



# Materials under irradiation PWR Structural Materials

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## Short bio



Engineering degree Ecole Centrale Paris (materials major)

PhD in Appied Physics California Institute of Technology (USA)

Research assistant at Los Alamos National Laboratory (USA)

Post doc at the EU Joint Research Centre of Petten (The Netherlands)

I joined CEA in 1996, held several management positions before becoming director of nuclear activities in Saclay in 2017

Adjunct professor at Centrale Supelec, ENSTA and Phelma Grenoble



universite

PARIS-SACLAY

# **Direction of Nuclear Activities of Saclay**





125 PhD students



# Outline



- Effects of irradiation on materials
- PWR structural materials
  - The reactor pressure vessel
  - The internal structures
- PWR fuel assembly materials (excluding fuel)
- Gen IV structural materials



# **Outline**



#### Effects of irradiation on materials

- Macroscopic effects of irradiation
- Neutron matter interaction
- Point defects, displacement cascades, irradiation damage
- •Long term evolution of point defects : structure, mobility, clusters and sinks
- Microscopic evolution

#### The reactor pressure vessel

- •PWR design
- PWR fabrication
- Internal cladding
- Fracture of ferritic steels
- Irradiation embrittlement
- Pressure vessel integrity assessment
- •Surveillance program

#### The internal structures

- Internals
- •IASCC Intergranular corrosion (internals)
- •Swelling



#### For further reading...







#### Structural Materials for Generation IV Nuclear Reactors

**Edited by Pascal Yvon** 

STRUCTURAL ALLOYS FOR NUCLEAR ENERGY APPLICATIONS

> EDITED BY G. ROBERT ODETTE AND STEVEN J. ZINKLE





Rudy J.M. Konings

Section Editors: Todd R. Allen Roger E. Stoller Shinsuke Yamanaka WP



#### World nuclear fleet



450 reactors operating in the world

>99% have a thermal spectrum

2/3 are PWR (or VVER)



So the focus will be on PWR materials





# Macroscopic effects of irradiation on materials



After irradiation an evolution of mechanical properties can be observed

For instance the tensile testing properties of steel





# **Mechanical behavior : tensile test**





Elastic deformation (fully reversible)

ε = σ/Ε

 $\sigma$  stress

E modulus of Elasticity

(Young modulus)









# Macroscopic effects of irradiation on materials





Dimensional changes With or without stress

> Corrosion Creation of H<sub>2</sub> and He





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# Effect of neutrons

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Depending on their energies, neutron can have

Nuclear effects (inelastic): - thermal neutrons

Fission

Capture (and subsequent nuclear reactions)



Ballistic effects (energy conservation) – fast neutrons

dpa - point defects





- For a transferred energy  $E_t < E_d$  (threshold energy) -> vibration of the crystal lattice -> heating

- For a transferred energy  $E_t > E_d$ , the atom can be ejected from its atomic site and move through the crystal to other atomic sites (mean free path ~ several atomic sites)

- This creates a vacancy + a self-interstitial atom. This is a Frenkel pair.

PKA : Primary Knock on Atom







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# Neutron spectrum and units of irradiation



The neutron of different energies have different effects on the materials

Unit of flux : n.cm<sup>-2</sup>.s<sup>-1</sup>

Unit of fluence: n.cm<sup>-2</sup>

Difficult to describe a spectrum by just one number

Therefore use of the dpa (displacement per atom)



PWR neutron spectrum



# Displacement cascade ( $E_t >> E_d$ )



- ... these other atoms can then displace other atoms.
- The primary knock on atom induces a displacement cascade





#### **Cascade evolution**

15 keV

0,02 ps





- Isolated interstitials
- Isolated vacancies
- Interstitials clusters
- Vacancy clusters

Vacancy

Interstitial

0,1 ps

0.28 ps

Few surviving defects after cascade relaxation : only 1/100 of displaced atoms remain

-> Cascade creation (in agreement with KP)

Figure 5a

0.02 ps



-> Cascade relaxation recombinations







Vacancy formation energy : low distorsion of the crystal lattice -> low formation energy



interstitial formation energy : High distorsion of the crystal lattice -> high formation energy

-> Out of reactor it is much easier to create a vacancy than a self-interstitial

Point defect concentration at thermodynamic equilibrium

$$c_{DPe} = \exp\left(-\frac{H_{DP}^{f}}{kT}\right)$$
 Formation energy

-> No interstitial at thermodynamic equilibrium





Irradiation damage : creation of point defects and mixing of the atoms (dpa)

But also

Evolution of these point defects

- Recombination
- Clustering
- Annihilation on sinks



## Mobility of point defects



nterstitial

Vacancy



$D = D \exp \left( -\frac{1}{2} \right)$	$\left(-\frac{H_{DP}^{m}}{H_{DP}^{m}}\right)$	
$D_{DP} - D_{DP0} CAP$	$\left( -\frac{kT}{kT} \right)$	

	Vacancy	Interstitial
Formation energy (eV)	1.4-2.1	2.8-3.5
Migration energy (eV)	0.5-0.9	Ea=0.01-0.06 Ec=0.1-0.3

# Anisotropic diffusion of the self-interstitial

-> High mobility for interstitials, low mobility for vacancies





- A self-interstitial close to a vacancy reacts spontaneously and the two defects are annihilated
  - The mutual recombination volume is about 100 atomes.
  - Saturation of the point defects (if no other sink) due to mutual recombination





# Mutual recombination :

 $\Box$  +  $\Im$  = nothing (if pure material)



#### **Point defect clustering**





Point defects clustering : loop, cavity  

$$\Box + \Box = \Box + \Box = \Box \Box + \Box = \Box \Box or \Box \rightarrow Point defect cluster$$
  
 $\Im + \Im = \Im + \Im = \Im \Im + \Im = \Im \Im$ 









• There is competition between the creation of point defects and their elimination

•At low temperature, the point defect mobility is reduced. High density of point defects. The point defects are mainly annihilated by mutual recombination.

• At high temperature, the vacancies concentration at thermodynamic equilibrium is high, the increase due to irradiation in point defects is low.

When the temperature increases, so does the mobility of defects. Therefore, the system tends to go back to the equilibrium state

Beware of accumulation of energy



# **Microstructural evolution**

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Effect of elastic collisions on precipitates

- Amorphization
- Dissolution

Enhanced diffusion due to the super-saturation of point defects

Precipitation

Nuclear reactions

Changes in chemical composition



# **Amorphization of precipitates**





Amorphization of the precipitates Dissolution of Fe into the matrix





Sursaturation of point defects Accelerated diffusion of atoms



Precipitation of  $\beta$  Nb under irradiation in Zr alloys with Nb

Zr-Nb alloys, solide solution supersaturated in Nb (out of thermodynamic equilibrium).

Under irradiation : the high vacancies concentration leads to a high vacancy flux that enable a fast return to thermodynamic equilibrium, and reprecipitation of  $\beta$ -Nb







- Point defects : vacancies and interstitials
- Under irradiation : creation of interstitial and vacancies (high V concentration)
- High mobility of interstitial low mobility of vacancy
- Anisotropic diffusion of the interstitials
- Vacancy and interstitial recombination
- Point defects clustering : loops
- Point defects elimination at sinks (dislocation, grain boundaries + loops)
- Complex evolution, depends on all the sinks present in the material, on temperature, on stress



#### The reactor pressure vessel











The reactor pressure vessel is the second safety barrier

The pressure vessel is the only component which cannot be replaced

it has to keep its functions for the lifetime of the plant (environment, irradiation damage) in operating conditions, but also in accidental conditions...



#### **PWR pressure vessel**





Temperatures :  $296 - 320^{\circ}C$ 

Coolant pressure: 155 bar

 $\emptyset = 4400 \text{ mm}$ e = 220 mm

Gross weight 330 (900 MW) 440 t (1300 MW) EPR (520 t)

Steel A508 Cl. 3 = 16MND5 (bainitic steel) Internal cladding: 304 L = Z2CN1810 (austenitic stainless steel)



#### **Fabrication process**







#### Forming of ingots





- Forging at 1100 1200°C
- Deformation ratio > 3
- Intermediate re-heating
- End of forming: hold at 600-650°C (H diffusion)
- Final heat treatments
  - γ -quench 850-920°C
  - tempered 635-665°C



#### Forged sections are welded









# Rolled and welded flats

# Forged cylindrical rings



Westinghouse



Le Creusot


## **PWR pressure vessel steels**

Ferritic steel (bcc) 16 MnNiMo5 (A 508 Cl 3)

Low carbon (easy welding) Strength by other elements, Mn....and structure (bainitic)

C <sub>max</sub>	Mn	Ni	Мо	$\operatorname{Cr}_{\operatorname{max}}$	Si
0.2	1.15/1.55	0.5/.8	0.45/.55	0.25	0.1/.3
	P <sub>max</sub>	S <sub>max</sub>	Cu <sub>max</sub>	Со	
ppm	80	80	800	300	

Low S, P et Cu to avoid irradiation induced embrittlement Low Co to avoid  $\gamma$  irradiation



## Internal cladding for vessel



- To protect against the corrosion of the primary coolant: welding of a stainless steel layer (*beurrage in french*)
- Two layers are welded from planar sheets
  - 24 Cr, 12 Ni (Cr rich to compensate the loss due to dilution with base metal melted)
  - 20 Cr, 10 Ni (other layer similar to 304L-316L)
- Thickness: 8 mm (vessel steel: 220 mm)
- Formation of cracks under the layer
  - Cracking at low temperature (during the cooling, contamination due to H diffusion during the welding)
  - Pre- and post-heating





# **Charpy**

- Indication of a <u>tendency to brittle fracture</u> (resistance to cracking)
- Small samples
- Easy irradiation
- Fracture toughness (K<sub>IC</sub>)
  - Mechanical value of a <u>resistance to crack</u> propagation (design)
  - Much larger testing samples



## Brittle - ductile transition in ferritic steels (bcc)



Quantification of the resistance to cracking



Measurement of the energy absorbed during the test



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## Fracture surfaces after Charpy impact test





### Brittle

**Ductile** : plastic deformation and rupture after coalescence of cupules, high energy absorbed during the tests

**Brittle** : cleavage = de-cohesion of the crystal along specific crystallographic planes, low energy absorbed during the test before rupture



#### Ductile



Evolution of the absorbed energy during the test as a function of the temperature



σ

σ

а

# Fracture toughness (K<sub>IC</sub>)



#### Resistance to crack propagation

At the root of a crack, the stress diverge => equal to infinity at the tip

$$\sigma_{loc} = \frac{K_I}{\sqrt{2\pi \cdot r}} \cdot f(\theta) \qquad \qquad K_I = \sigma \cdot \sqrt{\pi \cdot a}$$

The stress intensity factor  $K_l$  allows to give a value to the singularity (in MPa.m<sup>1/2</sup>)

The resistance of a material to crack propagation is measured by a toughness test. Fracture at  $K_l = K_{lC}$ (ASTM E 399) (no propagation if  $K_l < K_{lC}$ , if  $K_l > K_{lC}$  than the crack propagates suddenly)

Knowing the crack geometry and the stress state, allows to forecast crack propagation or not.











 Pressure vessel irradiation: 10<sup>-10</sup> dpa.s<sup>-1</sup>

 Dislocation loop formation, and other defects like clusters of minor elements induce an increase in mechanical properties. Saturation of the hardening due to the saturation of the microstructure (saturation of defects density)





## **Evolution of ductile to brittle transition temperature**



Higher strength increases the probability of failure by cleavage, leading to a higher transition temperature.







At higher temperature, continuous recovery occurs during irradiation and embrittlement is reduced.

For the same irradiation dose, the effect is higher at 120°C than at 290°C



Tirr. =290°C

Tirr. =120°C : lower elimination of PD, less recombination, more hardening



# **Saturation of irradiation effects**



**Ductile Brittle Temperature Transition** increase vs fluence

Énergie (J) Non irradié 80 60 Irradié  $\mathbf{d}$ 40 △ 3,58.10<sup>18</sup> n.cm<sup>-2</sup>  $\odot$  7,05.10<sup>18</sup> n.cm<sup>-2</sup> 20 • 2,22.10<sup>19</sup> n.cm<sup>-2</sup> 0 200 0 100 -100Température d'essai (<sup>O</sup>C)

Non linear increase of the **DBTT** as a function of the fluence, rapid saturation

Induced by hardening and also the formation of précipitates





### Modelling of Cu precipitation by Kinetic Monte Carlo





On each crystal site Fe or Cu Thermodynamics for interactions between species Kinetics, according to probability of occurrence Simulated time: One century

Sonde Atomique 3D

Simulation Monte Carlo





More complex chemistry





## **Surveillance Program**

Tensile and Charpy-V specimens are located at the periphery of the internal structures.

The materials submitted to the surveillance program are the central part of the vessel, the C1. C2 weldment with its HAZ and a reference material common to all French nuclear power plants.

Regulations stipulate that the surveillance program must be representative regarding the irradiation conditions (temperature, neutronic spectrum, <sub>Cuve</sub>, ...) and the materials

Base metal taken from overlength of the shell Weld and heat affected zone elaborated under identical welding conditions as the core zone components





### **Irradiation devices**



4 holders

Removed every 1/4 quarter design life 4, 7, 10 and 14 years Fast neutron dose integrators Samples: Charpy, tensile, K<sub>IC</sub>



Cea







	Capsule <b>W</b> <i>(u)</i>	Capsule (v)	Capsule <mark>X</mark> ( <i>z</i> )	Capsule (y)
Time of duration in vessel (years)	4	7	9	14
Equivalent time of irradiation of the Vessel (Years)	11.2	19.5	28.0	39.1

Extension of the RPV irradiation surveillance programme based on the introduction of reserve irradiation capsules is engaged on the French plants since 1999 for all reactors.

Two reserve capsules W and X in place of capsules U and Z after removing from reactor these capsules U and Z.



## Materials and fluxes



Largely inspired from American regulations Fulfills the french safety Authorities requirements

- For all 900, 1300 and 1450 MWe reactors, the core zone is generally made up of two shells and the associated weld. As these materials experience a marked embrittlement under their design end of life (40 years), mechanical properties and particularly the rupture characteristics through impact strength are monitored for each reactor zone
- Materials positioned in capsules at locations well characterized for temperature and neutronic conditions
- Neutronic flux is higher (x3) than the one undergone on the vessel in order to anticipate the embrittlement. The flux is evaluated for each capsule through a lead factor, corresponding to the ratio of the neutron fluxes of more than 1 MeV energy undergone by the capsule and the vessel at the most irradiated point.





#### <u>Embrittlement Formulas :</u>

The general form is indexed on the temperature shift of Charpy-V  $\,:\,$ 

$$\Delta RT_{NDT}(^{\circ}C) = CF \cdot \phi^{G}$$

where *CF* is the Chemical Factor,  $\phi$  is the fluence (10<sup>19</sup> n/cm<sup>2</sup> with E > 1 MeV) and *G* an exponent.

Formulation based on steels and welds from the French nuclear program :

This particular formulation is for the highest effect of irradiation (FIS). Another formula is available in RCC-M for mean irradiation effect (FIM).

$$\Delta RT_{NDT}(^{\circ}C) = 8 + \left[24 + 1537 \cdot \left(P - 0.008\right) + 238 \cdot \left(Cu - 0.08\right) + 191 \cdot Ni^2 \cdot Cu\right] \cdot \phi^{0.35}$$



# Non destructive examination (NDE)



Ultra sonic testing

- Elastic strain wave
- Under water
- Focalized probes
  - x, y, z examination
  - 3D description of the cracks
  - A few mm accuracy
  - Inspection techniques (5 years)





#### In service NDE



# US probes



Inspection device for a PWR Accuracy < 1 mm Defect sizes: 6 - 7 mm CPO: 31 known defects CPY: 2 known defects







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![](_page_59_Picture_0.jpeg)

![](_page_59_Picture_2.jpeg)

<u>Approach considered in relation with French codification</u> Demonstration of the integrity of the vessels in all conditions of loading, parameters :

- the RT<sub>NDT</sub>,
- all parameters fluence, defect distribution, transient, temperature.

The most severe conditions to be considered is the pressurized thermal shock (PTS) taking account for hypothesis shallow cracks beneath the cladding (subcladding area).

Justification of the Vessel integrity

Demonstration of the margin on

- brittle fracture
- ductile fracture (ductile tearing).

![](_page_60_Picture_0.jpeg)

### Assessment of vessel integrity

![](_page_60_Picture_2.jpeg)

![](_page_60_Figure_3.jpeg)

![](_page_61_Picture_0.jpeg)

### **Extended life of PWR vessels**

![](_page_61_Picture_2.jpeg)

#### **Old reactors**

Fuel management for reduced leakage Thermal recovery of pressure vessel Warm safety water tank

#### **New reactors**

Fine chemistry control during processing Reduced neutron flux by design (EPR heavy baffle)

![](_page_61_Picture_7.jpeg)

![](_page_62_Picture_0.jpeg)

### Irradiation damage recovery

![](_page_62_Picture_2.jpeg)

The clusters with different chemistry can be dissolved by intermediate temperature annealings. Yield strength increase is recovered as well as toughness.

![](_page_62_Figure_4.jpeg)

VVER: works at lower temperature ~ 270 °C and [Cu]<0.15% [P]<0.025% higher, RT<sub>NDT</sub> increases faster than PWR for instance

![](_page_63_Picture_0.jpeg)

![](_page_63_Picture_2.jpeg)

Important metallurgical factors influence the properties, in particular the toughness, of French PWR steel (16MND5). Careful control of elaboration, of microstructure and embrittlement under neutron irradiation are the key of good results.

- The surveillance program warrants that no unpredicted deviation occurs.
- Comprehensive work on the basic mechanisms at the origin of Copper embrittlement is also under investigation with cascade dynamic simulations and to be extended to get closer to real compositions

Enormous stakes to increase the lifetime of the vessel

![](_page_64_Figure_0.jpeg)

![](_page_65_Picture_0.jpeg)

## Internals N4 (PWR 1350MW)

![](_page_65_Picture_2.jpeg)

![](_page_65_Picture_3.jpeg)

![](_page_65_Picture_4.jpeg)

![](_page_66_Picture_0.jpeg)

![](_page_66_Picture_2.jpeg)

core internal structures (core mechanical support, hydraulic, neutronic protection of the vessel)

#### Baffle

Junction between pressure vessel cylinder and poly-square type fuel assembly core Thick SS plates screwed together Flow control Internal structures of PWR Internals (temperature, up to 380°C)

![](_page_66_Picture_6.jpeg)

cléaire

![](_page_67_Picture_0.jpeg)

![](_page_67_Picture_1.jpeg)

## **PWR Internals**

![](_page_67_Picture_3.jpeg)

18%Cr and 8%Ni (18-08) : 304 et 316

2 to 100 dpa : end of life dose

**Irradiation effects:** Aggregation of points defaults: loops, voids : **hardening** 

- Depending on the temperature
  Hardening, reduction of ductility, Quick increase then saturation
  - Swelling is possible at high doses
  - He formation in situ (hardening)

<sup>58</sup>Ni (n, $\gamma$ ) <sup>59</sup>Ni then <sup>59</sup>Ni (n, $\alpha$ ) <sup>56</sup>Fe

For PWR : 0.5 to 1 ppm He/an

![](_page_68_Picture_0.jpeg)

# Irradiation assisted stress corrosion cracking

![](_page_68_Picture_2.jpeg)

![](_page_68_Figure_3.jpeg)

![](_page_69_Figure_0.jpeg)

One can observe lowering of Cr content at GB which favor the intergranular rupture. Especially if mechanical loading appears (stress corrosion cracking). This phenomenon is easier when hardening due to irradiation occurs and the corrosive environment which can be confined

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![](_page_70_Figure_0.jpeg)

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![](_page_71_Picture_0.jpeg)

### Hardness of internal baffle bolts for PWR

![](_page_71_Picture_2.jpeg)

![](_page_71_Figure_3.jpeg)

-> Saturation of the hardness around 5 dpa

📫 High hardening


## (Irradiation Assisted Stress Corrosion Cracking)

Irradiation dose : 5 - 10 dpa



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-Modification of the working conditions of PWR (water flux=>thermohydraulic loading)

-Bolts design: stress concentration

-Replacing some bolts at mid life (at a cost ! To replace 150 bolts, the reactor needs a 3 week outing)

-Thinking about the improvement of the material (for all internals : search for low activation or rapid deactivation materials)