Emerging material degradation issues in nuclear materials under extended in-service irradiation beyond 80 years

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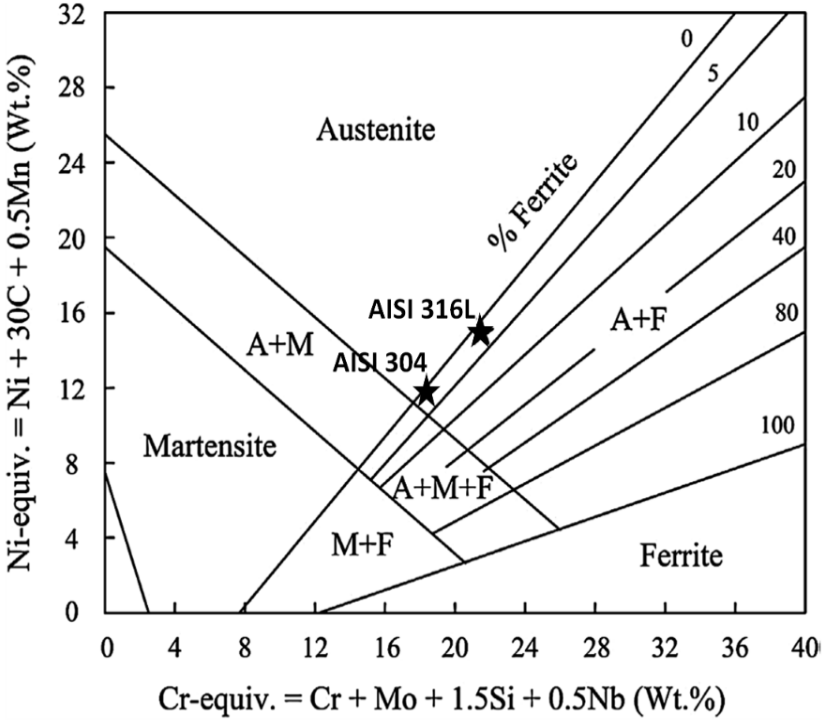
Second-order phenomena as a growing concern

- In 2023 the US average reactor age was 42 years old and the oldest was 54. Therefore, there are no materials degradation data available for predictions beyond 80 or even 60 years.
- Majority of US LWR core internals constructed from 304 SS with smaller amounts of 316, 347. These are metastable steels existing in a very destabilizing environment.
- Within the current 40-year LWR licensing period materials issues of first-order importance for austenitic internals are radiation-induced segregation, IASCC, and embrittlement.
- Second-order issues for LWRs have long been recognized but previously have not been considered to be life-limiting.
  - Void swelling and irradiation creep // will not be discussed here.
  - Transmutant (gaseous and solid) losses or additions.
  - Helium-hydrogen synergisms and possible impact on material performance.
  - Radiation-induced phase instabilities with possible impact on corrosion/cracking.
- However, the non-linear nature of some of these second-order processes and their possible synergisms causes worry that they might become first-order with life extension to 80+ years.

Transmutation concerns for phase stability of 300-series steels in PWRs and BWRs

Both 304 and 316 SS are very close to ferrite formation before irradiation.



- There is no adequate" phase diagram" for radiation-driven phase instabilities or radiation-driven processes that affect IASCC or cracking.
- Researchers frequently use as a default choice, the Schaeffler diagram, which is an empirical description of the microstructures of weld metal as a function of composition.
- Only starting compositions are considered, not any losses or additions occurring during irradiation via transmutation or precipitation.
- The martensite start temperature is also sensitive to Ni, Mn, N and V.
- Many published versions of this diagram ignore the role of N, V, Co, Ti, Cu and other minor elements.

- Ni equivalent Formula = (%Ni)+30(%C+%N)+0.5(Mn+%Cu+%Co)
- Cr equivalent Formula = %Cr + %Mo + 1.5(%Si) + 0.5(%Cb) + 2%Ti + 5%V

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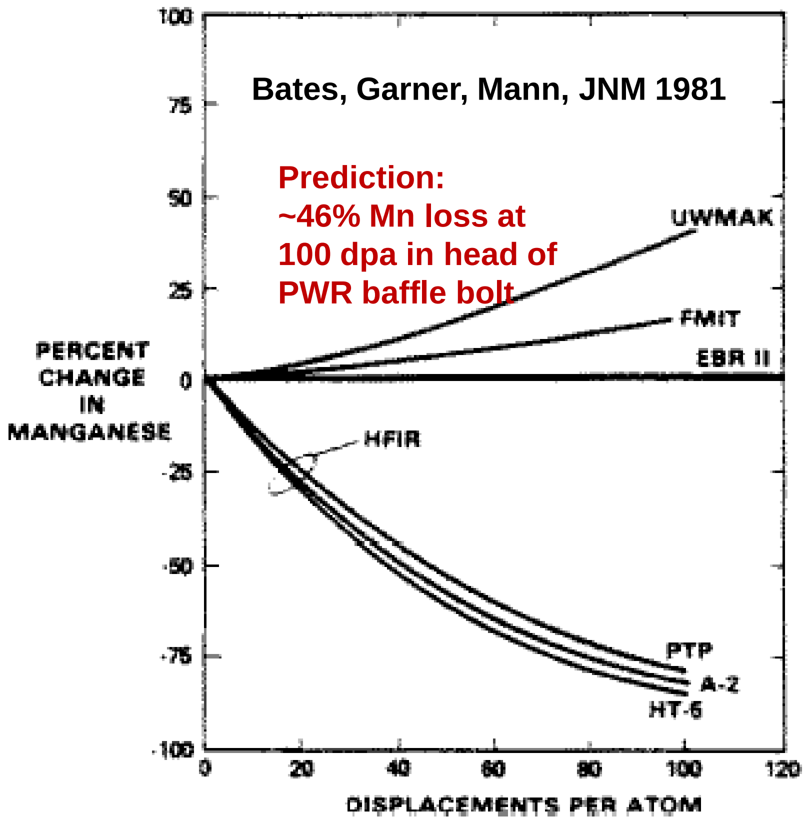
Transmutation becomes increasingly important at higher exposures

- Previous attention was focused only on He and H from Ni, but the detailed isotopic evolution of all Ni isotopes is required.
- Transmutation releases deleterious elements into the matrix.
- Transmutation directly decreases the concentrations three of the four major austenite-stabilizing elements, Ni, Mn and N.
- He and H produced from any Ni isotope removes Ni from solution.
- Transmutation produces V, which forms carbo-nitrides, decreasing the solubility of two of the four major austenite-stabilizing elements, C and N.
- Strong synergisms of He and H, allow storage of large amounts of H, with potential synergisms with phase stability, especially martensite.
- Large amounts of cavities may allow removal of N from solution (N_2).

Mn in thermal neutron spectra transmutes to Fe

Mn has one isotope Mn-55 which transmutes to Mn-56 (with Fe-56 as product) at 13.2 barns thermal.



Mn is an austenite stabilizer.

Mn retards martensite formation.

Mn contributes to solubility of N.

Major role of Mn is to sequester S and trace levels of F and keep them off grain boundaries.

MnS precipitates are thermally very stable, but FeS precipitates are not very stable.

Mn is a fast diffuser, migrating up vacancy gradients by inverse Kirkendall effect at MnS precipitate surfaces.

Combined effect of Mn out-migration, Fe-56 recoil, and transmutation promote MnS dissolution, releasing S and F into the matrix and eventually to grain boundaries.*

*Experimentally verified by Chung, Sanecki, Garner, ASTM STP-1325, 1999

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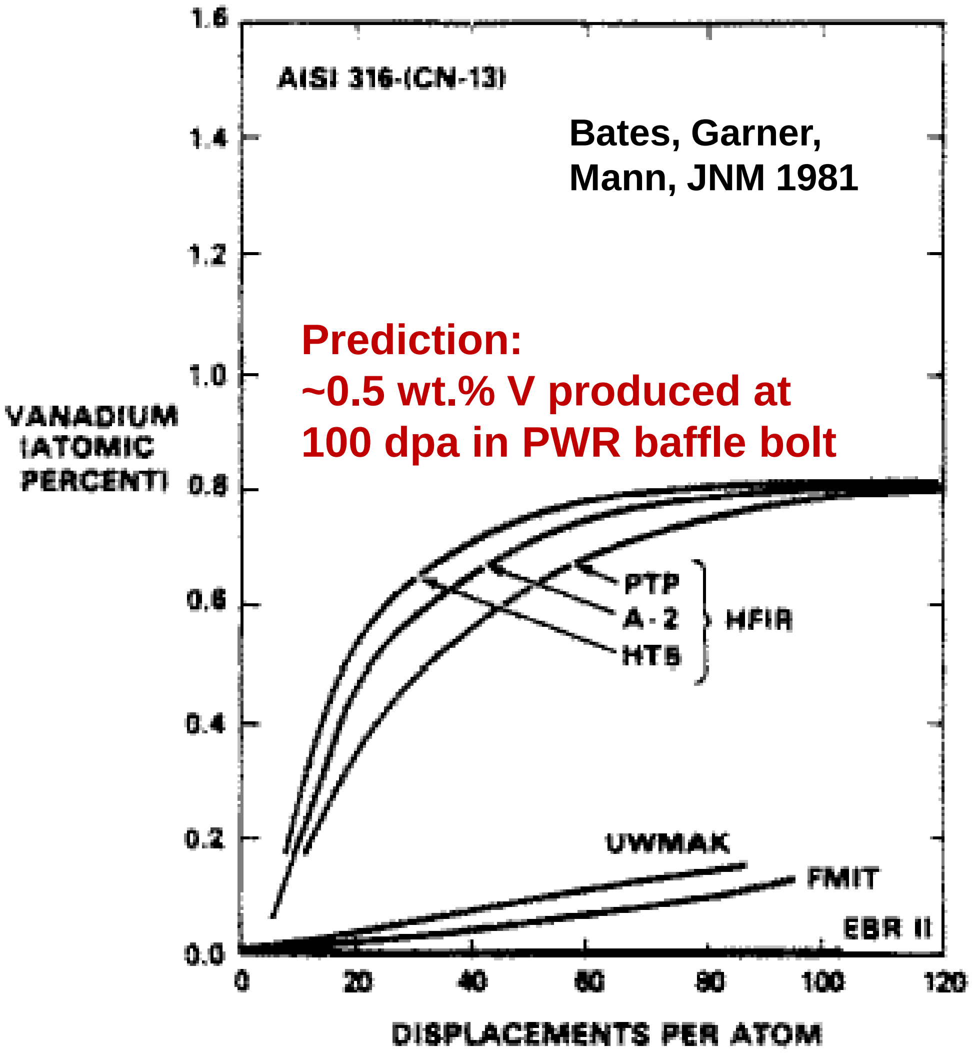
Cr in thermal neutron spectra transmutes to V



Cr has four isotopes with numbers <u>50</u>, 52, 53, 54 with abundances of <u>4.3</u>, 83.8, 9.5 and 2.4%.

$^{50}Cr(n,\gamma)^{51}Cr \rightarrow ^{51}V$ 15.4 b thermal

Total burnout of ^{50}Cr produces only 0.8% V in 316 stainless steel, but with respect to forming carbide precipitates, this is a rather large amount.

Activity of carbon is one of the important factors that determine swelling, and also influences other processes such as corrosion and cracking.

V and Cr are both ferrite stabilizers, but V is <u>five times stronger</u> ferrite stabilizer than the Cr that it replaces.

V also reacts strongly with N, a strong austenite stabilizer, removing it from solution.

Transmutation loss of N via N-14 (n,p) reaction

N-14 has 99.6% natural abundance

MT	Reaction	0.0253-eV	Maxwellian Average	g-factor	Resonance Integral	14-MeV	Fiss. Spec. Average
1	(n,total)	12.40 (b)	13.74 (b)	1.108	–	1.628 (b)	1.964 (b)
2	(n,elastic)	10.37 (b)	11.70 (b)	1.128	–	984.1 (mb)	1.832 (b)
4	(n,inelastic)	(E-thr = 2.480 MeV)				399.3 (mb)	11.36 (mb)
16	(n,2n)	(E-thr = 11.31 MeV)				5.670 (mb)	1.006 (μb)
22	(n,na)	(E-thr = 12.45 MeV)				29.95 (μb)	113.6 (nb)
28	(n,np)	(E-thr = 8.095 MeV)				44.52 (mb)	22.89 (μb)
32	(n,nd)	(E-thr = 11.01 MeV)				3.826 (mb)	654.7 (nb)
102	(n,γ)	75.00 (mb)	75.05 (mb)	1.001	33.86 (mb)	1.036 (μb)	34.69 (μb)
103	(n,p)	1.930 (b)	1.931 (b)	1.001	992.2 (mb)	54.03 (mb)	35.13 (mb)
104	(n,d)	(E-thr = 5.710 MeV)				32.66 (mb)	319.6 (μb)
105	(n,t)	(E-thr = 4.304 MeV)				10.00 (mb)	773.8 (μb)
107	(n,a)	(E-thr = 169.4 keV)				60.10 (mb)	84.07 (mb)
108	(n,2a)	(E-thr = 9.458 MeV)				34.48 (mb)	5.639 (μb)

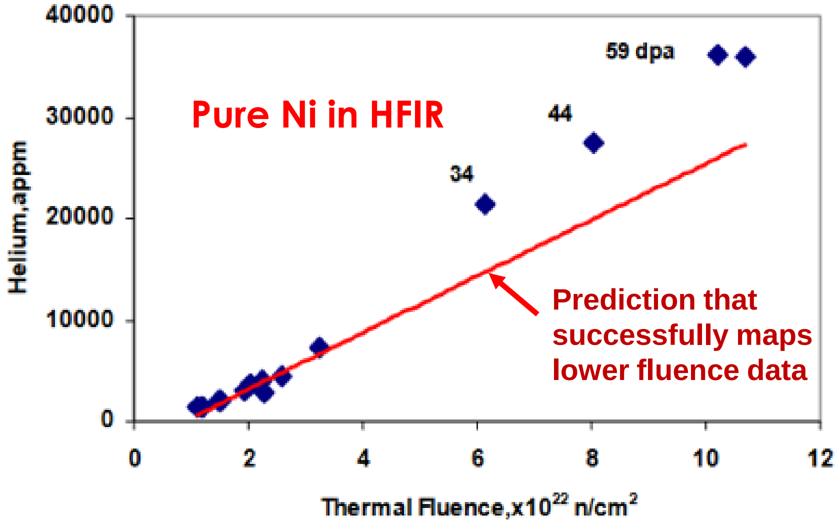
These cross sections are calculated from **JENDL-4.0** at **300K**.

Both thermal cross-section and resonance integral for the (n,p) reaction are large enough to significantly reduce N in LWR flux-spectra.

304 and 316 SS have 0.1-0.15 wt% N = 0.4-0.6 at%, equivalent to 3-4.5% Ni.

Complexity of Ni isotope evolution …. non-linearity?

Greenwood, Garner, Oliver, Grossbeck, Wolfer, 2004



Well-known nonlinearity at low fluence arising from two-step Ni-58, Ni-59 sequence

New strong increase at higher exposures arising from unidentified daughter or granddaughter isotopes?

Similar increases seen in hydrogen measurements.

Is a mistake to focus only on thermal neutron reactions?

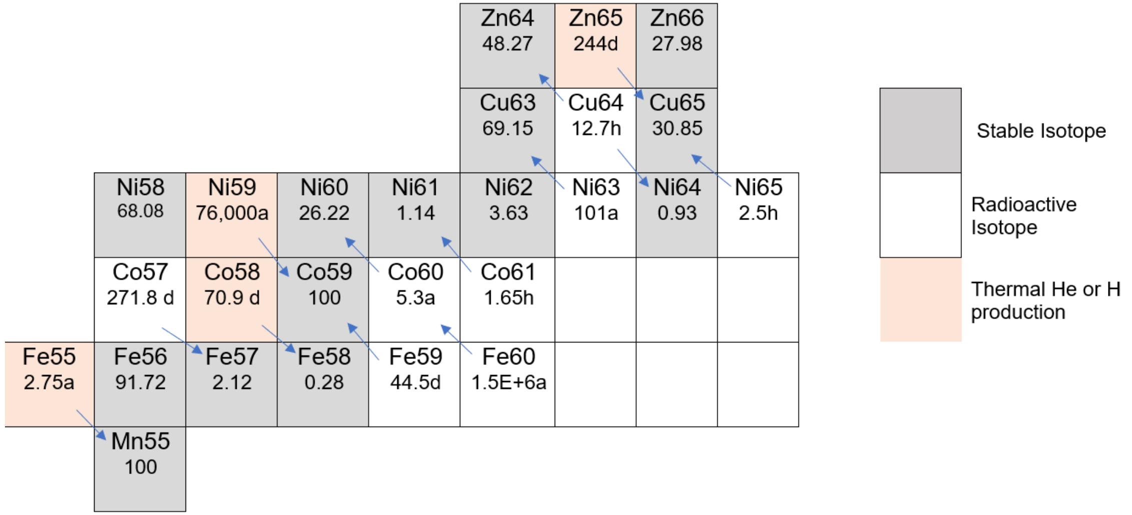


TABLE 3 — *Thermal neutron Q-values and cross sections.*

	(n,α) Helium Reactions		(n,p) Hydrogen Reactions	
Isotope	Q,MeV	Thermal σ,b	Q,MeV	Thermal σ,b
Ni-59	5.096	12.0	1.855	1.96
Zn-65	6.481	4.7	2.134	?
Fe-55	3.584	0.011	1.014	?
Co-58	3.511	?	3.089	?
Co-57	1.858	?	1.618	?

Other potential sources such as Ni-61 (γ,α) are being investigated.

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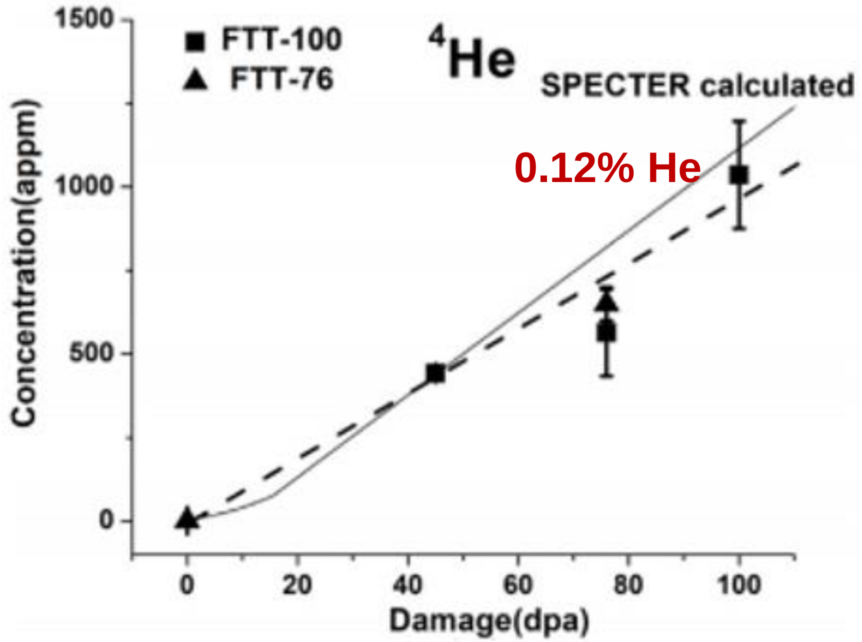
Recent measurements of 1200 appm He in nano-cavities generated in PWR 316 SS flux thimble tubes to 100 dpa at 25.3 EFPY

Miao Song, Kevin G. Field, Richard M. Cox, Gary S. Was , JNM 541, 2020



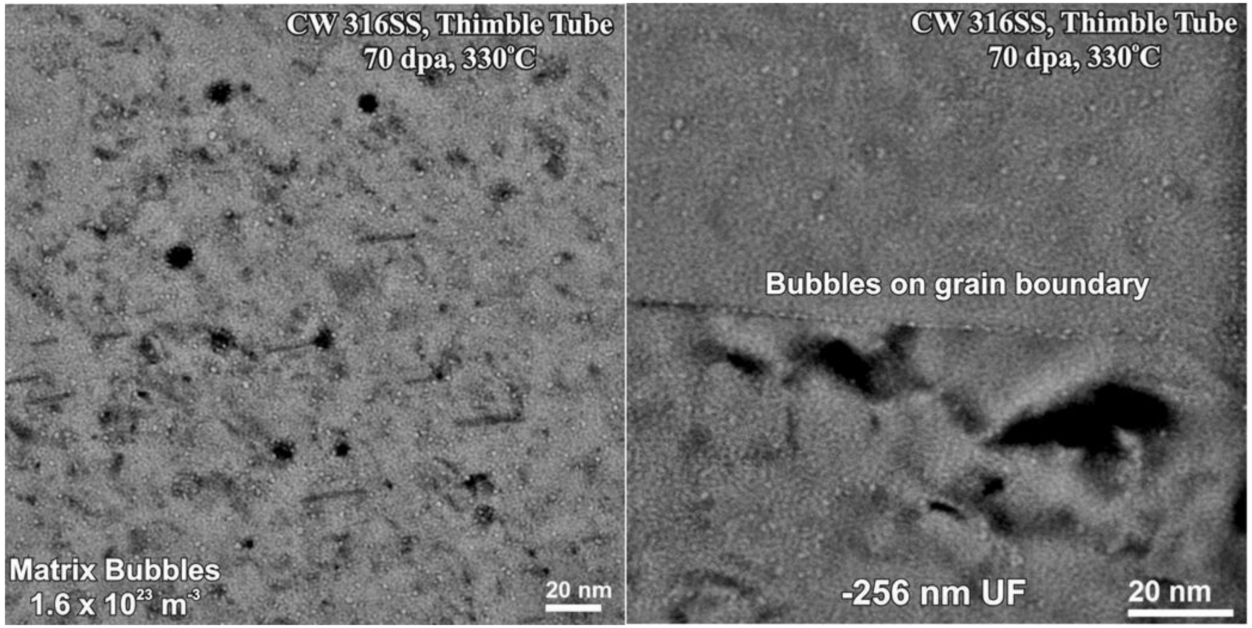
At 80 EFPY (80/23.5) (0.12) = 0.48 % loss of Ni in 316 SS.

0.56% Ni loss of Ni at 80 EFPY in 316 SS to produce He ad H.

304 SS with ~9.2% Ni would lose ~0.40%Ni.

He and H generation remove the most potent austenite stabilizer.

Synergisms between He, H and cavities



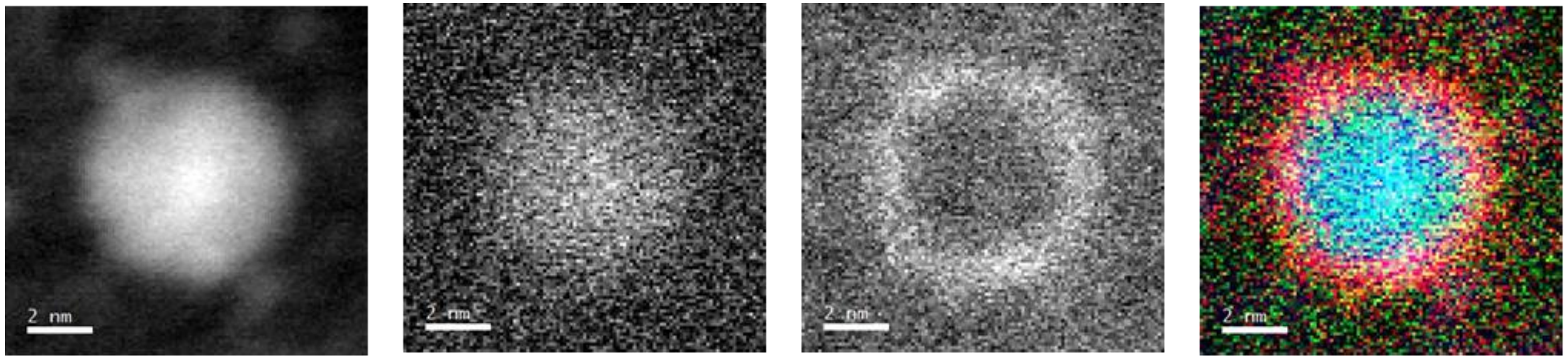
Nano-cavities in a PWR Flux Thimble Tube at 70 dpa.

Edwards, Garner, Bruemmer, Efsing, 2009

Measured~600 appm He, with ~2500 appm H, including significant amount of <u>captured</u> environmental hydrogen.

Bubble coating weakens grain boundaries, providing crack nuclei, and storing nascent hydrogen at the tip of any advancing crack.

Where is the H or H_2, inside or outside of the cavity? Other gases in the cavities (N_2)?

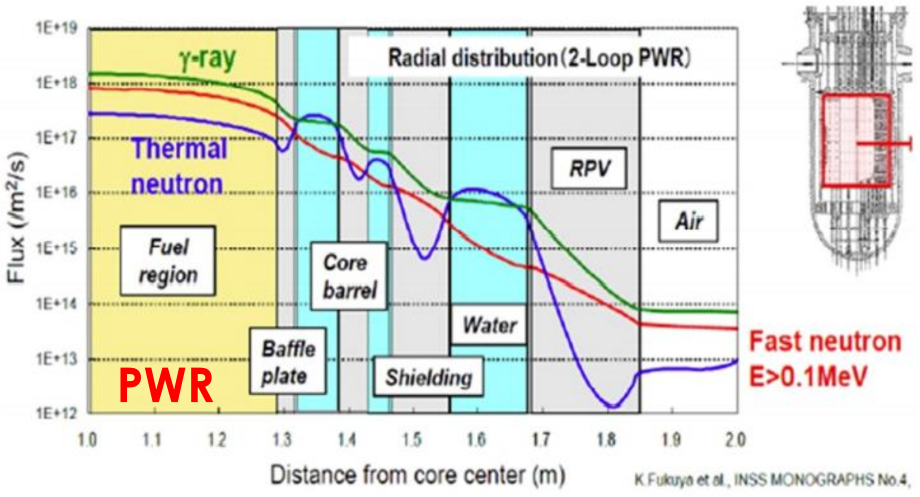


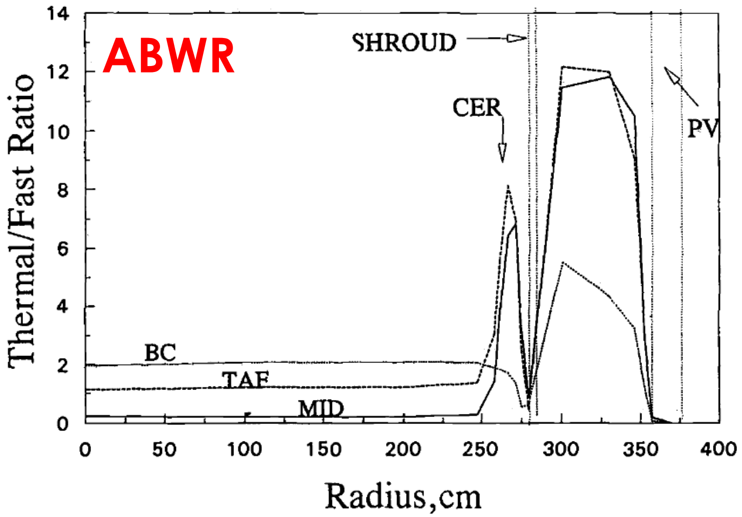
Zero Loss Filtered Image | Helium | Hydrogen | RGB

Transmutant He is inside the cavity with H coating the surface.

Judge, C. D., H. Rajakumar, A. Korinek, G. A. Bickel, 19th Intern. Env. Deg. 2019.

Transmutation will be greatest at water-metal interfaces due to thermalization of neutrons in water gaps

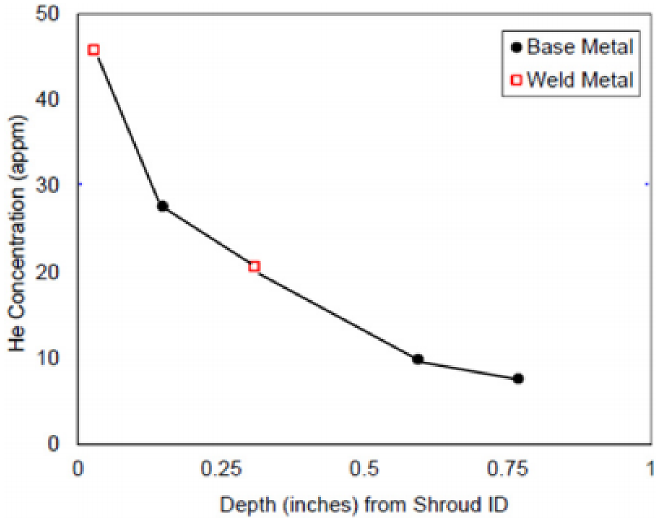




Thermal to fast neutron ratio **(T/F)** is a measure of transmutation to displacement damage (dpa) and varies strongly across LWR cores.

The water-contacting surface of the metal will be the most vulnerable to the effects of transmutation (Ni, Mn, N, V, H, H) on phase stability.

Transmutant helium measured in BWR shroud shows that the T/F ratio is strongest at the water-contacting surface.



Helium can be used as a retrospective dosimeter to measure the spatial variation in thermal neutron fluence.

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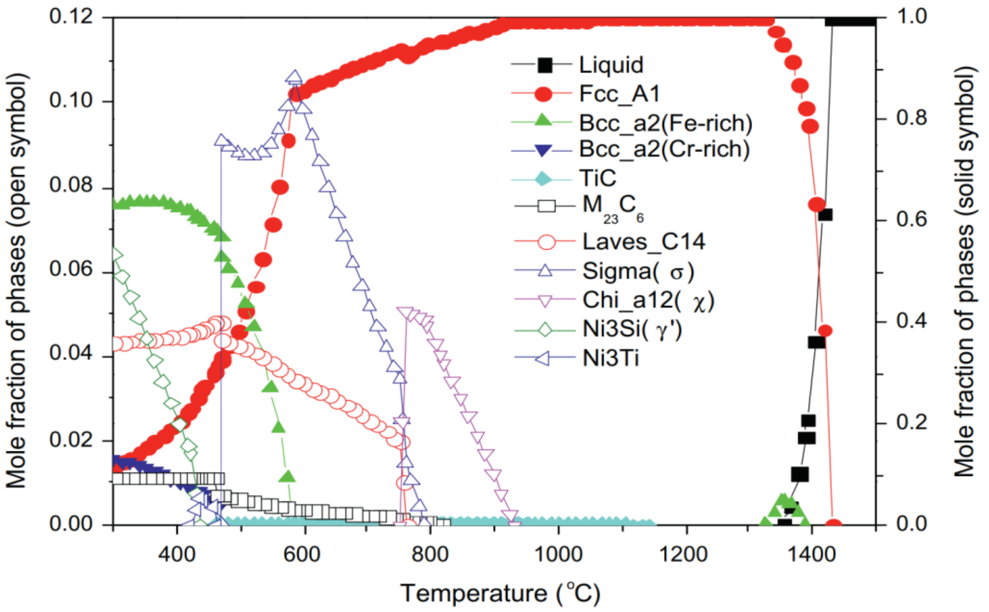
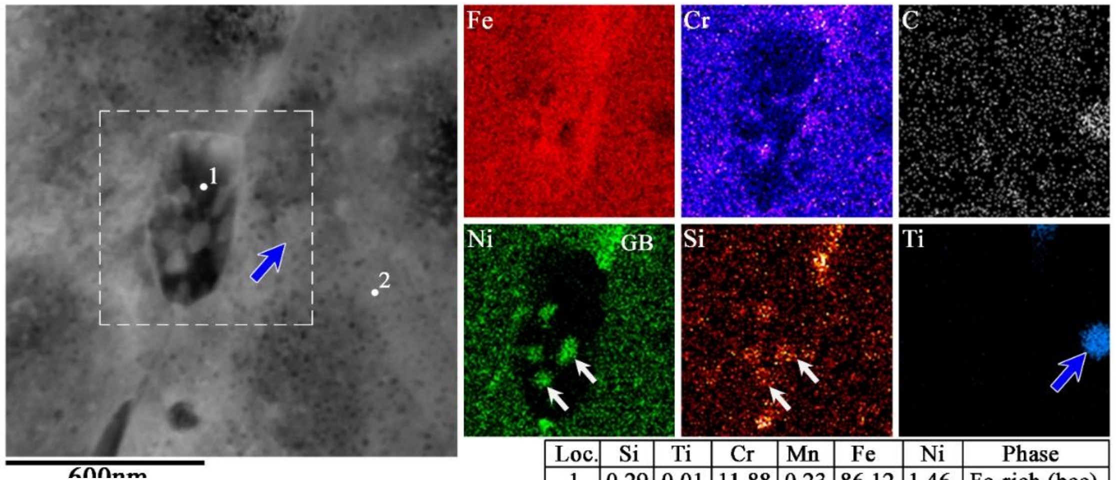
Phase instabilities resulting from transmutation and long life with special focus on new modes of corrosion and cracking

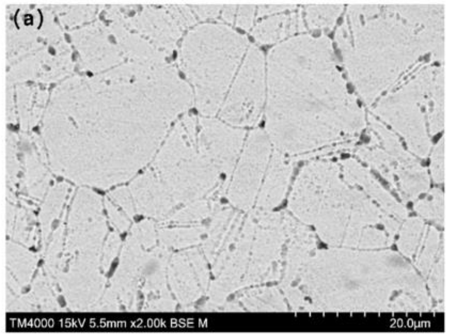
- **Transmutation and segregation will be strongest at intersection of grain boundaries and water-metal interface, providing new driving forces for corrosion.**
- **Primary concern is high-energy phases (deformation-induced martensite) and especially low-Cr, Fe-rich ferrite, forming at LWR-relevant temperatures.**



Thermodynamic calculations of equilibrium diagram showing two bcc-phases (Fe-rich ferrite and Cr-rich ferrite) can exist in 316 SS at 300°C. Yang and Busby, 2014



Loc.	Si	Ti	Cr	Mn	Fe	Ni	Phase
1	0.29	0.01	11.88	0.23	86.12	1.46	Fe-rich (bcc)
2	0.26	0.23	19.55	1.38	70.21	8.36	Matrix (fcc)



Fe-rich ferrite observed at low levels inside grains but at high densities on grain boundaries in 18Cr-10NiTi (321 SS) at 354°C and 58 dpa in BN-350. Merezhko et al., 2022.

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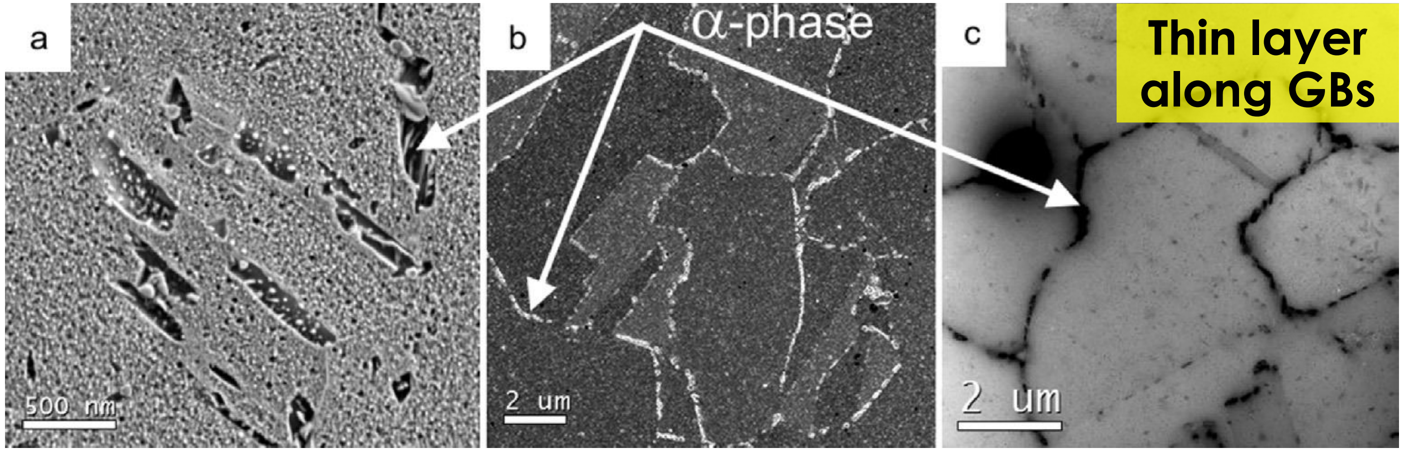
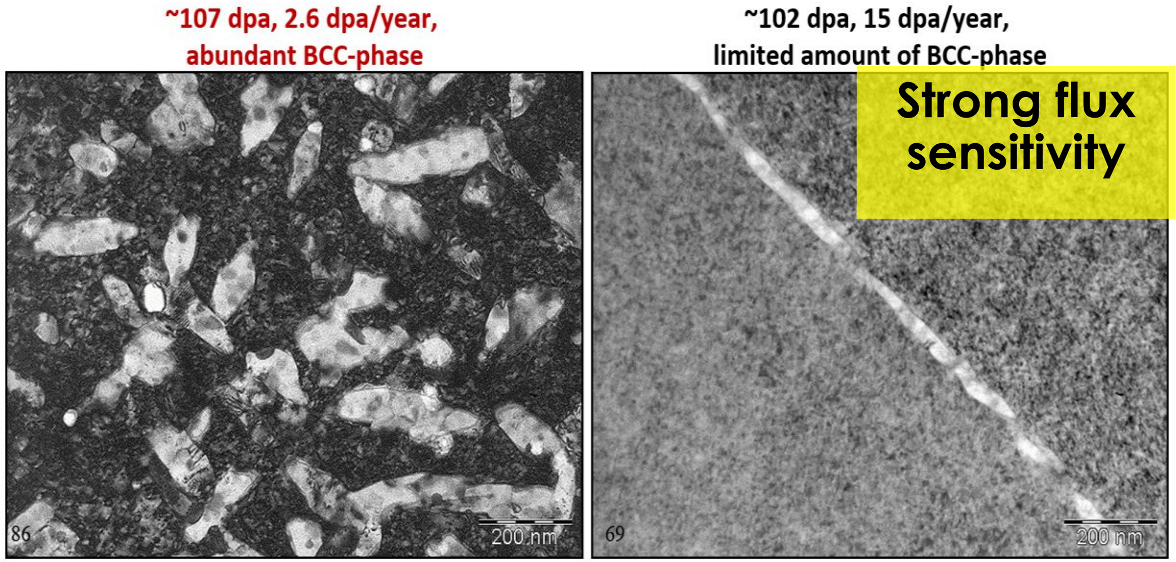
Radiation-induced ferrite in 18Cr-10Ni-Ti (321 SS) in BOR-60 ducts



SEM (a, b) and STEM (c) images of grain boundary α-phase in specimens obtained from different elevations on an 18Cr-10Ni-Ti steel wrapper after radiation in low-flux reflector region of BOR-60 for 41 years at 330-350°C. Gurovich and coworkers, 2015).



Comparison of ferrite phase developed in in-core and outer-reflector ducts. Neustroev and coworkers, 2015

Irradiation-induced ferrite tends to form along grain boundaries, making material susceptible to grain boundary fracture and corrosion in water.

Ferrite phase in image (c) was lost during electropolishing, indicating strong corrosion potential.

Ferrite formation is very sensitive to dpa rate where lower fluxes stimulate a larger degree of phase instability.

While carbide and silicide phases are limited by the C and Si content, BCC-ferrite is not limited by minor concentration of minor alloying elements.

Ferrite may easy reach a several percent or even tens of percent volumetric fraction.

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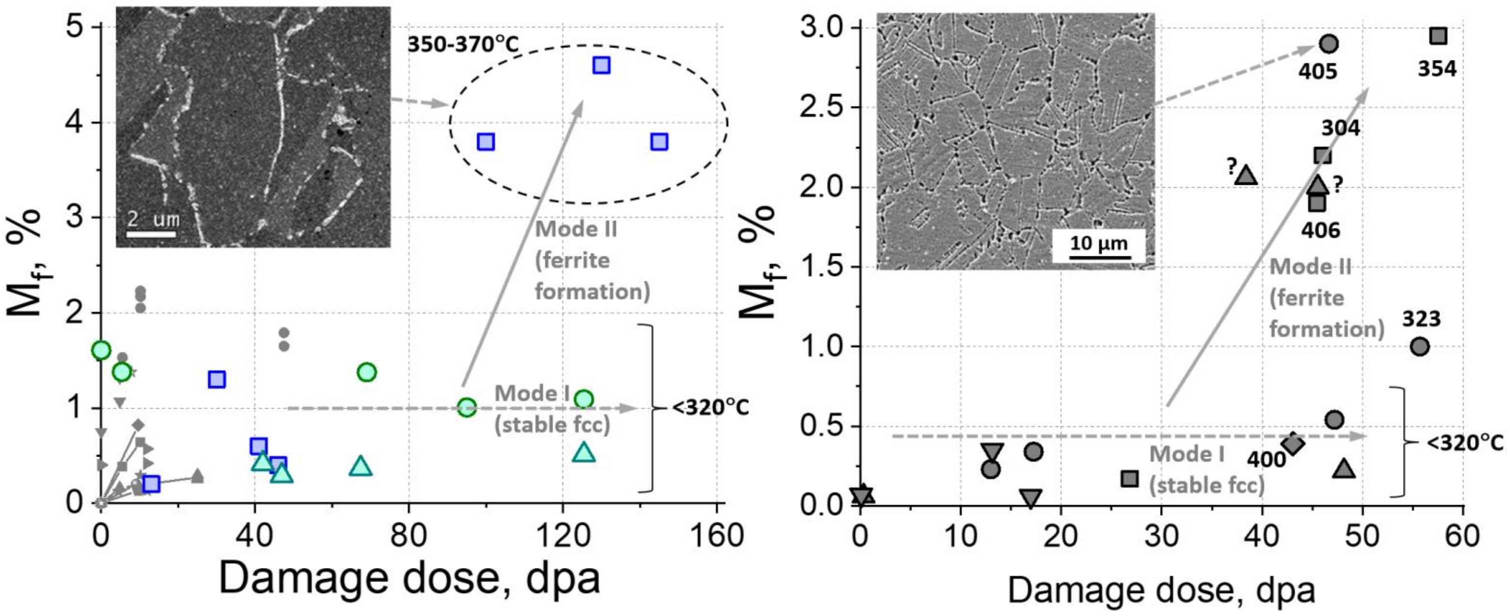
Ferrite formation under PWR-relevant conditions



Compilation of the available post-irradiation magnetic measurements performed using an industrial ferro-probe. The inset images show radiation-induced ferrite along grain boundaries.

Numbers near symbols show irradiation temperature (t_{irr}), and the "?"-signifies unknown temperature values; all other points have t_{irr} < 320°C.

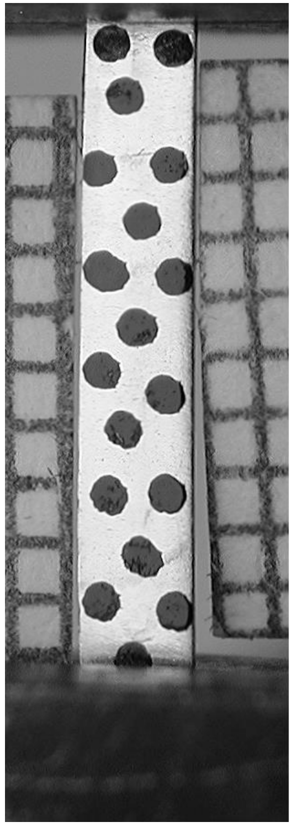
Ferritic phase amount is limited to ~3-5% in this compilation.

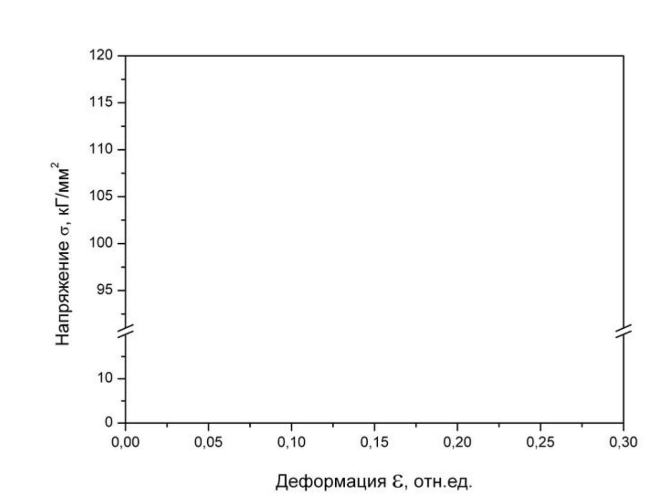
Most data came from fast reactor irradiation at higher fluxes, higher temperatures and neutron spectra that minimizes transmutation.

Breakaway behavior observed at some significant dpa level, followed by accelerated ferrite formation.

The concern is that lower fluxes and higher rates of transmutation per dpa in LWRs will shift the breakaway to lower temperatures, yielding much higher ferrite amounts.

“Deformation wave” as visual manifestation of martensitic instability

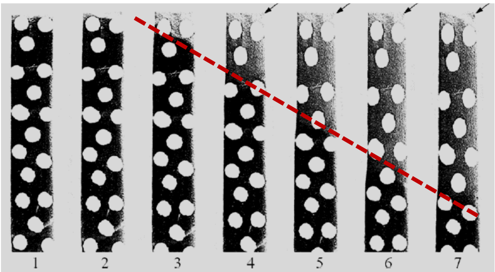


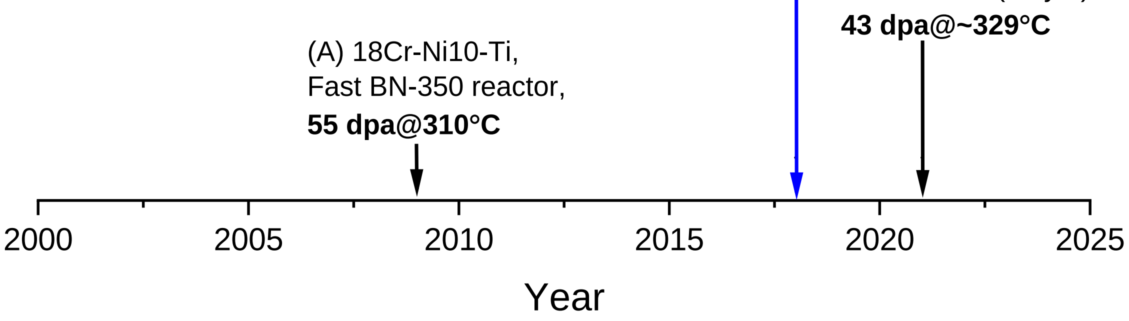


55 dpa, 310°C
in BN-350

Russian analog
of 321 stainless
steel

Test at room
temperature





Animation with “deformation wave” and timelapse of deformation wave observations in neutron-irradiated 300-series steels; the plot shows only cases confirmed with video recording or extensometer results. A: M. Gusev, O. Maksimkin et al, JNM, 386 (2009) 273–276; B: J. Hure et al, in Fontevraud 9, 2018; C: B. Margolin et al, JNM, 549 (2021) 152911.

The propensity toward deformation martensite increases with increasing dpa and lower test temperature.

Transmutation and possible synergism with H may accelerate the onset of martensite instability.

Once formed, martensite is a high energy-containing phase that is more prone to initiate corrosion.

The concern here is that during refueling at low temperature the inside of the baffle assembly may experience some minor scratch or physical impact, creating martensite on the surface that will serve as a corrosion source at operating temperatures.

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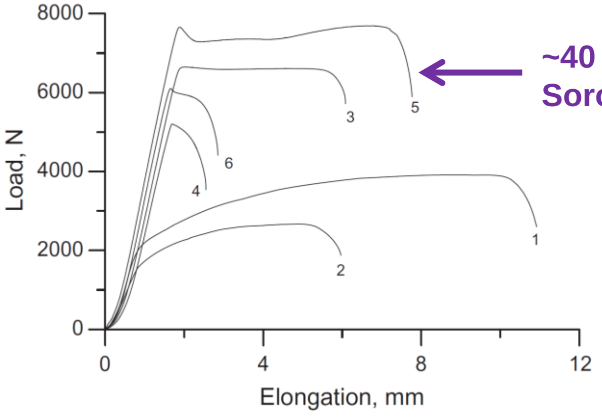
Growing evidence of abnormal mechanical behavior

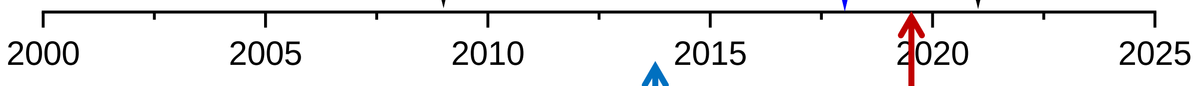


~40 dpa@400-450°C, Sorokin et al, JNM, 2014.

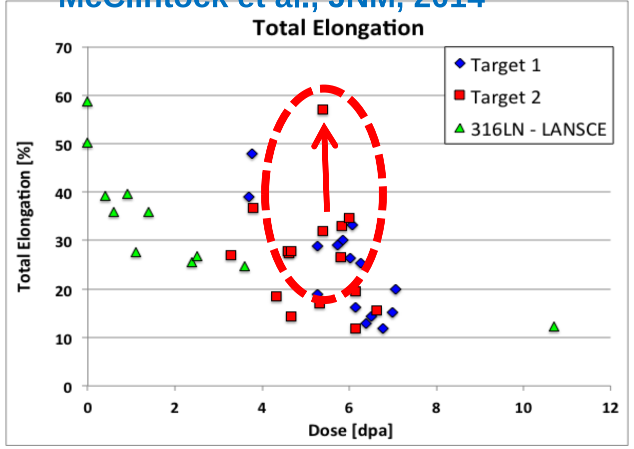
(B) 304 AustSS,
PWR Chooz A (decomm.),
25 dpa@~329°C

(C) 18Cr-10Ni-Ti,
WWER-440 (45 yrs),
43 dpa@~329°C

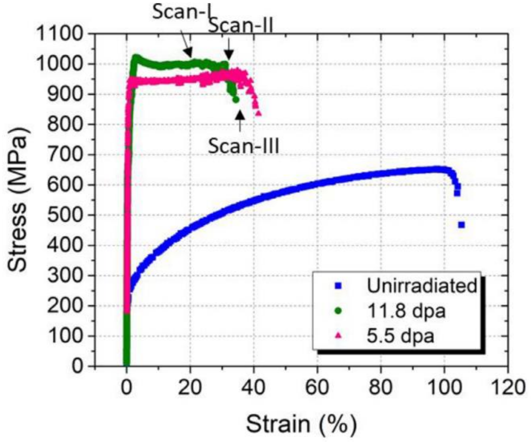
(A) 18Cr-Ni10-Ti,
Fast BN-350 reactor,
55 dpa@310°C



316L steel irradiated at SNS, McClintock et al., JNM, 2014



316L steel, irradiated at 320°C, Zhang et al, Acta Materialia, 2020



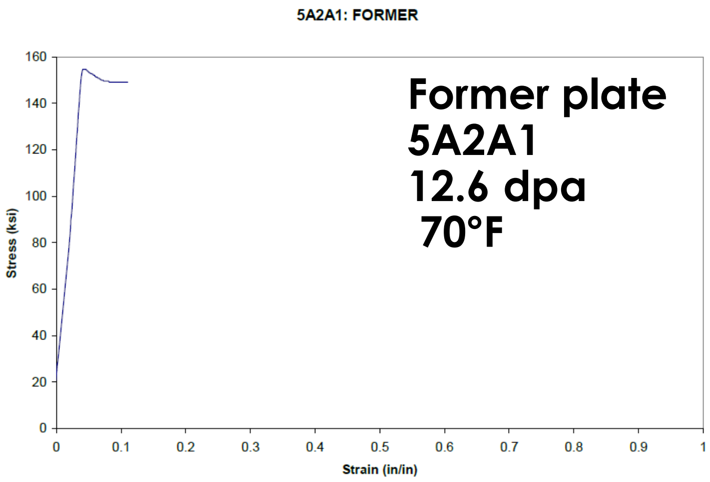
It appears that intense martensitic transformation may develop in 300-series steels irradiated in PWRs, as well as in fast reactors.

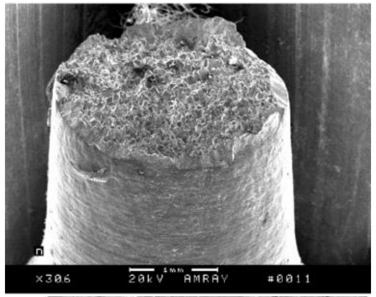
There are several reasons, currently not very transparent, shifting phase stability and initiating transformation. Hydrogen trapping, swelling, transmutation at high doses all may strongly influence material instability.

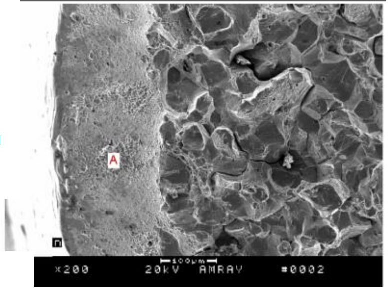
A severe risk here is the amount of new phase: the whole or significant portion of the material may be suddenly transformed.

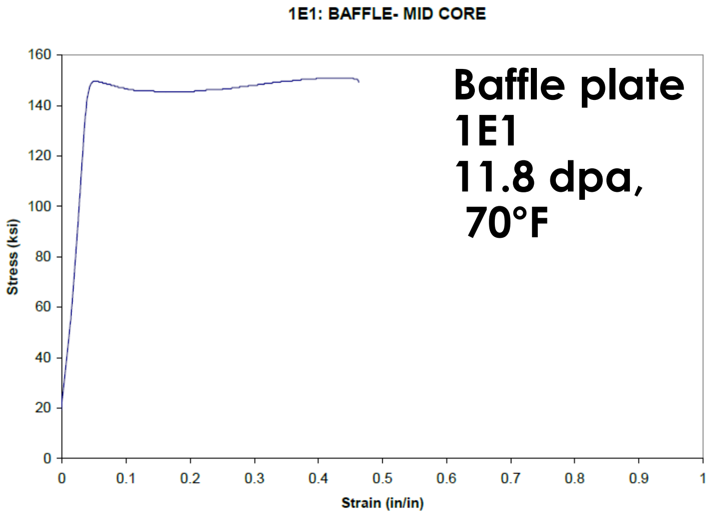
If happens while in service, it may bring additional risks since martensite phase has different radiation hardening, embrittlement and corrosion behavior.

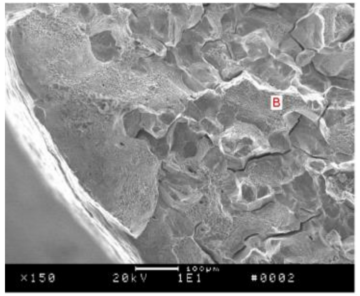
Brittle fracture of SONGS baffle-former plate material











Tensile curves show plateau behavior that suggests traveling wave phenomenon involving martensite instability in operation when tested at room temperature.

Only small amounts of strain and low dpa values are needed to stimulate "deformation wave".

Intense transformation may lead to embrittlement arising from complex interplay with trapped hydrogen.

Although there is no direct confirmation yet, it may be expected that martensitic transformation is the cause of brittle fracture seen in SONGS material.

EPRI report, "Materials Reliability Program Characterization of Decommissioned PWR Vessel Internals Material Samples—Tensile and SSRT Testing (MRP-129)," 1008205.

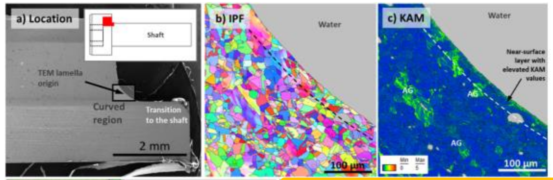
Conclusions

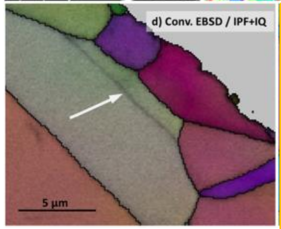
- Phenomena that previously appeared to be second-order and negligible in LWRs at <40 years, may become of first-order upon life extension.
- Evidence is accumulating that suggests a number of phase instabilities are occurring, inducing new forms of corrosion and accelerating IASCC.
- Potential changes in failure mechanisms may also be developing.
- The major driver is transmutation, persistently pushing metastable 304 and 316 stainless steels toward ferrite and martensite instabilities.
- Transmutation-induced changes will be strongest at metal-water interfaces.
- Steels in operating LWRs were poured 50-70 years ago and are relatively dirty by modern standards. S and F are tied up in MnS precipitates which are dissolving because of Mn loss, releasing S and F to grain boundaries.
- Harvesting efforts followed by PIE are important to support risk-free PWRs life extension.
- There are synergisms between various phenomena that need investigation, especially concerning hydrogen trapping at very high levels.

Back-up slides

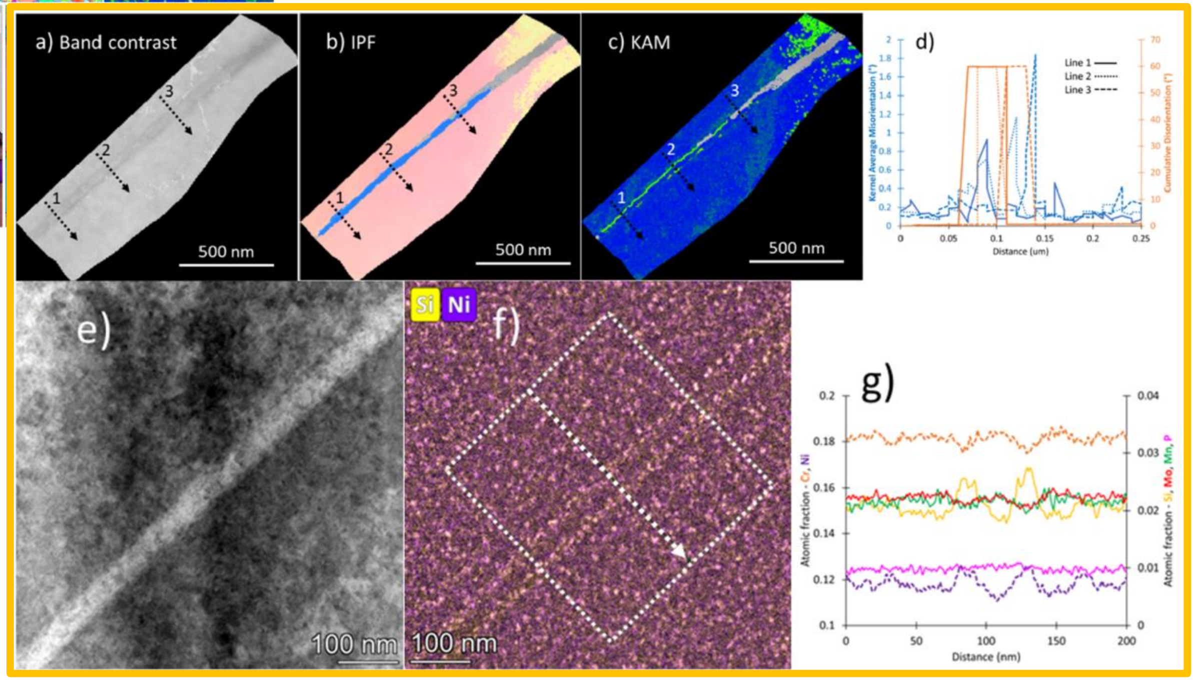
The necessity of material harvesting efforts

A recent example of interesting new phenomena: precipitations at defect-free channels formed in **baffle bolt**:





Left: a) Analyzed location of baffle former bolt; b,c) EBSD maps representing grain structure at the head-to-shaft transition area. d) Conventional EBSD map showing channel formed in a sub-surface grain (white arrow);



Right: tKD a) band contrast, b) IPF, and c) KAM. d) KAM and cumulative disorientation point-to-point profiles; **e) STEM-BF and f) STEM-EDS Ni and Si map of same channel; g) concentration profile based on box in f) across the channel;**

T. Lach, M. Gussev, X. Chen, "**Complexity of segregation behavior at localized deformation sites formed while in service in a 316 stainless steel baffle-former bolt.**" *Scripta Materialia* 255 (2025): 116371.

- Once NPPs or other nuclear facilities enters previously unexplored temperature and flux ranges (e.g., because of lifetime extension), new phenomena appear.
- An examples from the past is swelling.
- In vast majority of cases, no predictions were made, or predictions were wrong.
- Unexpected behavior(s) may appear even in well-explored dose/flux range (e.g., brittle fracture of baffle plate material).
- **In this context, harvesting materials irradiated in-service, within the conditions of interest, is important.**
- Material harvesting campaign may be a condition of granting life-extension license.

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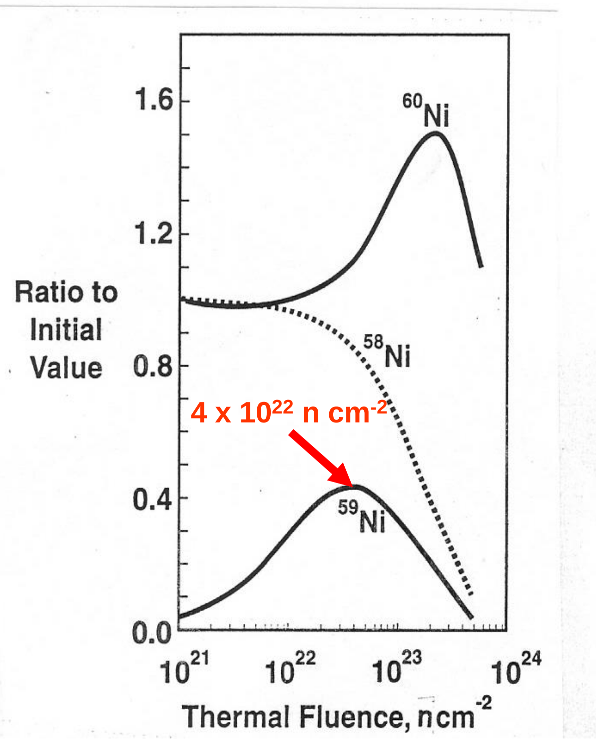
Complexity of Ni isotope evolution

Natural nickel has 5 isotopes with Ni-59 and Ni-63 missing.

Ni-59 has large thermal cross-sections to produce Ni-60 by (n, gamma), He by (n, alpha) and H by (n, p) reactions



Natural nickel

Ni-58 67.85%

Ni-59

Ni-60 26.2%

Ni-61

Ni-62

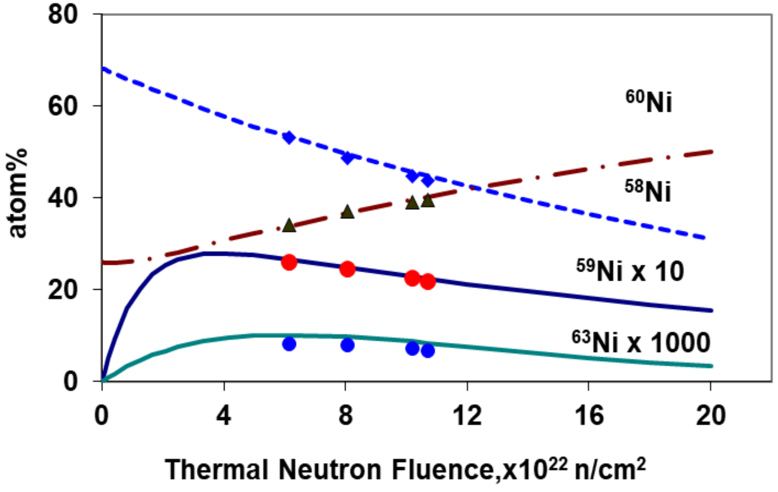
Ni-63

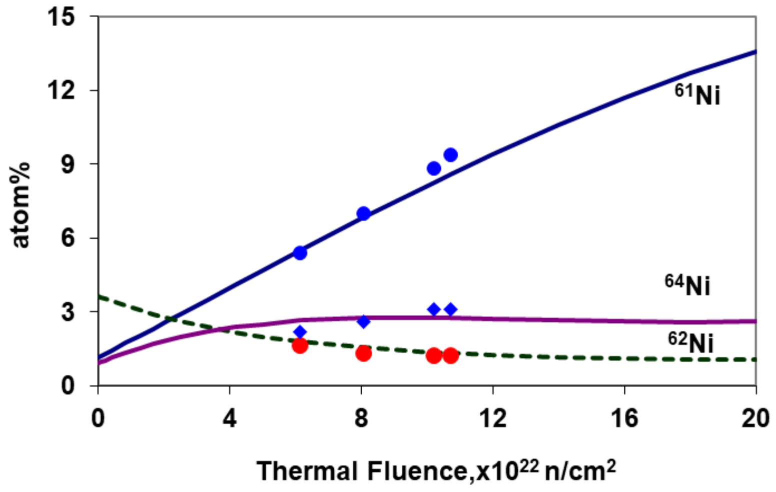
Ni-64

} **5.7% total**

Isotopic shift

Greenwood, Garner, 2024





Ni-61 is reaching double-digit values leading to possible increases in He and H production.

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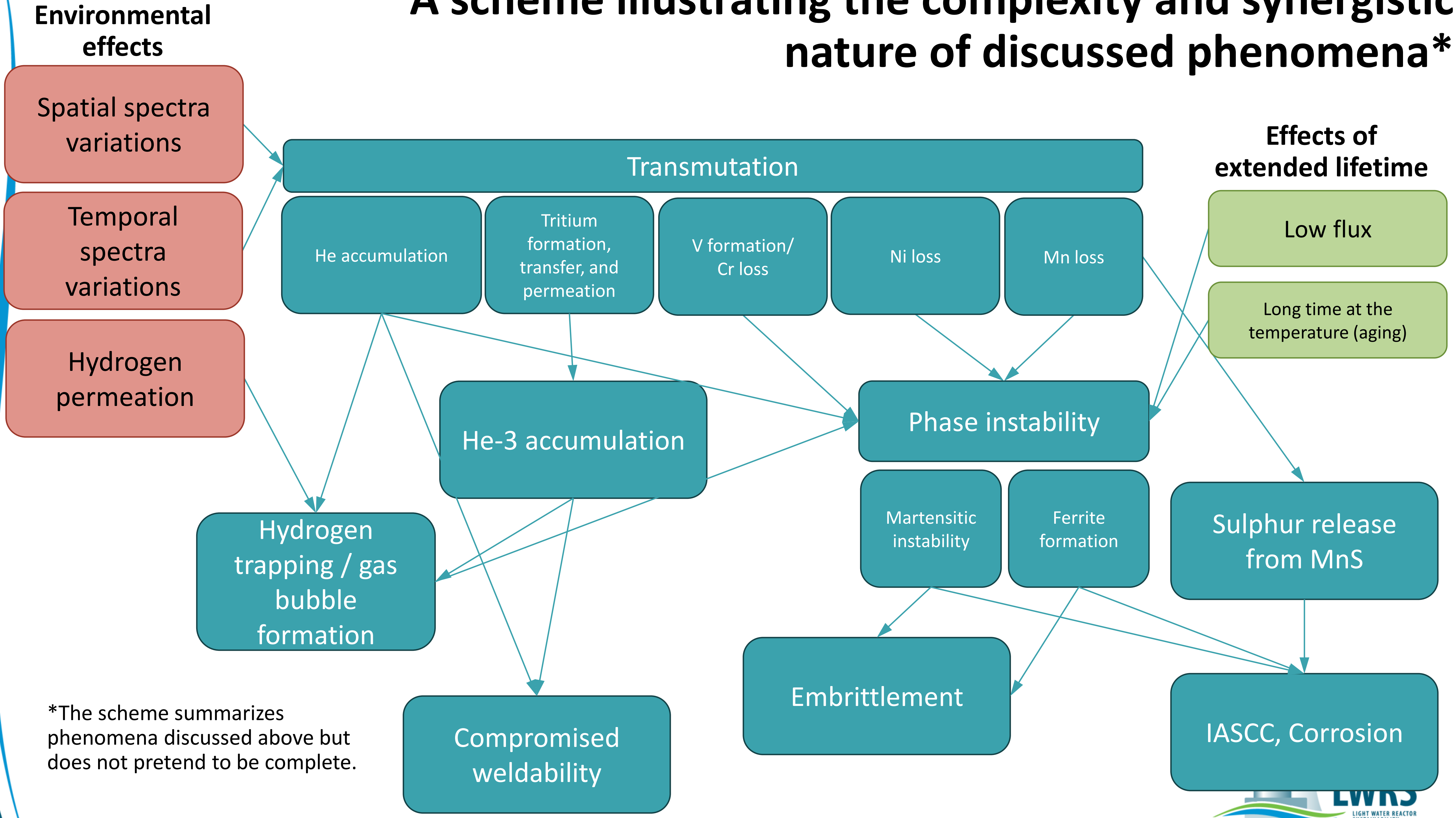
A scheme illustrating the complexity and synergistic nature of discussed phenomena*



*The scheme summarizes phenomena discussed above but does not pretend to be complete.