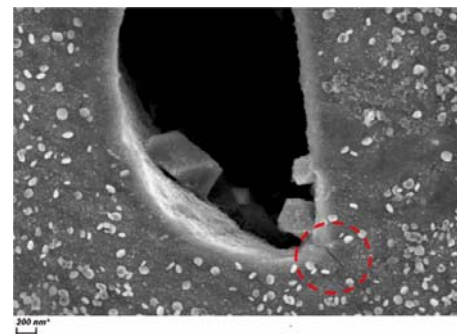
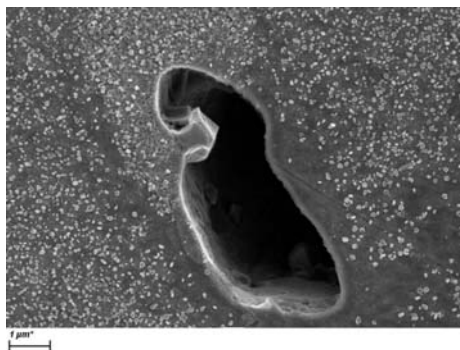
Irradiated sample



PAGE 15

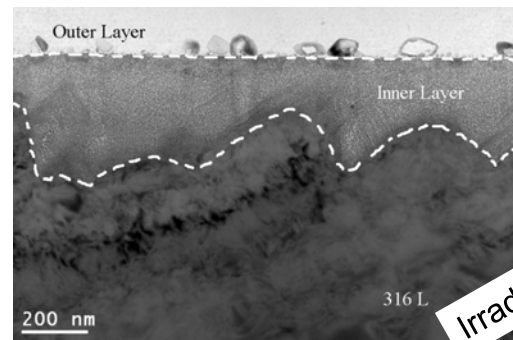
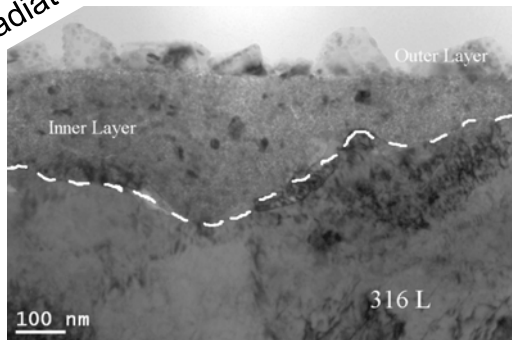


SEM micrographs of irradiated 316L stainless steel in the irradiated zone (zone1) at various magnifications
Cavities with small crystals inside and some cracks



PAGE 16

Unirradiated



Irradiated

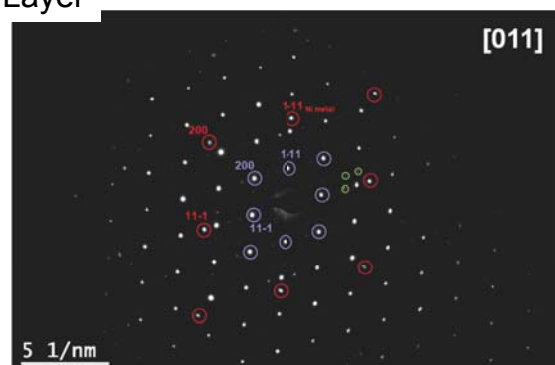
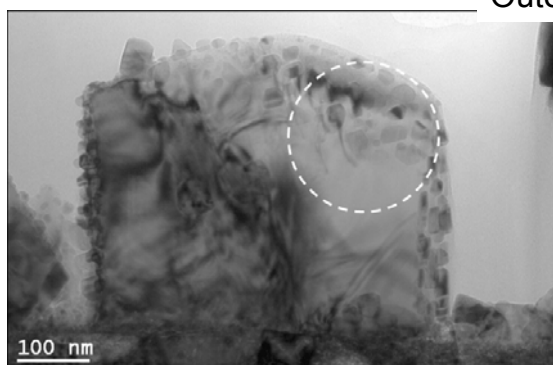
Both unirradiated and irradiated oxide film

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

| PAGE 17

Mi Wang & 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

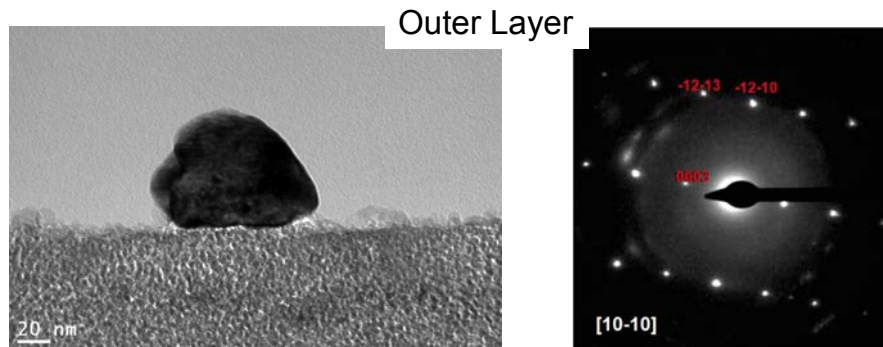
- Spinel oxide with polycrystalline structure $(\text{Ni,Fe})(\text{Fe,Cr})_2\text{O}_4$
- Red dots: metallic Nickel

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)

| PAGE 18



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**

| PAGE 19

CORROSION UNDER IRRADIATION IN THE LITTERATURE

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

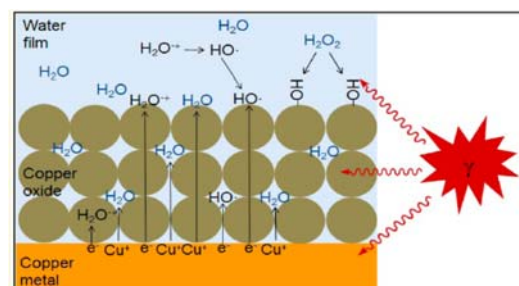
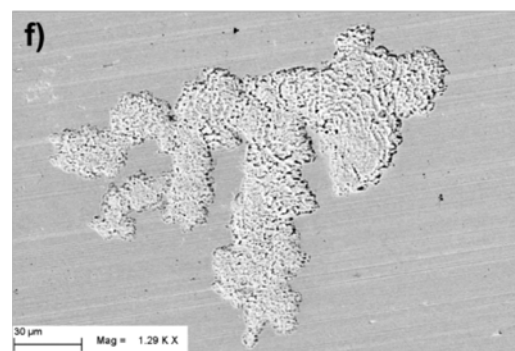
These degradation are attributed to:

- 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 O_2 , H_2O_2 (in the order of 10^{-6}) and $\text{HO}\cdot_{\text{aq}}$ (in the order of 10^{-7}) under our irradiation conditions.



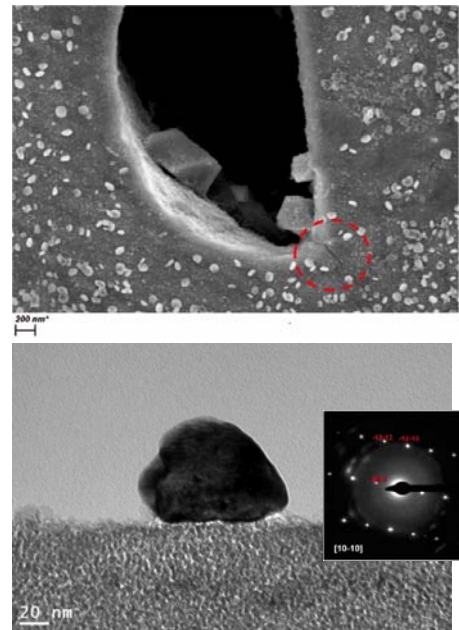
From Björbacka A. et al., J. Phys. Chem. C, 2016

| PAGE 20

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_{aq}^{\cdot} (in the order of 10^{-7}) under our irradiation conditions.



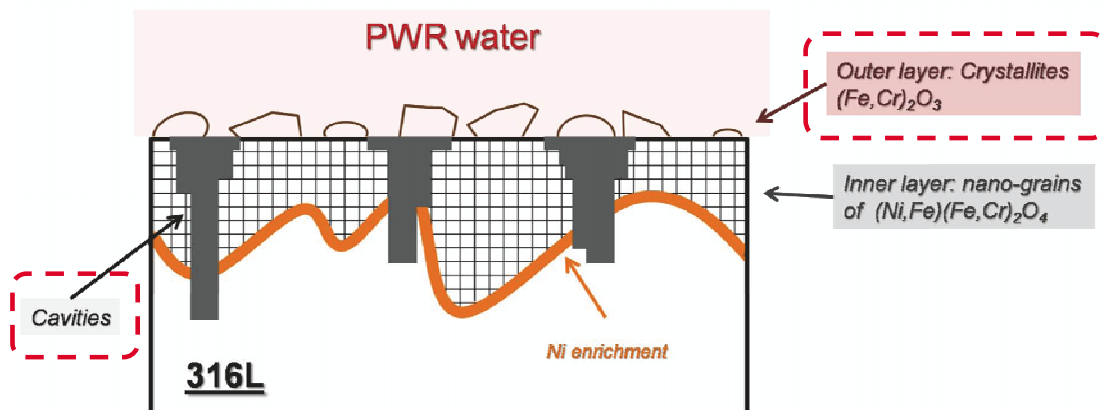
From Mi Wang, thesis, Ecole polytechnique, 2013

| PAGE 21

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

| PAGE 22

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

| PAGE 23

Thank you for your attention