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Irradiation Assisted Degradation of LWR Core Internal Materials: Brief Review

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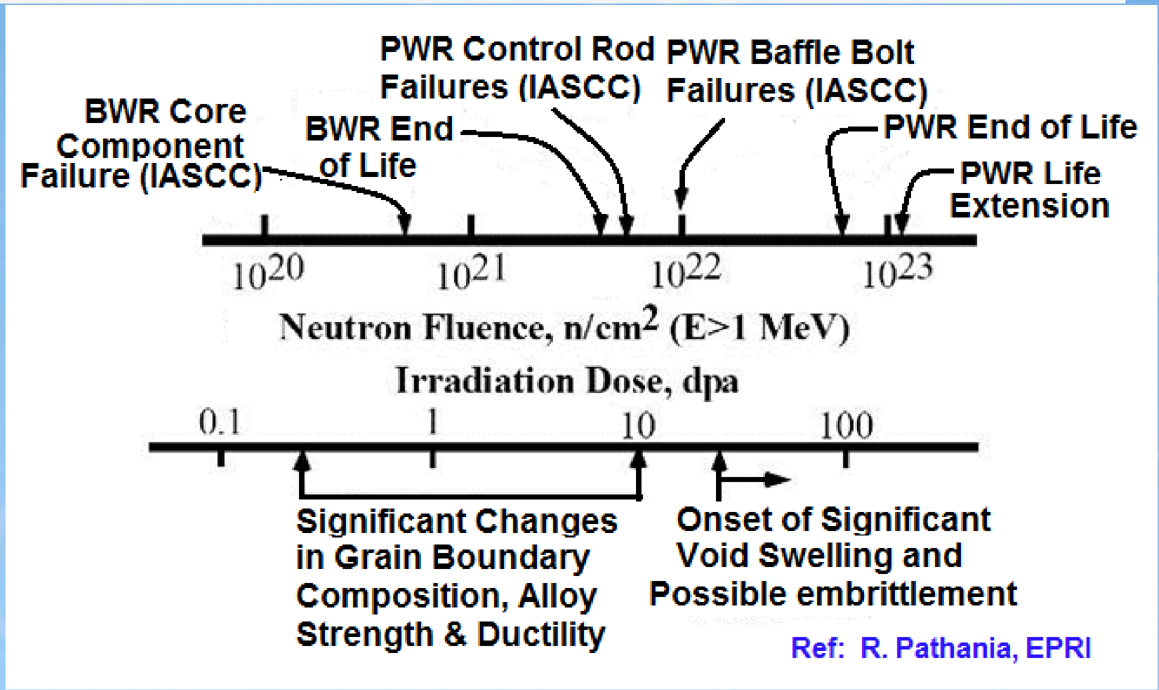
Contents

Introduction

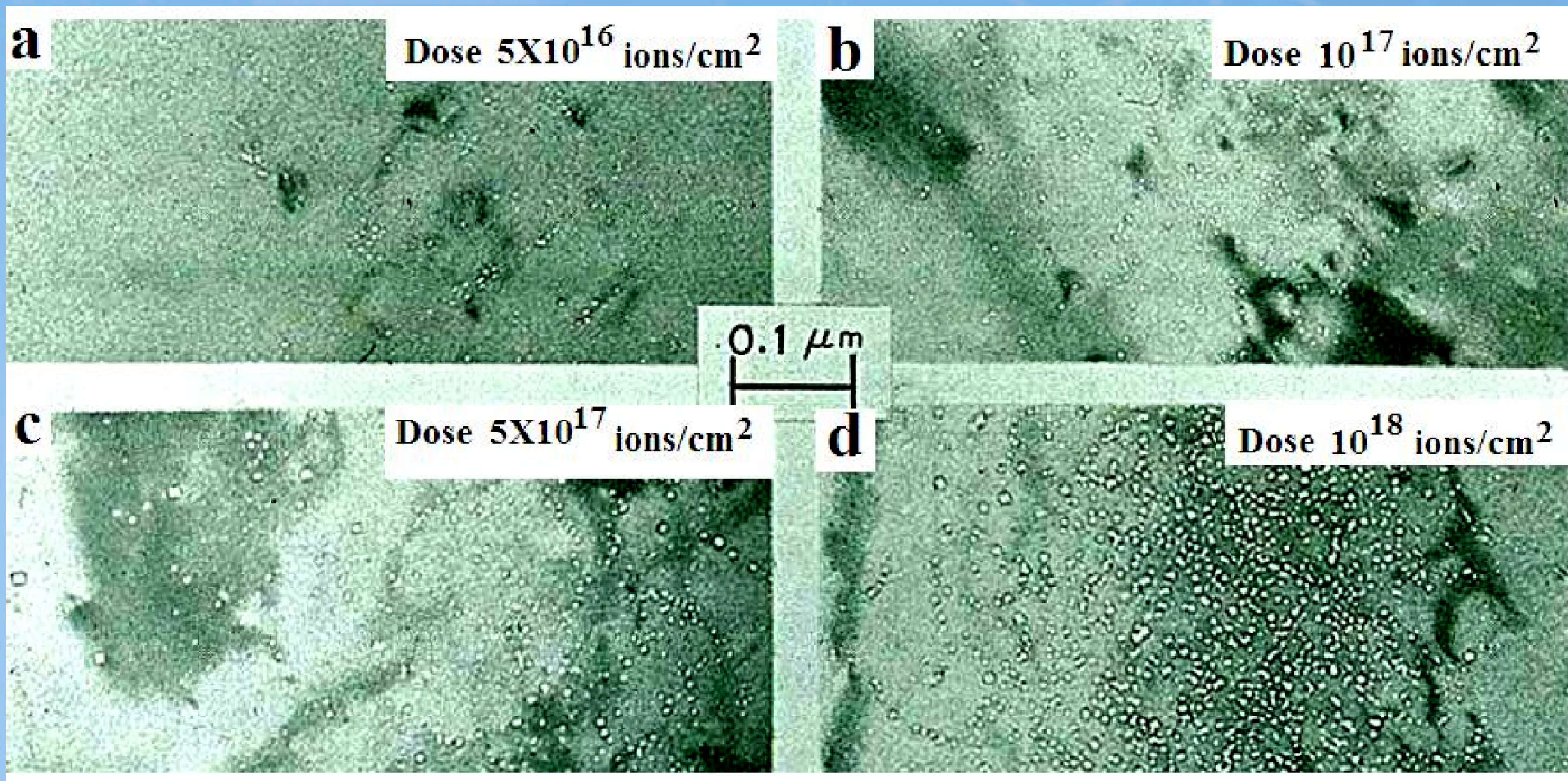


Technical Issues

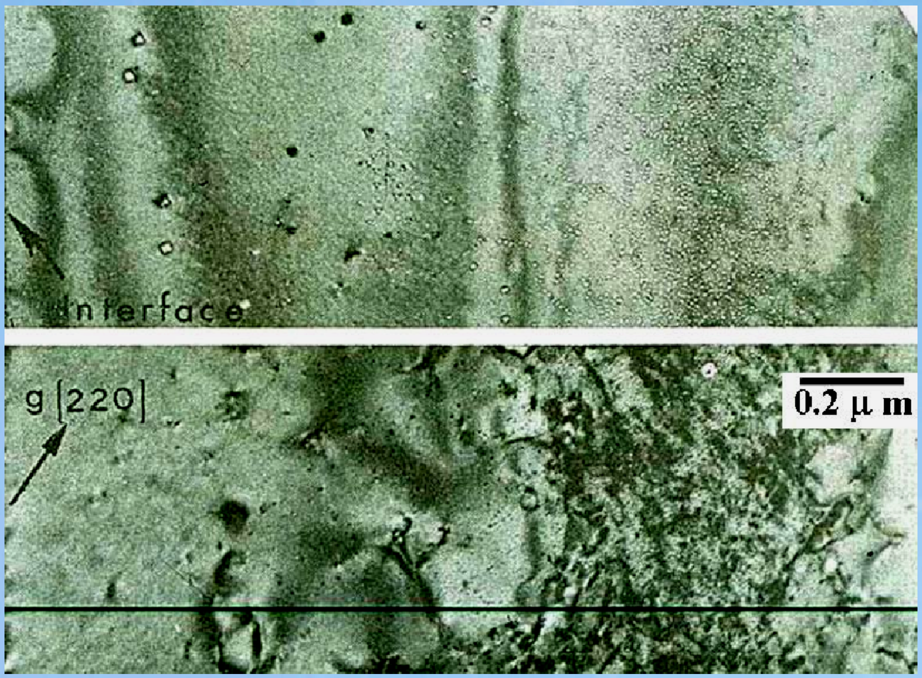
- identify susceptible materials & conditions,
- determine crack growth rates to assure that the selected inspection intervals are adequate,
- verify effectiveness of proposed mitigative measures
- investigate potential of radiation embrittlement, including synergistic effects of thermal & neutron embrittlement
- evaluate effects of void swelling, including the associated decrease in ductility

Void Swelling

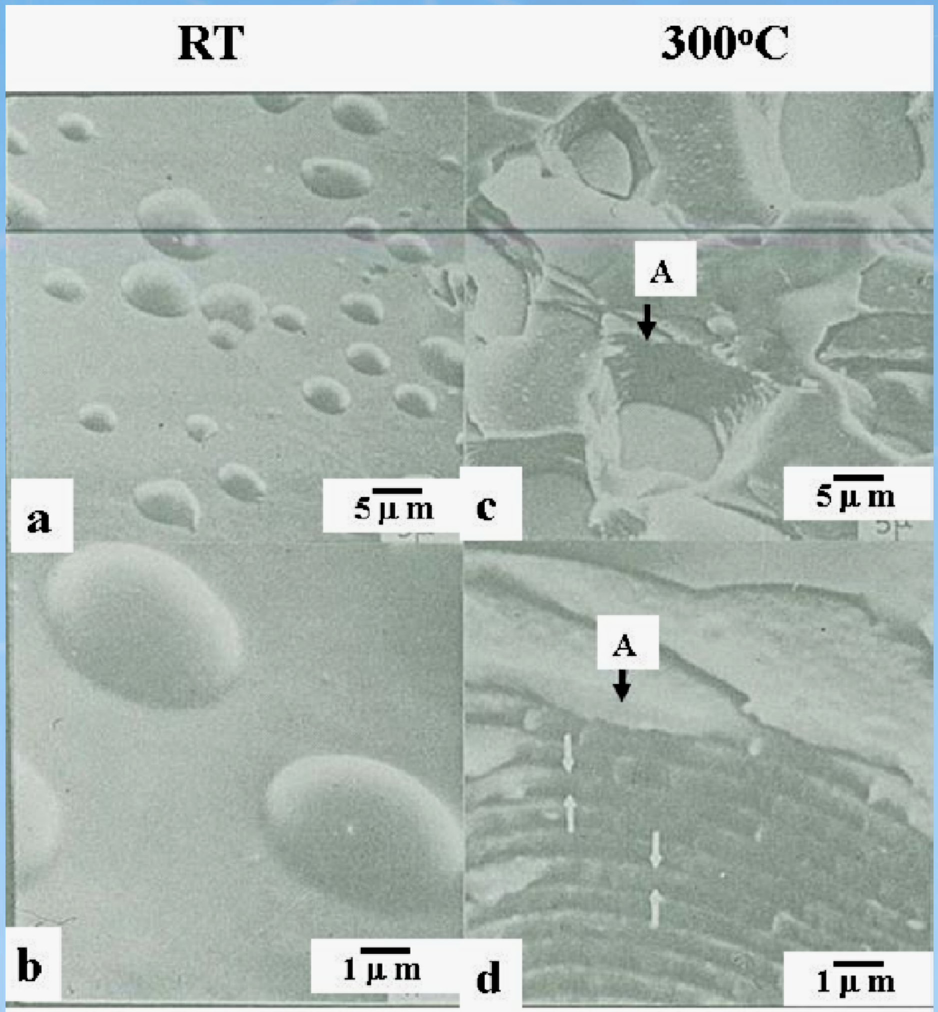
- Void swelling of most reactors internals is not expected to be limiting over the current licensing period
- Continued research work will explore the extent of void swelling over the extended operating life of present reactors (i.e 54 EFPY)



Helium bubbles in Mono crystalline Nickel (110) Irradiated with 100 keV ions



Interface
g [220]
0.2 μ m



RT
300ºC
a
5 μ m
c
5 μ m
A
b
1 μ m
d
1 μ m
A

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Background

- **Neutron irradiation changes the *material microstructure* (radiation hardening) & *micro-chem.* (radiation induced segregation) that leads to:**
  - ➔ **increase in yield strength & decrease in ductility**
  - ➔ **degradation of fracture toughness**
  - ➔ **increased susceptibility to IASCC**
  - ➔ **void formation, coalescence and swelling**
  - ➔ **creep relaxation**

- **Neutron irradiation also changes the *water chemistry* (radiolysis);**
  - **BWR normal water chemistry results in an increase in corrosion potential,**
    - ➔ **E_{corr} ≈ 200 mV (SHE);**
  - **PWR water contains H_2 to scavenge radiolysis products,**
    - ➔ **E_{corr} ≈ - 800 mV (SHE);**

- **Extent of micro-structural & micro-chemical changes vary with irradiation temperature, neutron fluence, flux, & energy spectrum**

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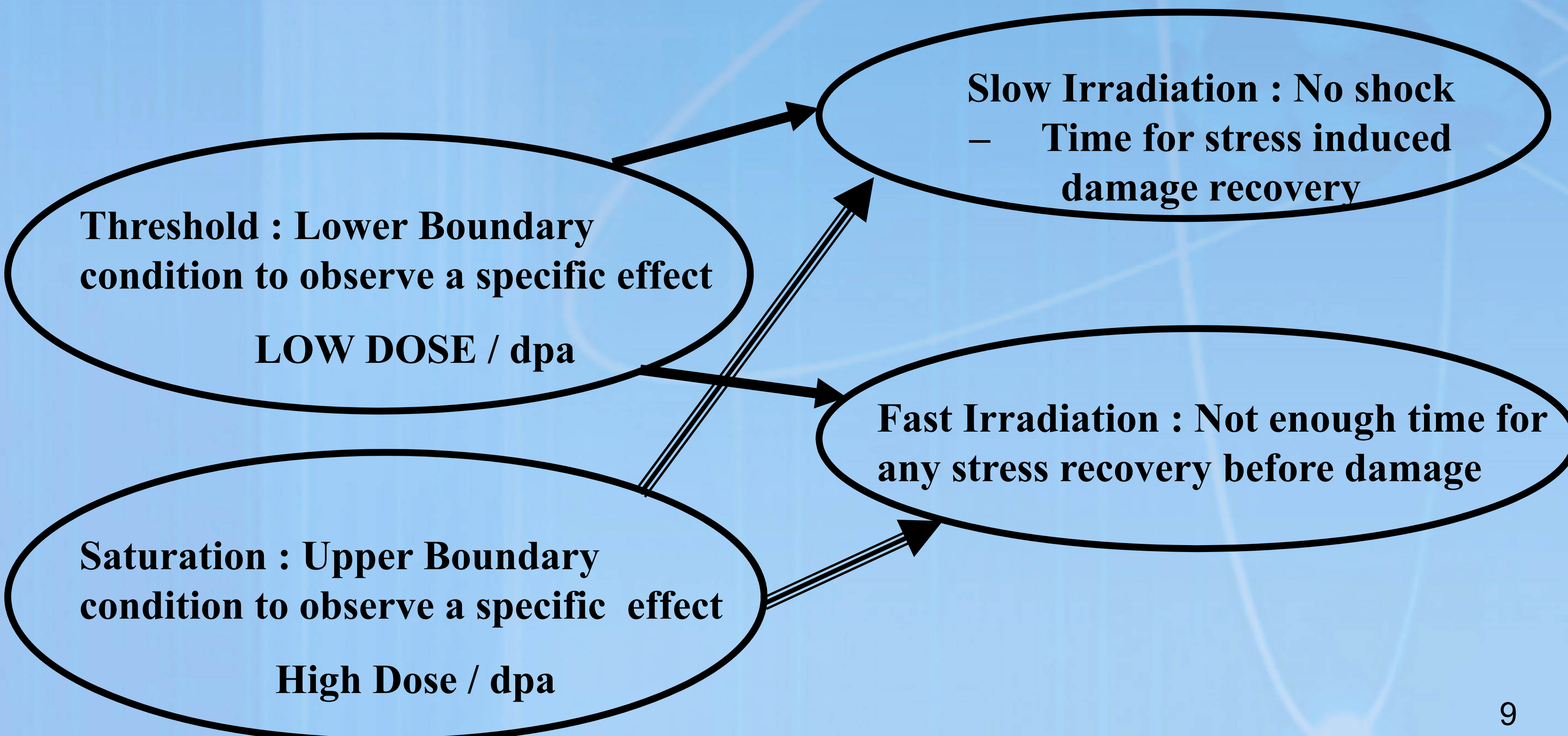
- **Materials series with low dose exposure**
  - **Help to understand the thresholds for irradiation effects:**
    - ➔ **Fracture and tearing toughness,**
    - ➔ **Irradiation-assisted stress corrosion cracking (IASCC)**
- **Materials with high dose exposure**
  - **Help to understand if saturation of mechanical properties occurs:**
    - ➔ **Radiation-induced segregation (RIS)**
    - ➔ **Fracture toughness (FT) and tensile properties**
    - ➔ **Irradiation-assisted stress corrosion cracking (IASCC)**
  - **Help to understand the dose dependence for the :**
    - ➔ **Onset for the void swelling and the extent of the void swelling (if any at a given temperature and exposure)**

Threshold and Saturation



Chemical composition of austenitic stainless steels

Materials	Composition								
	Ni	Si	P	S	Mn	C	N	Cr	Other Elements
304 CW	8.23	0.47	0.018	0.002	1.00	0.060	0.070	18.43	B <0.001
304 L SA/CW	8.91	0.46	0.019	0.004	1.81	0.016	0.083	18.55	B < 0.001
HP 304L SA, High - Oxygen	9.03	0.03	<0.005	0.005	1.11	0.005	0.003	19.21	O 0.008, Mo < 0.005
HP 304 L SA, Low - Oxygen	9.54	0.01	0.001	0.002	1.12	0.006	<0.001	19.71	O 0.0047, Mo 0.02
316 LN SA	12.20	0.70	0.007	0.002	0.97	0.019	0.103	17.23	Mo 2.38, Cu 0.21
316 LN – Ti SA	12.30	0.72	0.007	0.002	0.92	0.012	0.064	17.25	Mo 2.38, Ti 0.027, Cu 0.021
316 SA/CW	10.24	0.51	0.034	0.001	1.19	0.060	0.020	16.28	Mo 2.08, B < 0.001

SA Solution Annealed; CW Cold Worked

Ref: Y, Chen et al., NUREG/CR – 7018(2010) and 6965 (2008)

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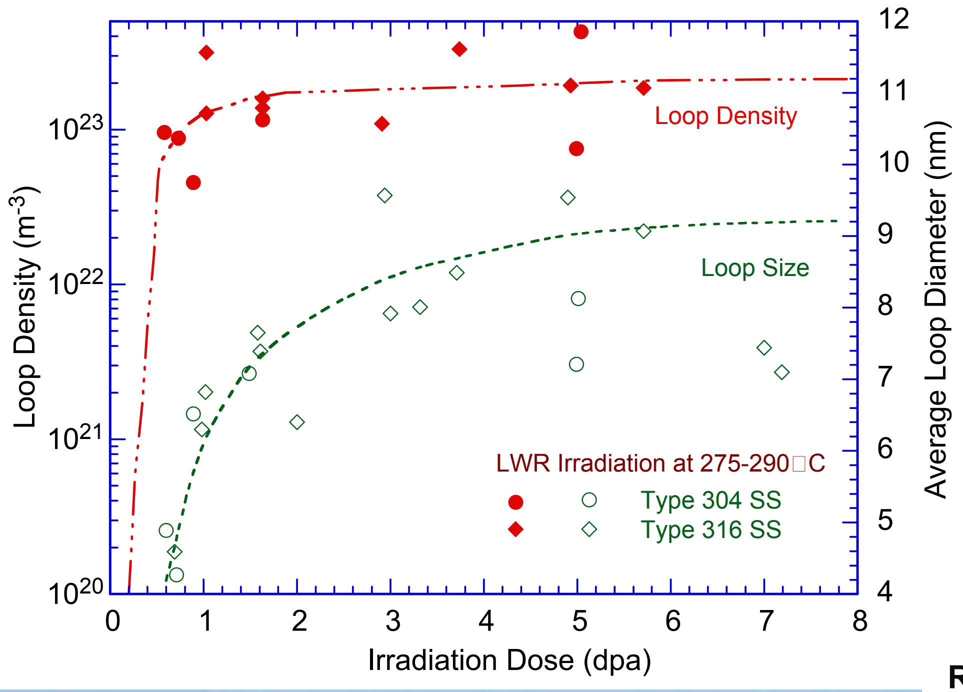
- **Neutron irradiation of SSs leads to the formation of:**
  - **Point defect clusters (black dots)**
  - **Dislocation loops**
  - **Dislocations network s**
  - **Cavities**
  - **(voids of vacancies and/or gas bubbles)**
  - **Precipitates**

Ref: O. Chopra and A. S. Rao, NUREG/CR-7027 (2010)

- **Based on experimental observations it has been suggested that:**
  - **Microstructural changes vary with irradiation condition, i.e., temperature, fluence, dose rate, & spectrum, and material condition & composition**
  - **Below 300°C: black spot defect clusters & faulted dislocation loops**
  - **Above 300°C: large faulted loops, network dislocations, cavities/voids, & precipitates**
  - **Depending on material & irradiation condition, loop density & size reach saturation**
  - **Microstructural changes correlate well with change in yield strength**

☛ **Continuing increase in IASCC susceptibility at higher dose can not be explained readily**

Irradiation Microstructure - Density/Size of Loops with Dose



- Neutron irradiation of SSs leads to the formation of:
  - Point defect clusters (black dots)
  - Dislocation loops
  - Network dislocations
  - Cavities (voids of vacancies and/or gas bubbles)
  - Precipitates

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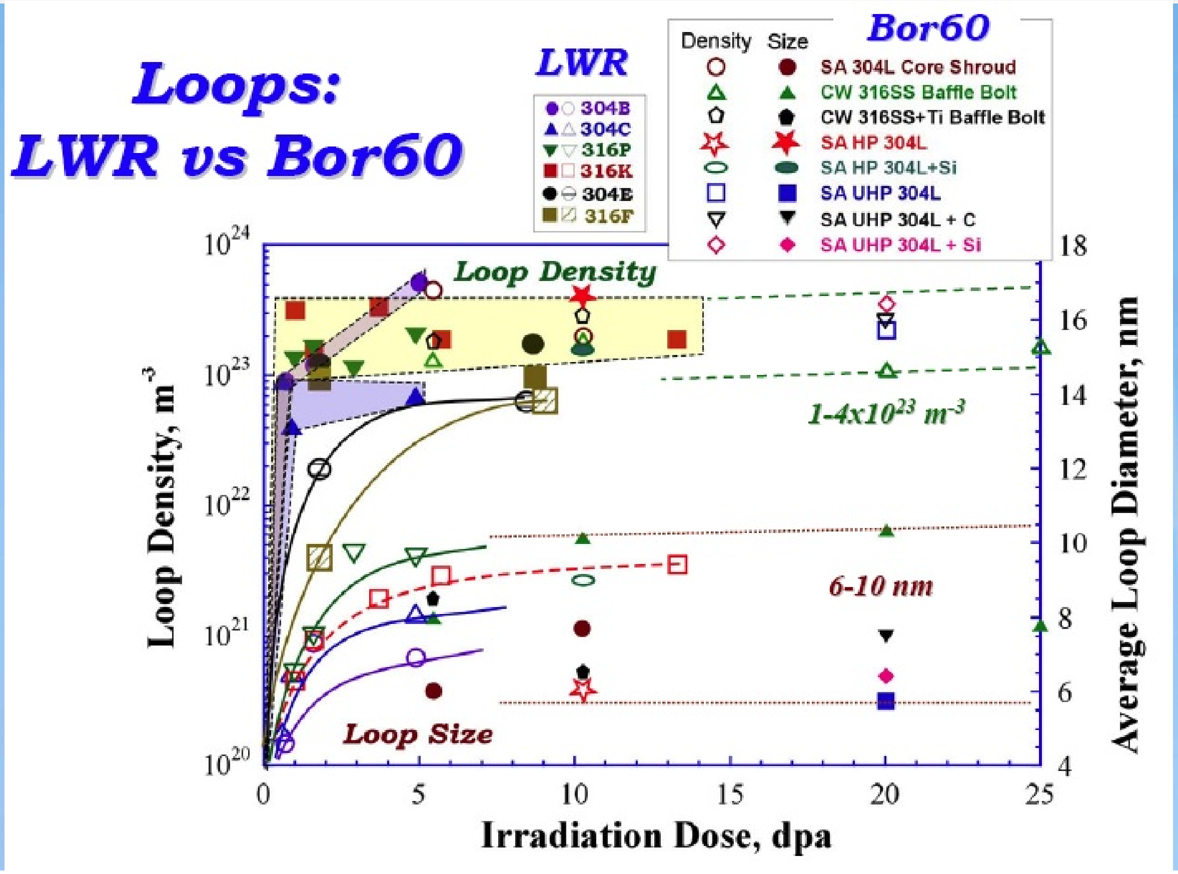
Density & Size of Loops in LWR vs BOR-60 Irradiation



Small symbols LWR
Big symbols BOR-60

LWR → 275°C
BOR-60 → 320°C

Edwards et al. , also observed (Ref: 12th Intl. Conf. Env. Deg., 2005)

- Loop size is similar for both LWR and BOR -60 reactor irradiations.
- Loop density is higher for BOR-60 than LWR
- Both temperature and thermal spectrum has effect .
- Irradiation temperature 275°C versus 320°C has some effect in loop evolution initially (dose < 5 dpa). However for dose levels > 5 dpa irradiation temperature has very little effect .

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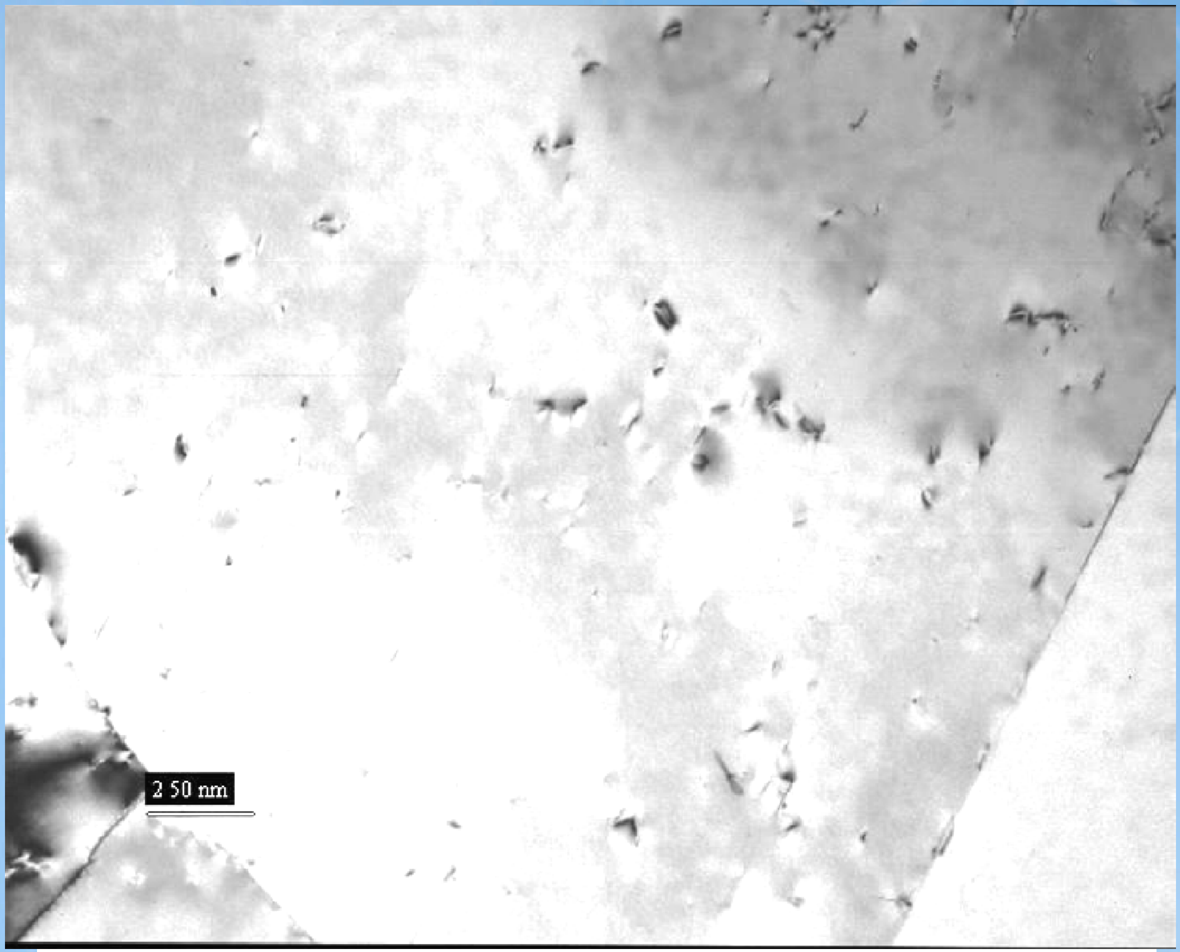
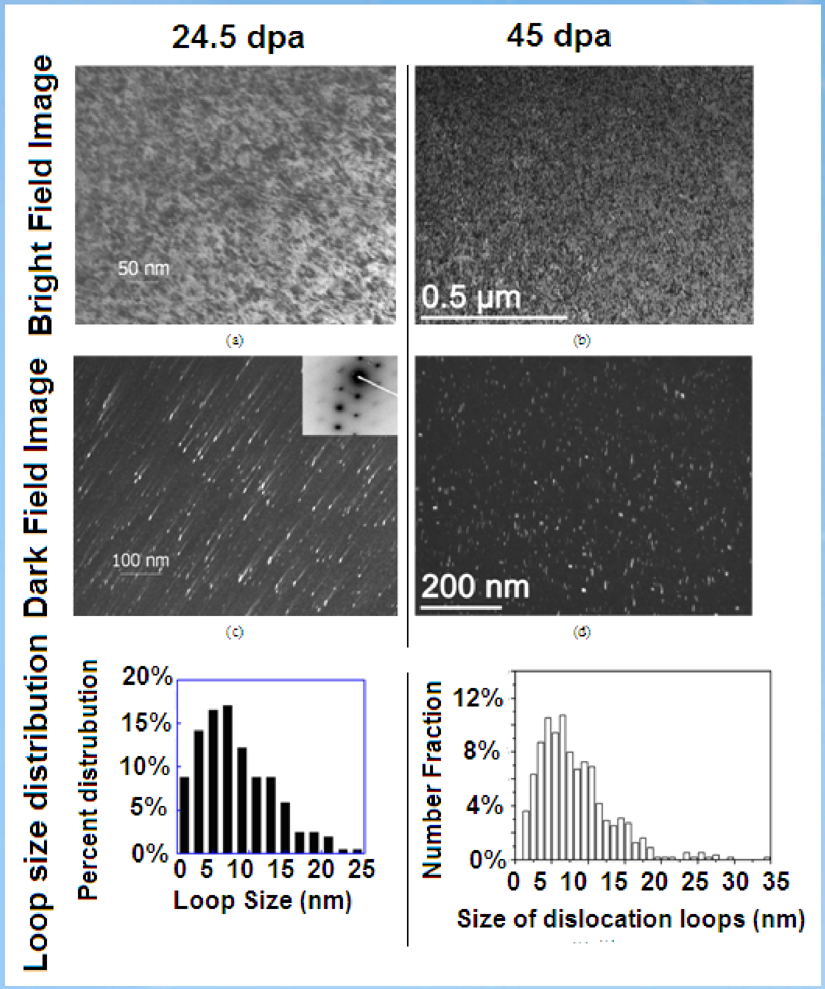
Recent NRC Research on Irradiation Microstructure - Density/Size of Loops with Dose (Y. Chen et al., NUREG/CR-7128, 2012)



Typical microstructure of un-irradiated solution annealed 304 stainless steel

Irradiated SA 304 SS
Irradiation BOR -60 reactor

Bright Field (BF) images ➔



🡐 Dark Field (DF) images

🡐 loop size distributions

Microstructure of irradiated solution annealed 304 SS

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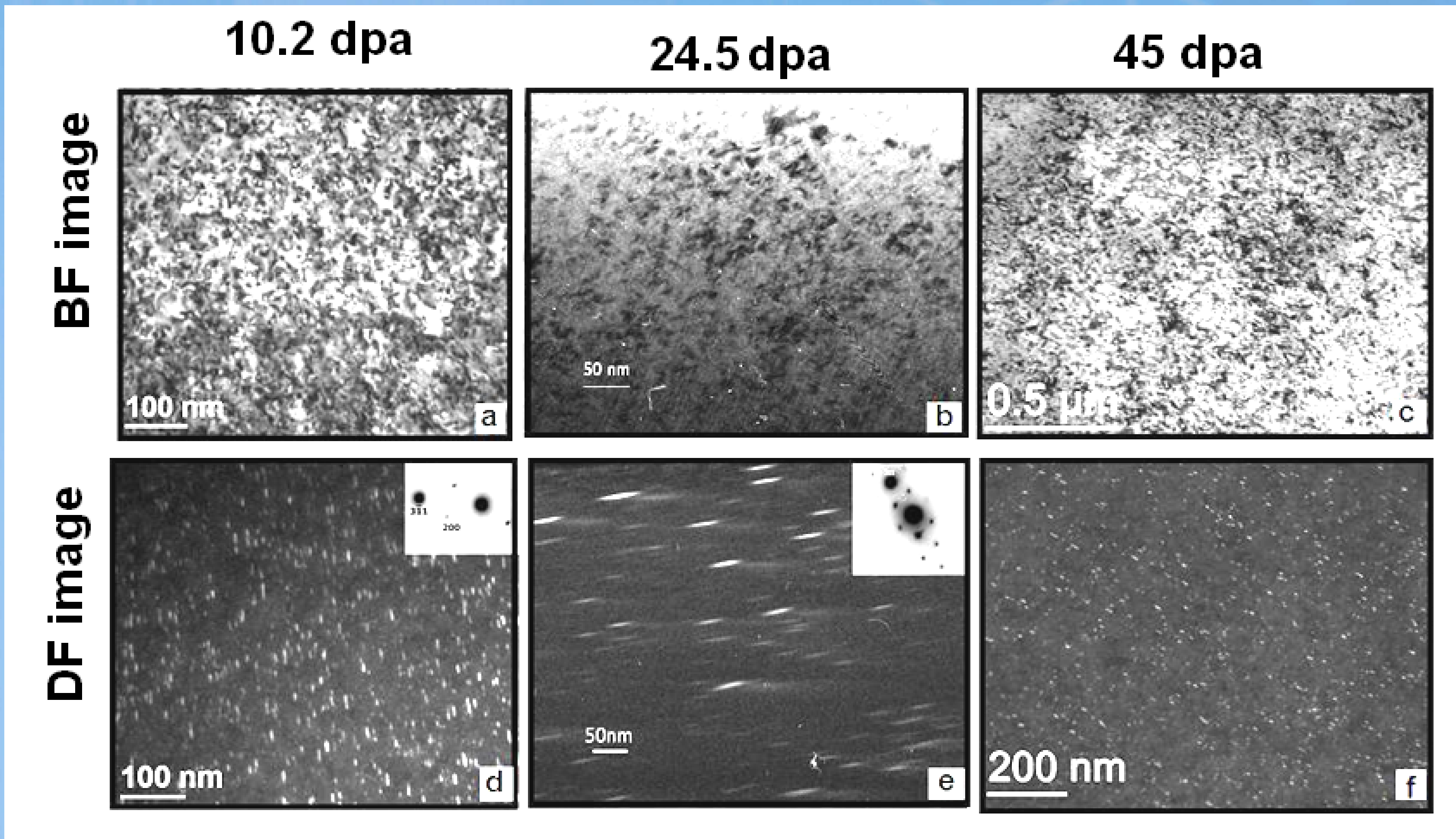
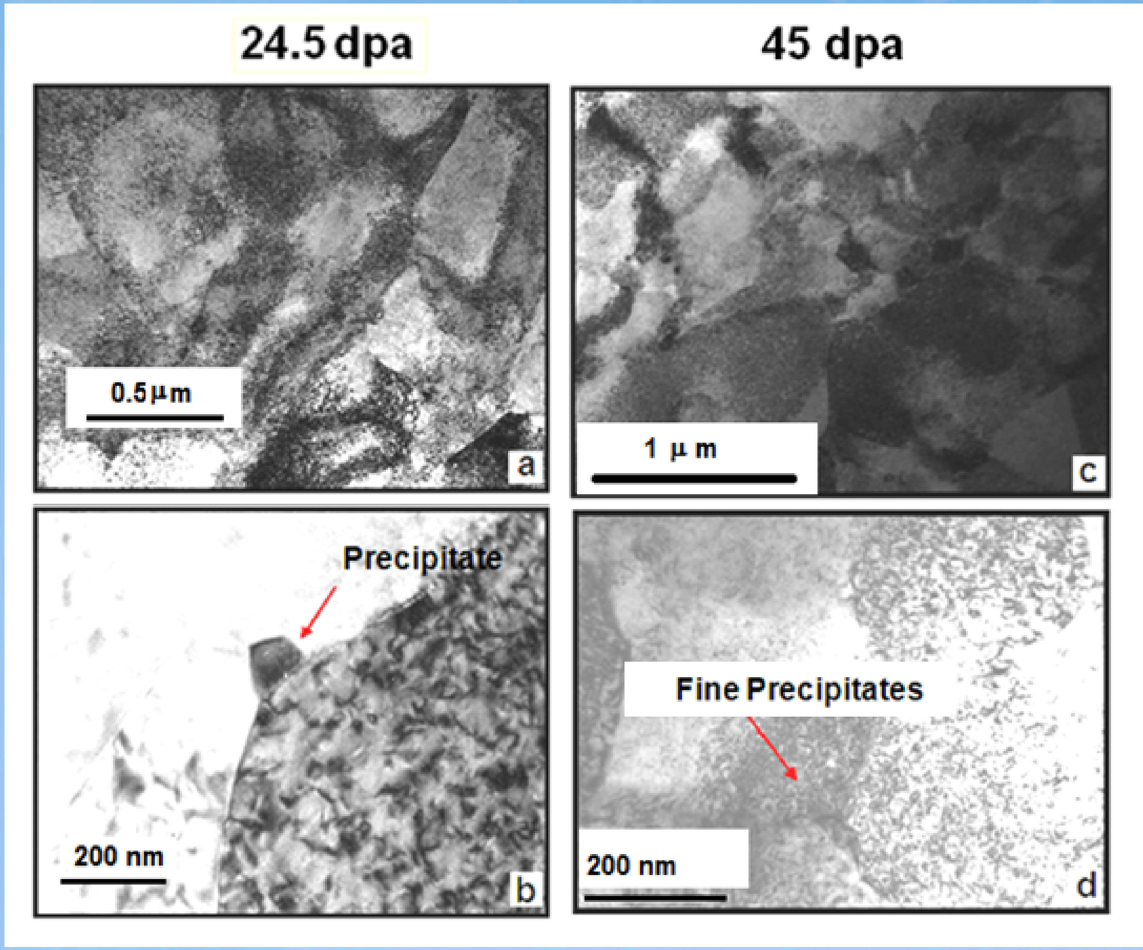
Irradiated SA 304 SS
Irradiation BOR -60 reactor



Microstructure of irradiated solution annealed 304 SS with low sulfur

Irradiated 316 LN SS

Irradiation BOR -60 reactor



Microstructure of 316 LN SS irradiated to doses of (a) 24.5 and (c) 45.0 dpa. (b) and (d) are magnified view of (a) and (c) respectively.

Irradiation BOR -60 reactor

SS	Dose (dpa)	Void	Precipitation	Average loop size (nm)	Loop density ($X10^{22}$ m^{-3})
304 SS-SA	5.5 10.2 24.5 45.0	Not observed Not observed Not observed Not observed	Not observed Not observed Not observed Possible	7.9 8.2 8.1 7.8	3.3 4.2 4.6 6.7
304 SS-SA low S	10.2 24.5 45.0	Not observed Not observed Not observed	Not observed Not observed Possible	8.1 25.5* 7.3	2.7 3.0 5.8
316LN - SA	5.5 10.2 24.5 45.0	Not observed Not observed Not observed Not observed	Not observed Not observed Present Present	8.7 8.8 5.8	3.5 5.8 1.7

Ref: Y, Chen et al., NUREG/CR – 7128(2012)

* may be multiple defects. Measurement was difficult

Quantitative data on the average loop size and loop density and qualitative conclusion on the presence of voids and precipitates in the irradiated stainless steel samples.

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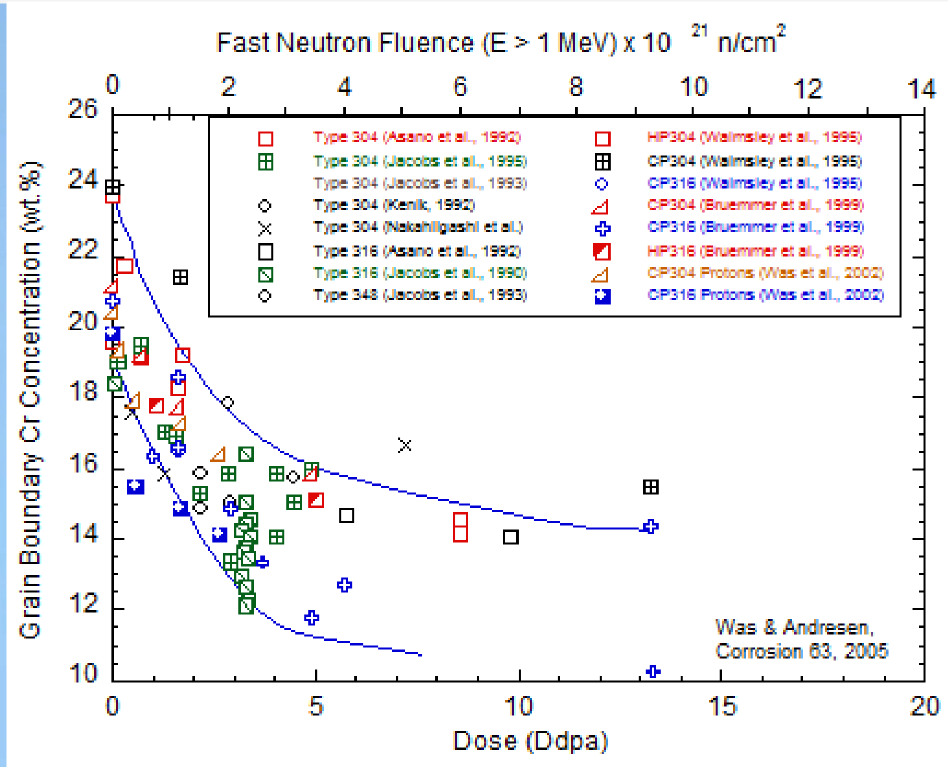
Micro-chemical changes at the grain boundary of Steels due to Neutron Irradiation

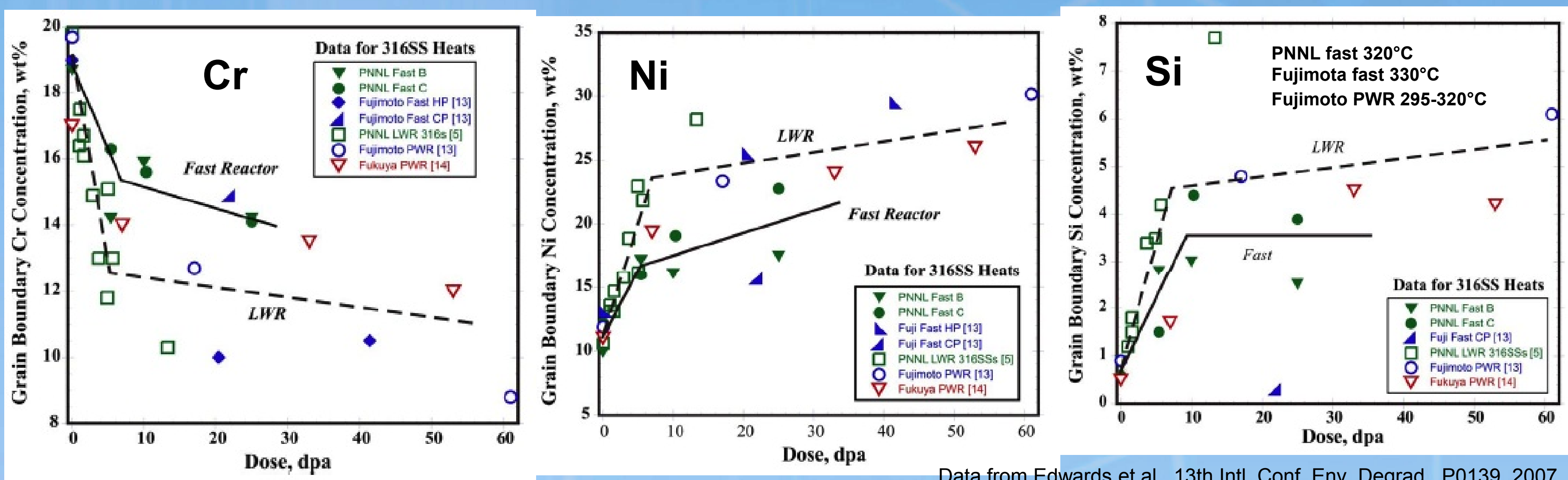
(Ref: O. Chopra and A. S. Rao, NUREG/CR-7027 (2010))

Micro-chemical changes at the grain boundary of Steels versus Neutron Irradiation



- RIS results in GB depletion of Cr, Mn, Mo & enrichment of Ni, Si, P, C, B
- Segregation depends strongly on irradiation temperature, dose, & dose rate
- In LWRs, RIS increases with neutron dose, peaks at intermediate temp, & increases at lower dose rates
- At 300°C, saturates at ≈5 dpa

Dose Dependence of Grain Boundary Cr, Ni & Si Contents for Stainless Steels Irradiated in LWRs & Fast Reactors



Data from Edwards et al., 13th Intl. Conf. Env. Degrad., P0139, 2007

- **RIS results in GB depletion of Cr and the enrichment of Ni, Si. (also P, C, B – not shown here)**
- **Stronger RIS in LWRs than BOR-60 (except Fujimoto HP), particularly above 5 dpa**
- **Irradiation temperature comparable, differences most likely due to dose rate**
- **Edwards et al. conclude, BOR60-produced GB compositions provide reasonable representation of LWR-irradiated SSs; however, PWR-irradiated SSs contain cavities that may effect fracture properties**
- **Fujimoto et al. conclude from SSRT data, IASCC susceptibility of FBR-irradiated SSs is significantly lower than PWR irradiated SSs - <5%IGSCC vs 50-100%IGSCC**
- **Data suggest FBR irradiations may not be prototypical of LWRs, particularly >5 dpa**

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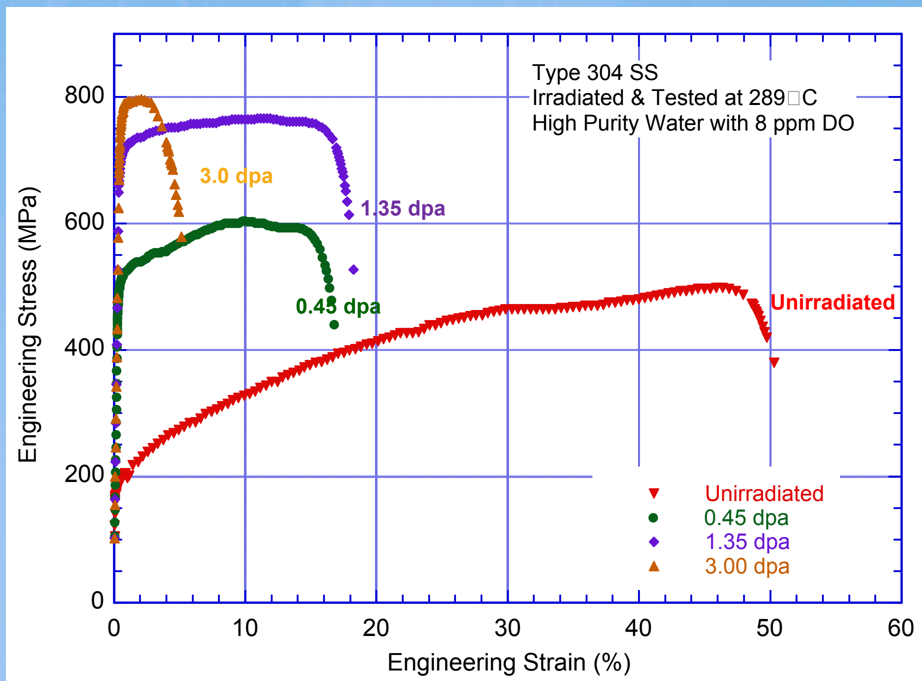
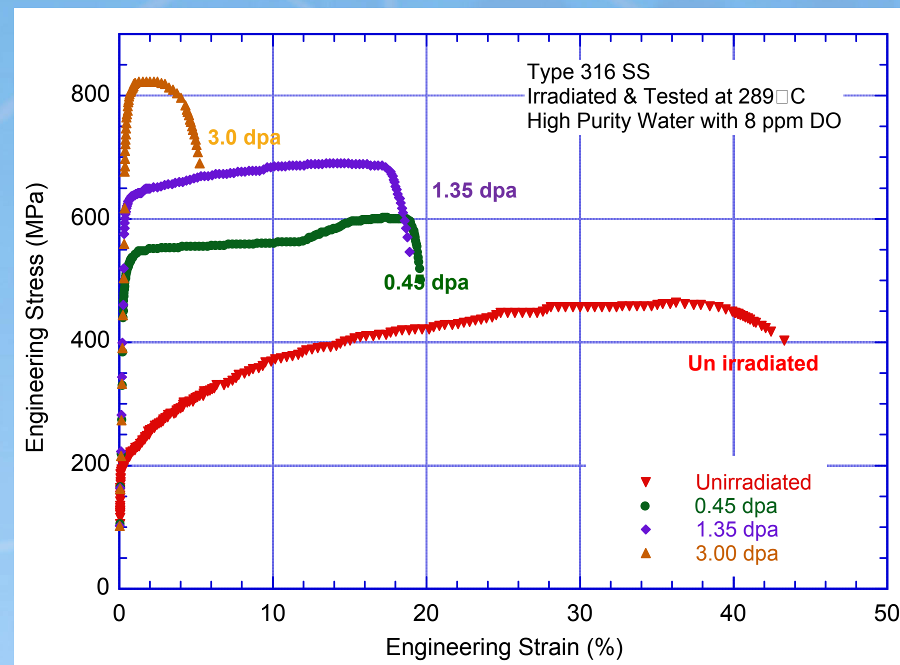
Irradiation Hardening



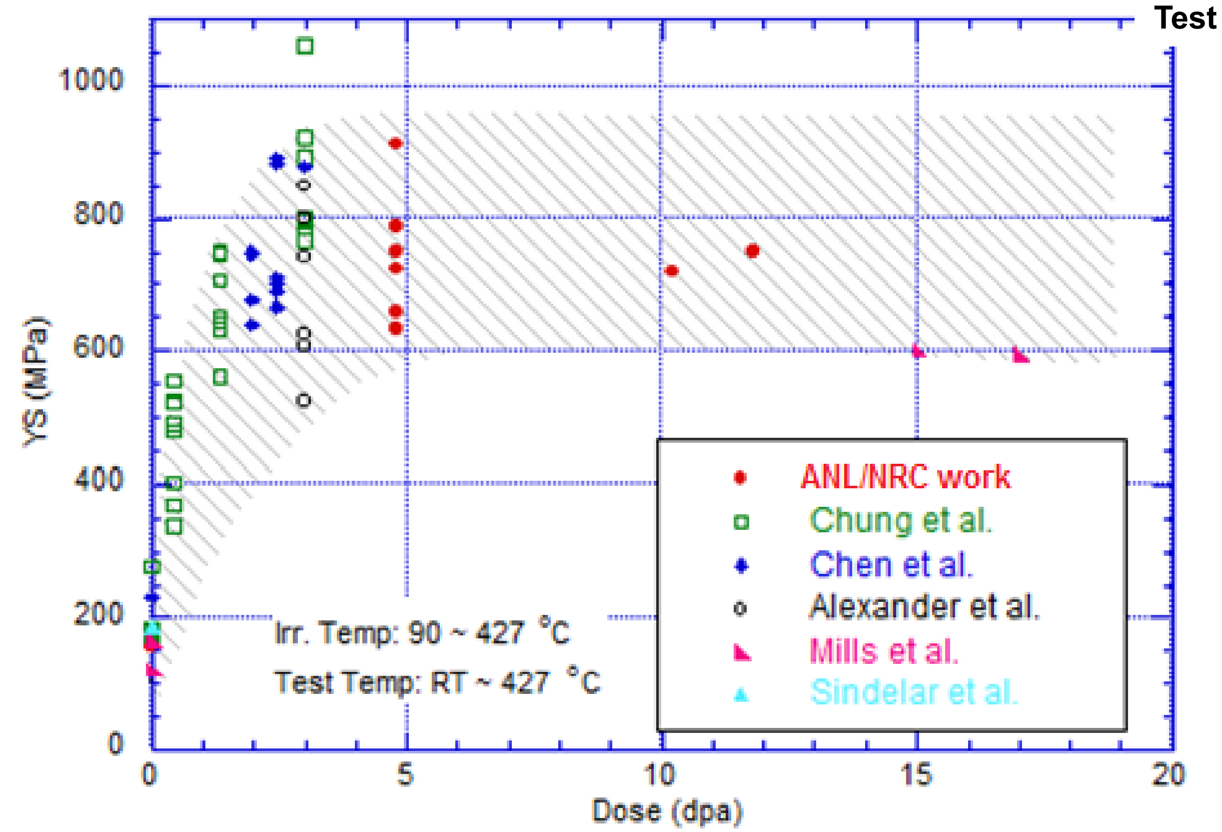


Ref: Y, Chen et al., NUREG/CR – 7128(2012)

- **Defect structure & precipitates act as obstacles to dislocation motion that lead to matrix strengthening - increase in yield strength & decrease in ductility**
- **In general, cavities (voids) are strong barriers, large faulted dislocation loops are intermediate barriers, & small loops & bubbles are weak barriers**

Effect of Irradiation Dose on Tensile Yield Strength

Irradiation temperature 100-427°C
Test temperature 125-427°C



- Yield strength can increase up to five times by 3 to 5 dpa
- Increase in yield strength follows a square root dependence on dose
- Yield strength of solution annealed SSs saturates between 3 & 5 dpa
- At higher dose(>5 dpa), drastic change in deformation mode - dislocation channeling

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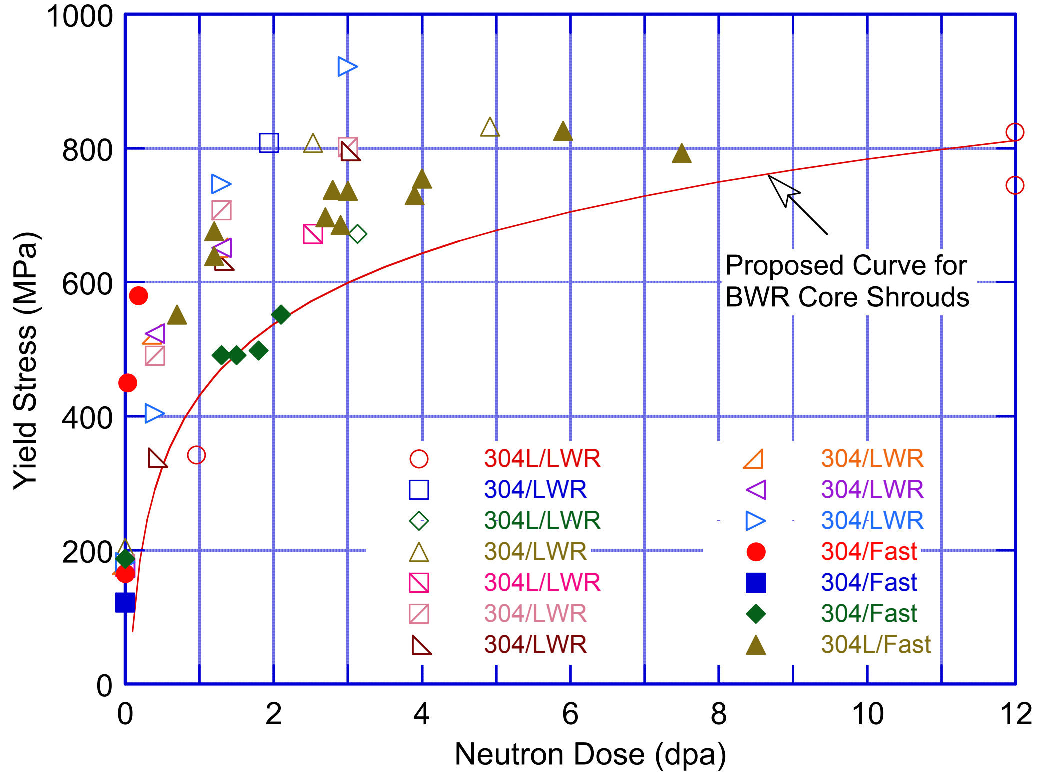
Increase in Yield Stress - Type 304 SS

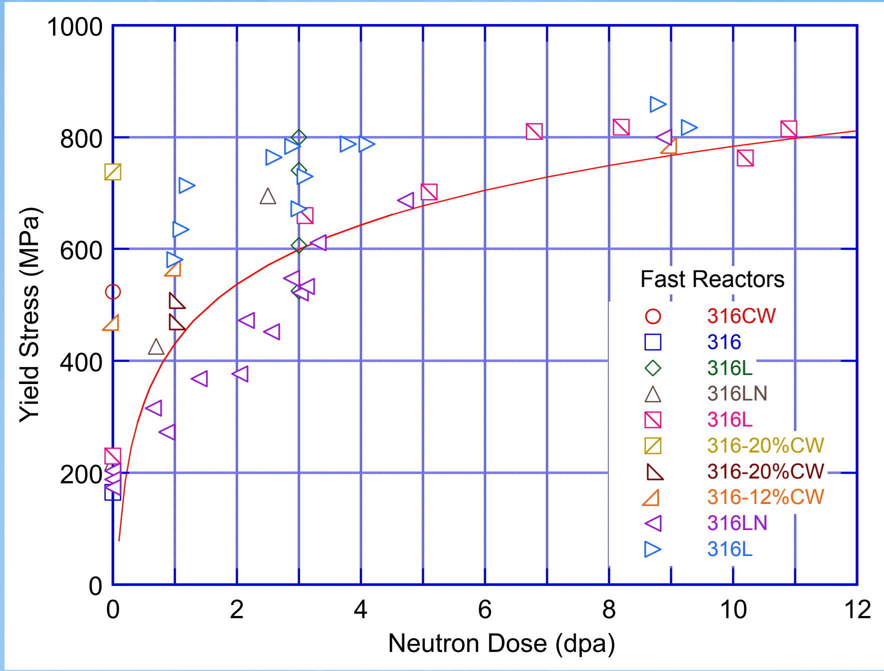


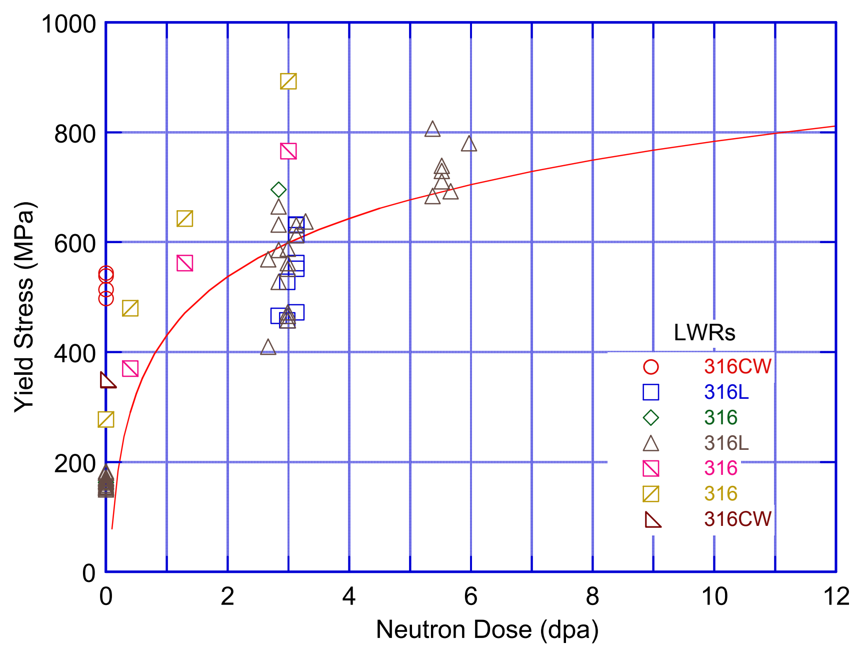
Irradiation temperature 100-427°C test temperature 125-427°C

- **YS of solution annealed SS increases from 150-200 to ≈800 MPa at 3-5 dpa**
- **Yield stress of SA SSs saturates between 3 & 5 dpa; nearly all SSs show strain softening at higher dose & little or no uniform elongation**
- **Proposed curve for BWR core shrouds represent lower bound of the data for Types 304 & 304L SS & their welds**

Increase in Yield Stress - Type 316 SS

Irradiation temperature 90-427°C, test temperature 100-427°C





- YS of SA SS increases from 180-250 to ≈800 MPa at 3-5 dpa
- YS of cold worked SS increases from 500-700 to ≈1000 MPa at 3-5 dpa
- Both Fast reactor and LWR irradiation results on the YS of materials is the same
- SSs irradiated >3 dpa show strain softening & little or no uniform elongation

SLOW STRAIN RATE TENSILE TESTING (SSRT)

Ref: Y, Chen et al., NUREG/CR – 7018(2010) and 6965 (2008)

Tests performed in PWR water

Material Type	Material	Dose (dpa)		
		5	10	48
304, 304L	304 CW	-	-	√
	304L SA	-	√	-
	304L CW	-	√	√
	HP 304L [1] SA, High O	-	√	√
	HP 304L [1] SA, Low O	-	√	√
316, 316L	316LN [2] SA	√	√	-
	316LN-Ti [2] SA	-	-	√
	316 SA	-	-	√
	316 CW	√	√	√

[1] High purity 304L stainless steel with high (0.047 wt.%) and low oxygen (0.008 wt.%) content

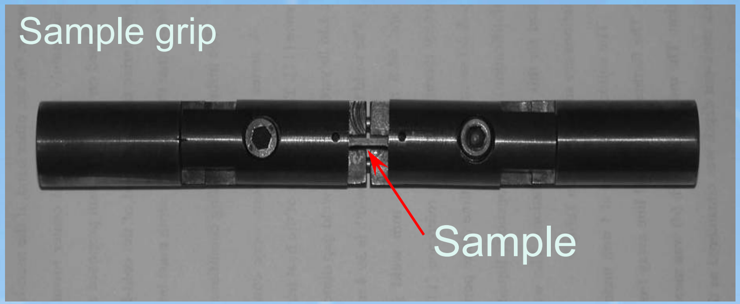
[2] Low carbon, nitrogen 316 stainless steels with and w/o Ti addition (N≈0.06-0.1 wt.%, Ti≈0.027 wt.%)

SA – Solution Annealed, CW – Cold Worked

Irradiation and SSRT Tests

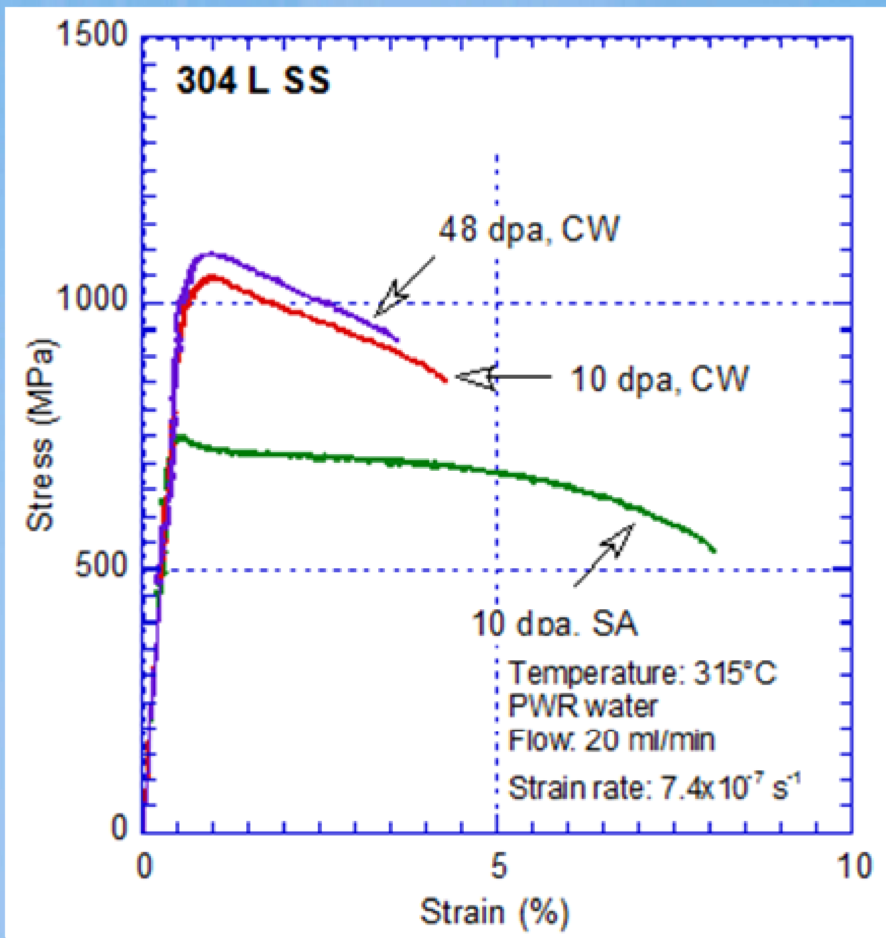
- **Irradiated in BOR-60 (a fast flux reactor)**
  - **Irradiation temperature ~ 320°C**
  - **Damage rate ~ 10^{-6} dpa/s (<10^{-7} dpa/s in Halden)**
  - **Three doses: 5, 10, 48 dpa**
- **SSRT strain rate: *7.4×10^{-7} s^{-1}***
- **Test Conditions:**
  - **In *PWR* water *DO* < 10 ppb**

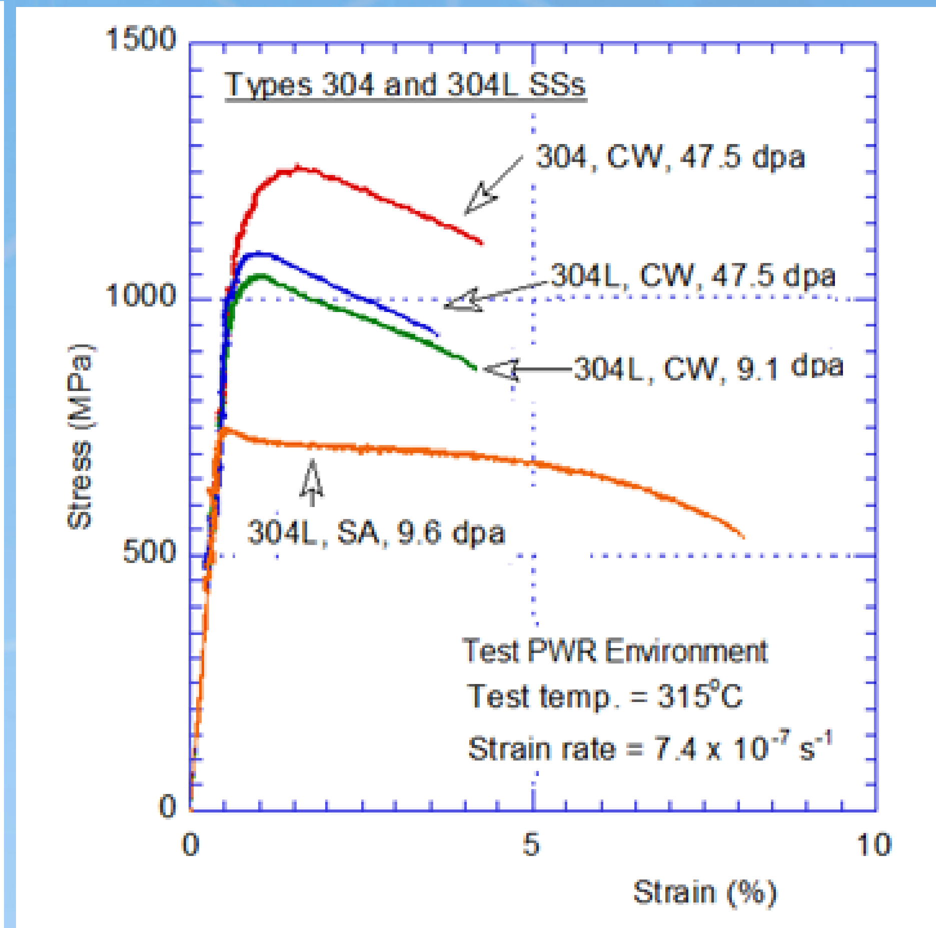
    ***Temperature:* ≈ 315°C**
    ***Pressure:* 1800 psig**
    ***Conductivity:* 20 mS/cm**
    ***pH:* 6.6 *ECP:* - 650 mV (ss)**
    - 700 mV (Pt)
    ***Flow rate:* 25 ml /min**



A fractured sample

Type 304 and 304L SSs
Irradiation BOR -60 reactor





- CW samples exhibit much higher yield stress and less elongation.

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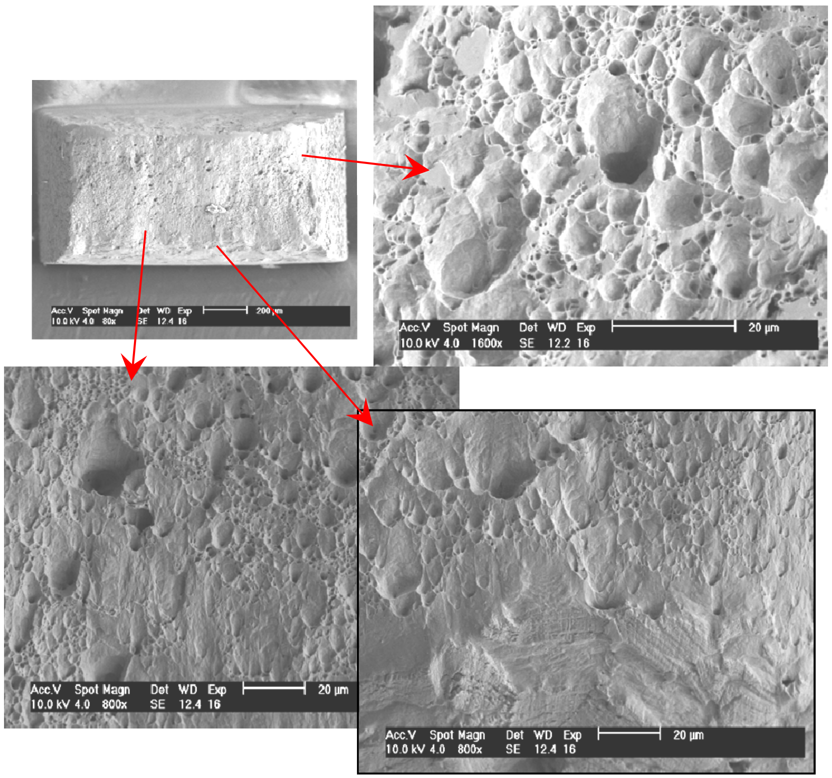
Microstructure of SA and CW Type 304L SS

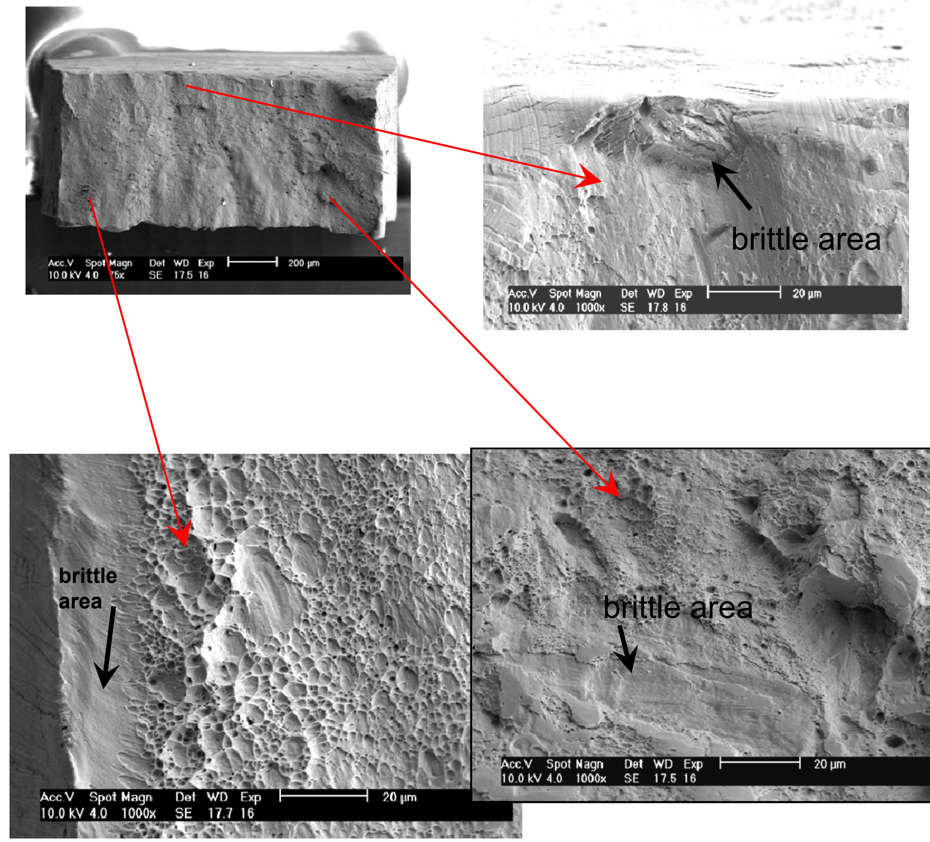
304L SA, 10 dpa

Large dimples



304L CW, 10 dpa

Small dimples with some brittle areas

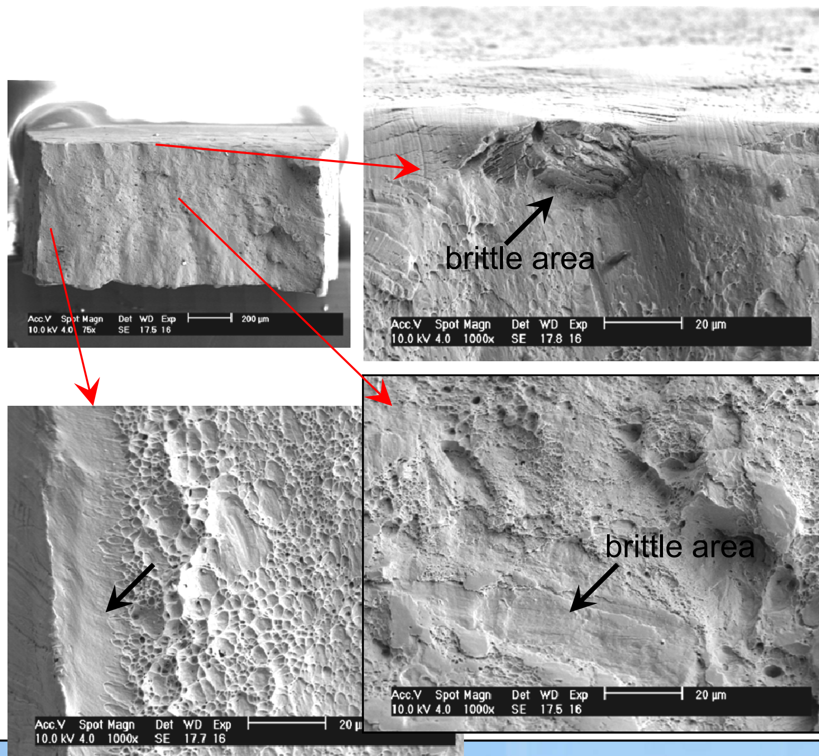


- **SA samples possess fully ductile features while brittle features can be seen in CW samples.**

Microstructure of irradiated Type 304L CW SS

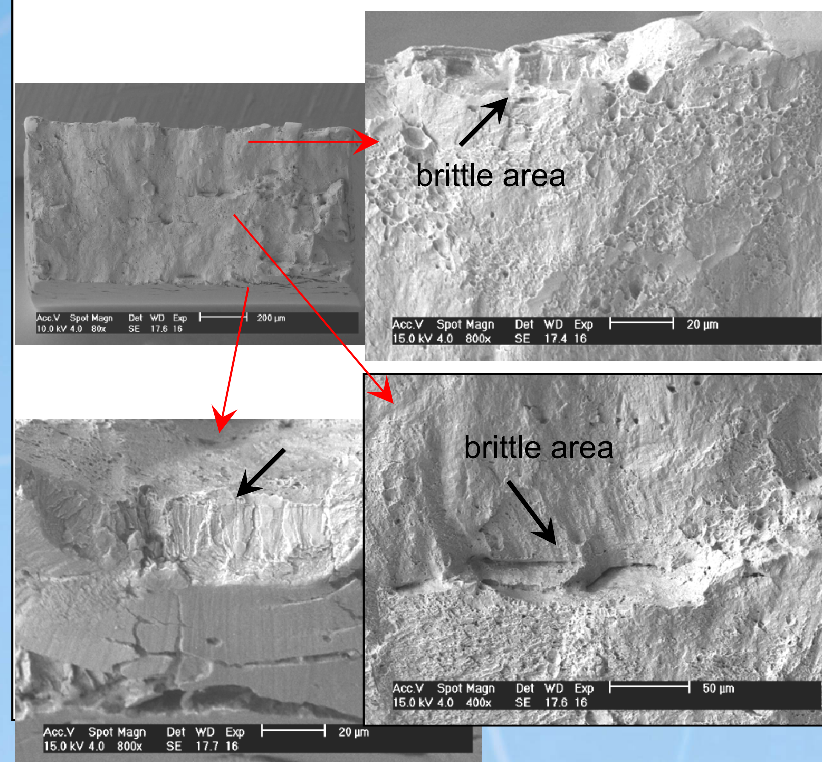
10-dpa

Small dimples with some brittle areas



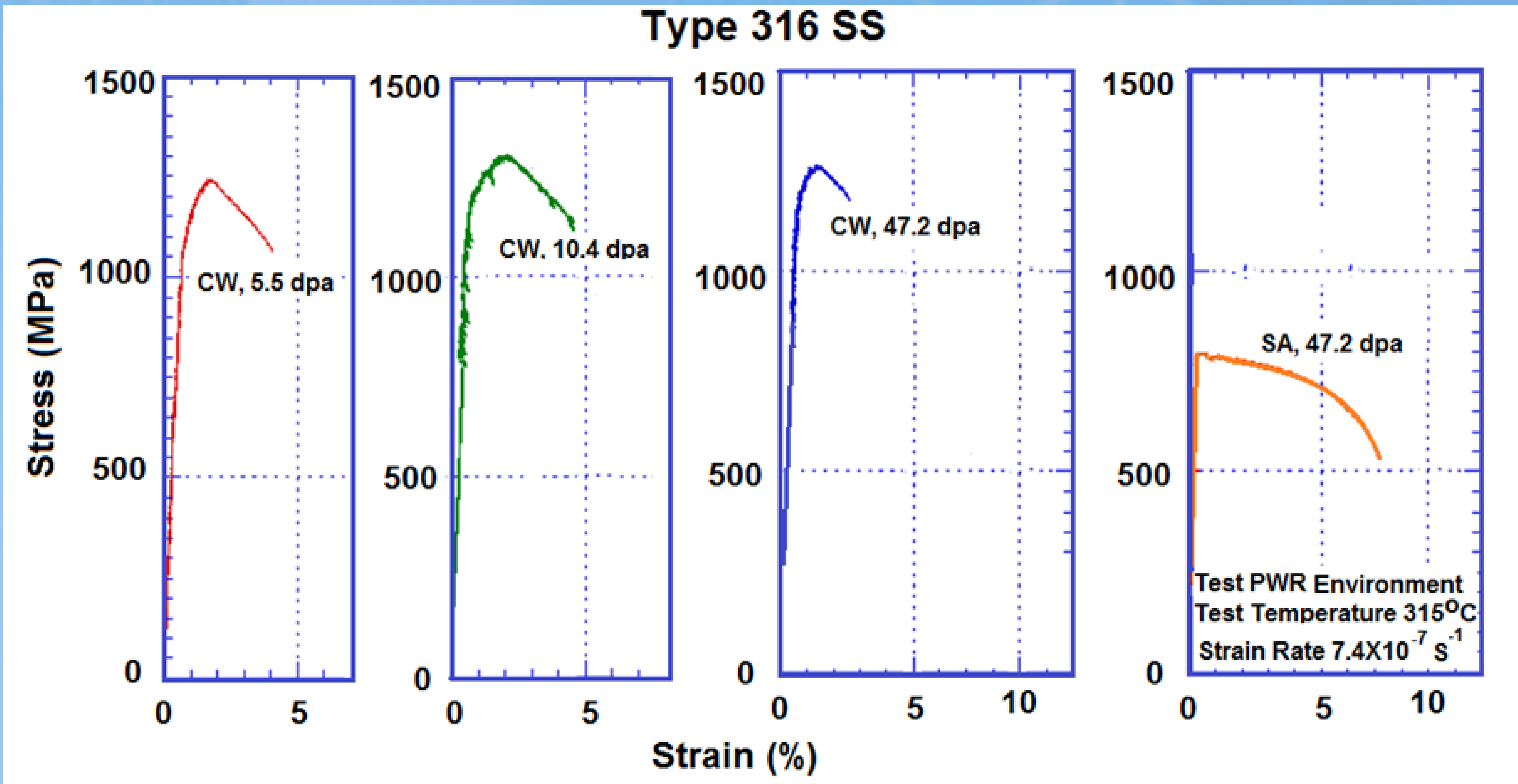
48-dpa

More brittle areas in higher dose sample and cleavage on sample surface.



Type 316 SS – Effect of Dose

Irradiation BOR -60 reactor



- Yield stress is higher and elongation is lower for CW SS than that of SA SS at 48 dpa.
- For CW SS, yield stress ($\sigma_{0.2}$) increases with dose from 5 to 10 dpa, and saturates above 10 dpa.

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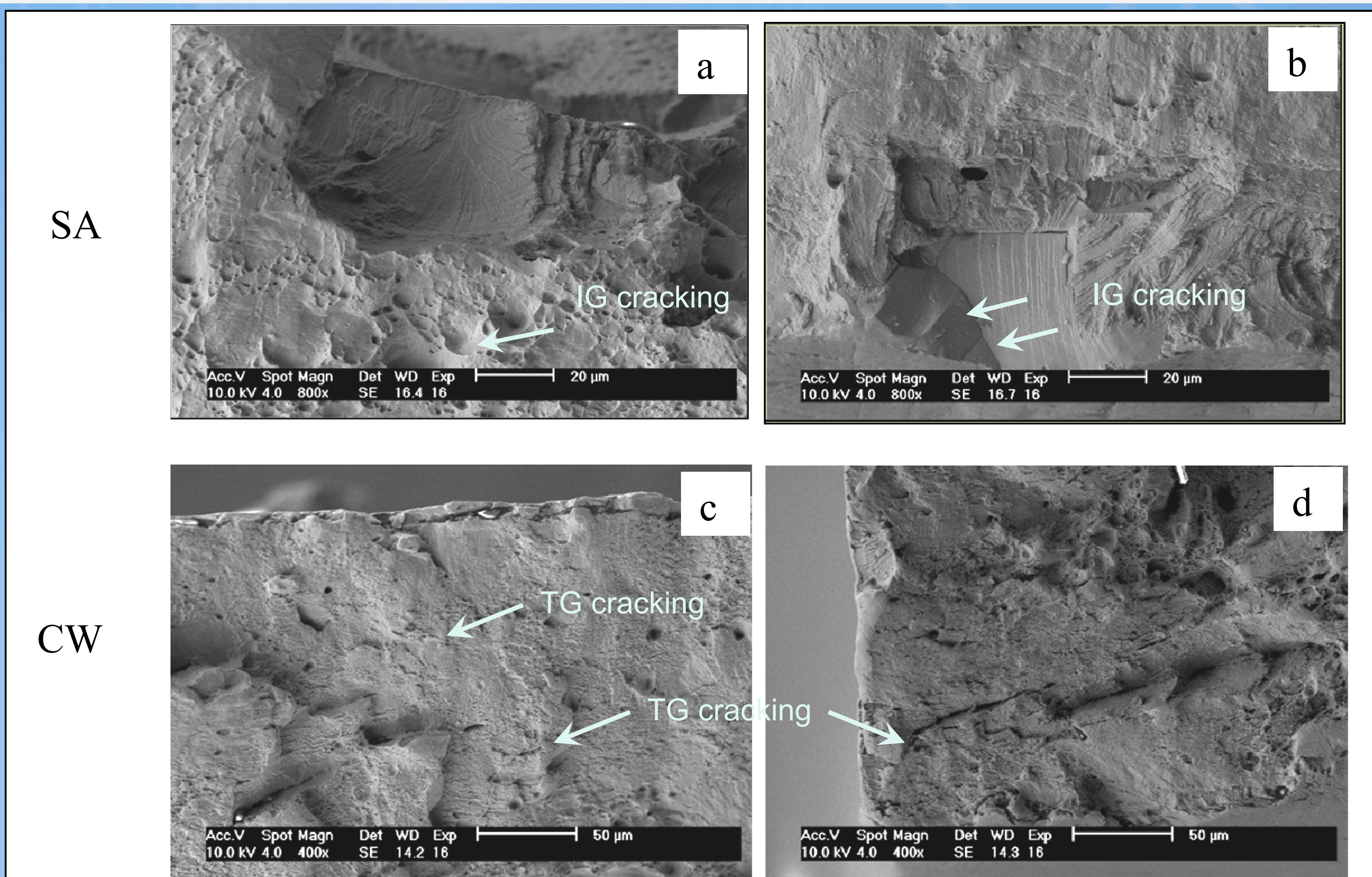
Type 316 SS
Irradiated to 47 dpa



- **Some IG features in SA samples, only TG cracking in CW samples.**
- **Despite a much lower elongation, the failure surface of the CW sample does not appear more susceptible to cracking than the SA sample at 48 dpa.**

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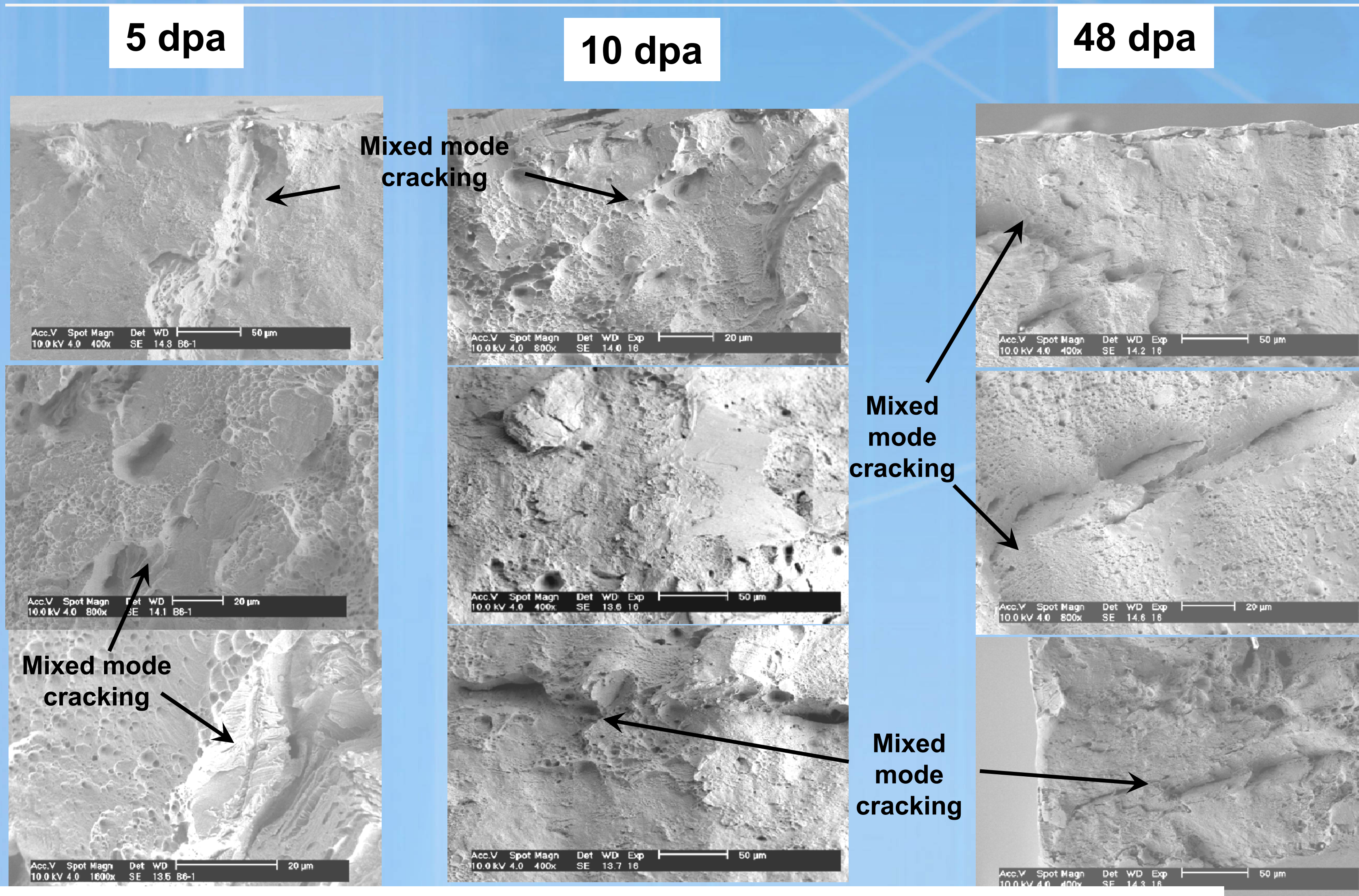
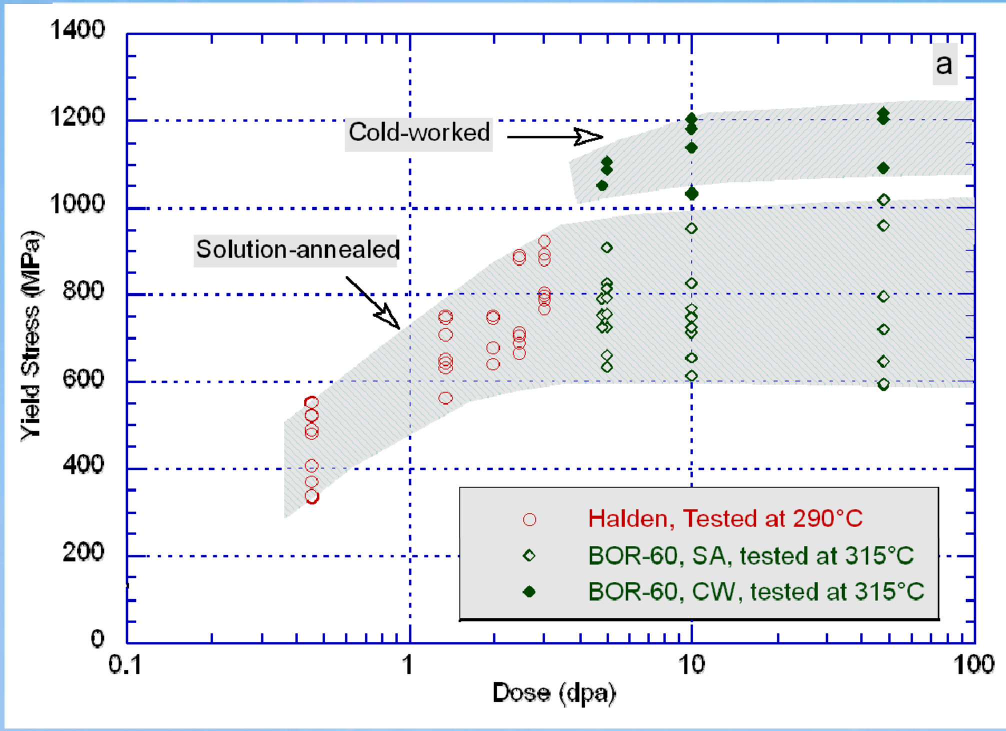
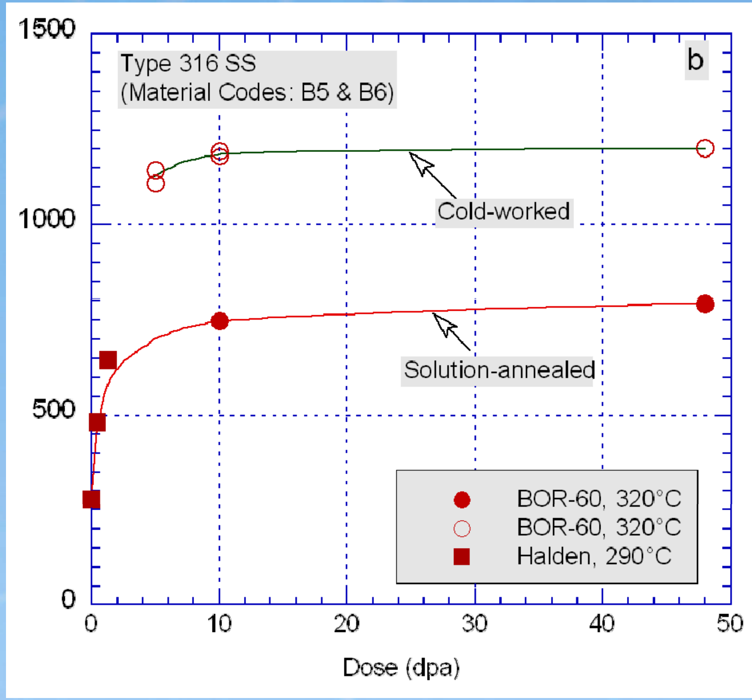
Type 316 SS – CW, 5, 10 and 48 dpa



- Dimple fracture with small mixed-mode cracking areas at all dose levels.

Yield Stress - Dose effects SA versus CW

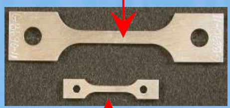




- The increase of yield stress by CW is not affected by irradiation beyond 10 dpa.
- The yield stress differences between SA and CW materials are consistent between 10 to 48 dpa.
- The yield stress seems saturate at 5-10 dpa.

Loss of ductility - Dose effects SA versus CW

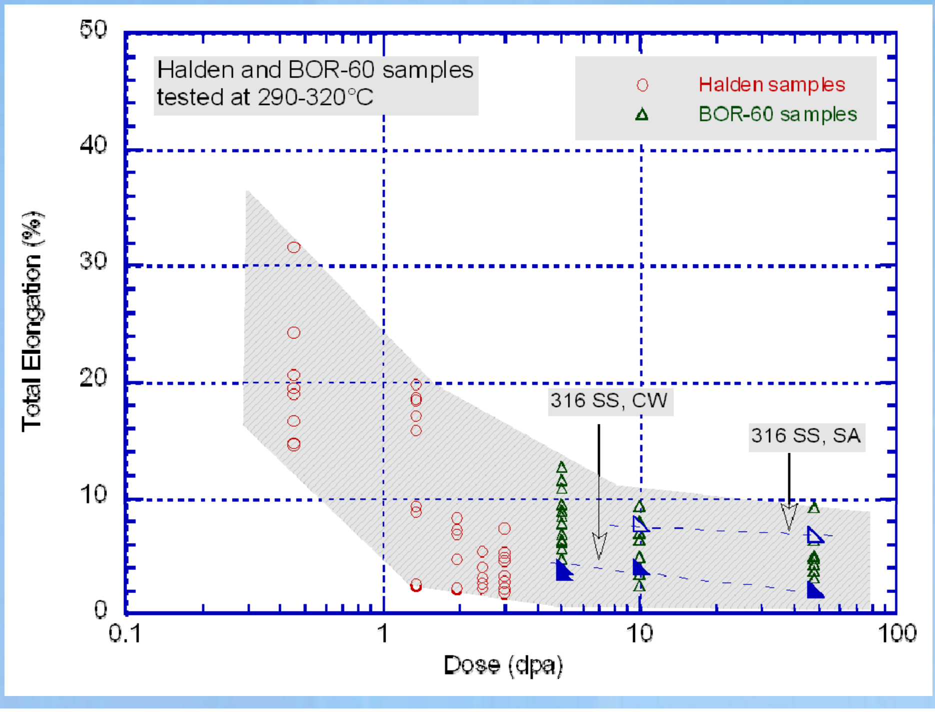
Halden



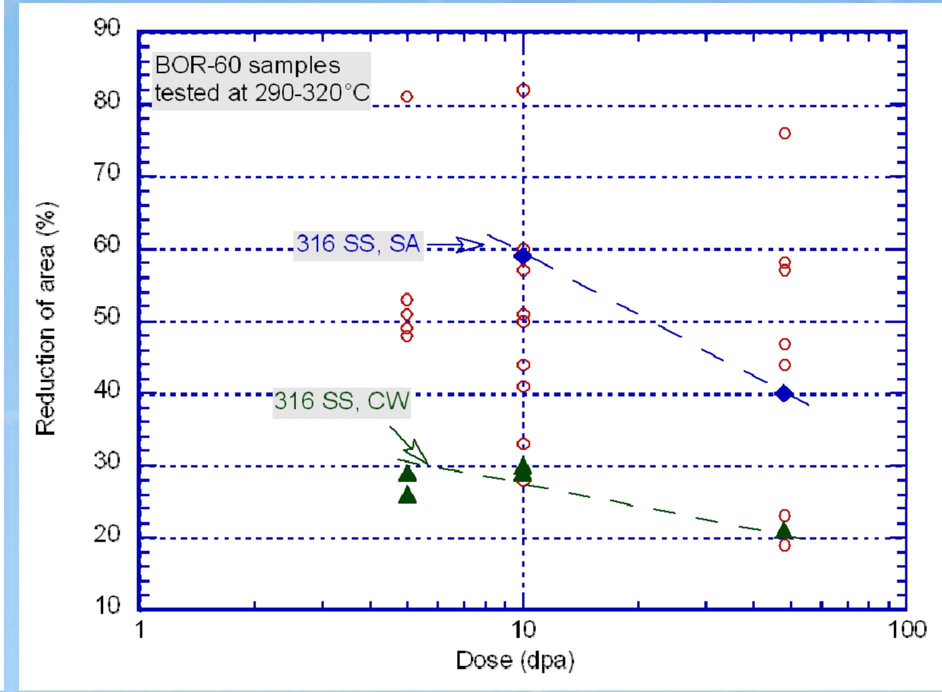
BOR60

Test in Environment

Total elongation

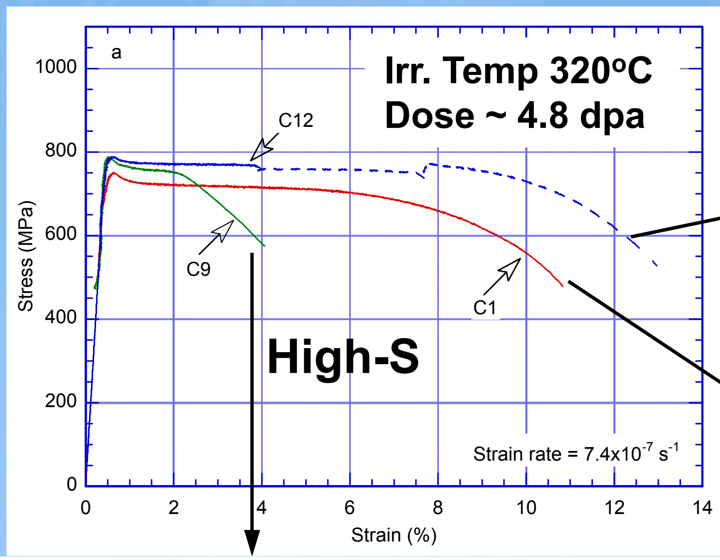


Reduction of area

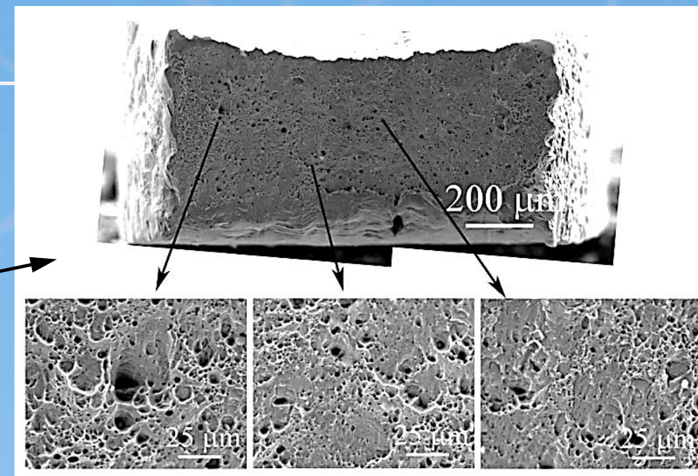


- **Total elongation and reduction of area decreases with increasing dose up to 48 dpa.**

SSRT Tests - Effect of S Content

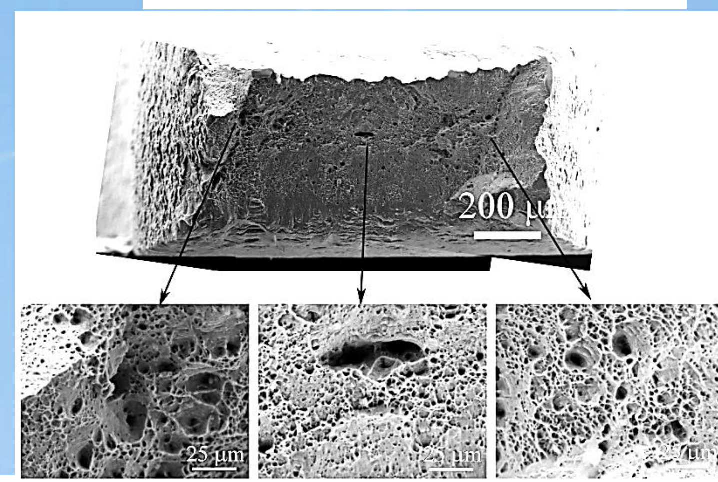


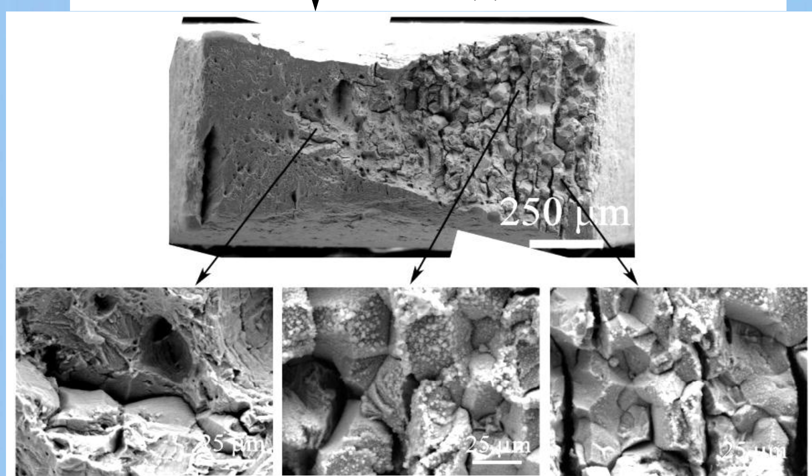
Low-S



Low-S (0.003%)

Low-S





High-S (0.016%)

- IG cracking is severe in the high-S Type 304 SS, but no IG fracture in the low-S Type 304 SS

HP Type 304L SS SA with high - O (0.008%) and low-O (0.0047%)

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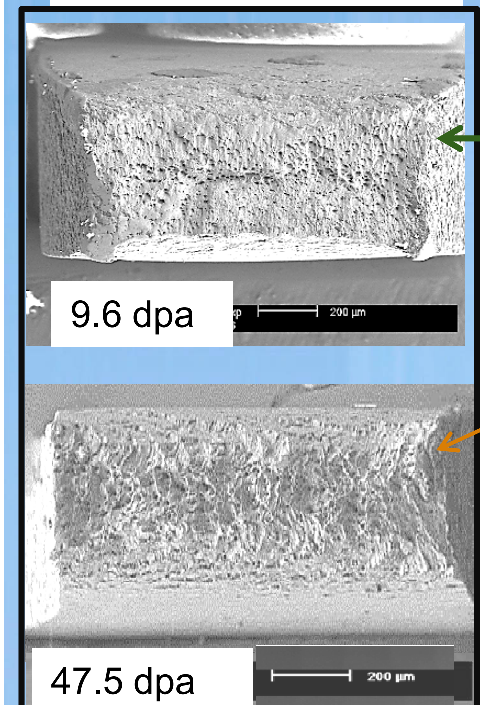
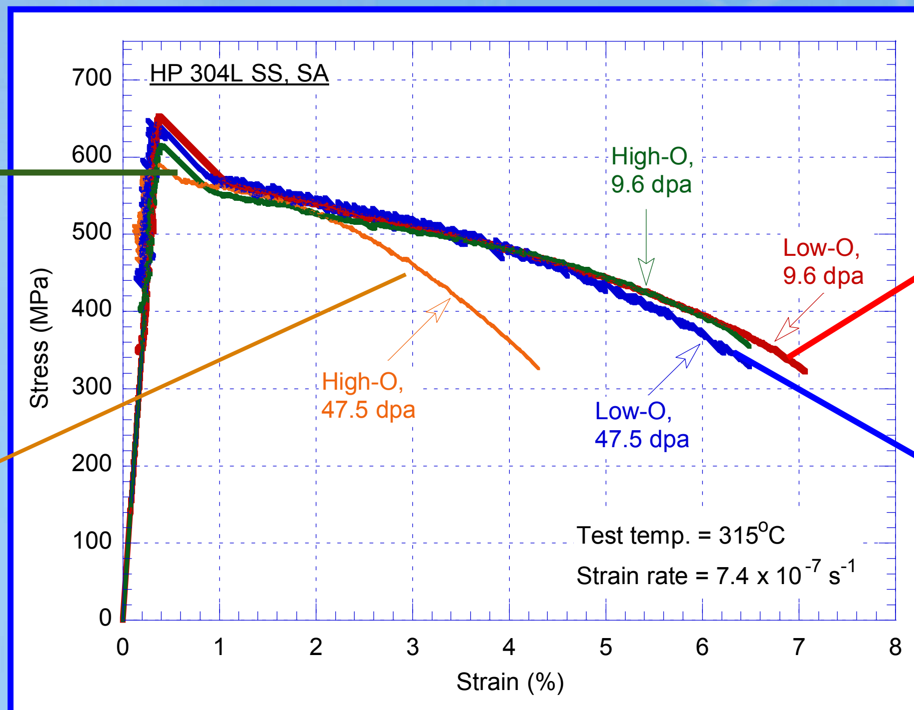
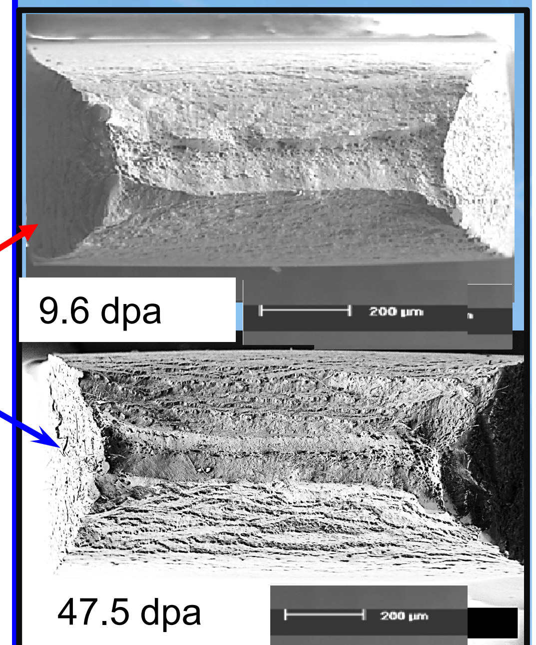
Test DO Environment

High-O, RA ~ 60%





Low-O, RA ~ 80%



- **A load drop beyond yield is observed for all HP 304L samples, regardless of their O content.**
- **The low-O specimens are more ductile than the high-O specimens.**
- **No IG cracking was observed in low-O specimens .**

RA - reduction of area

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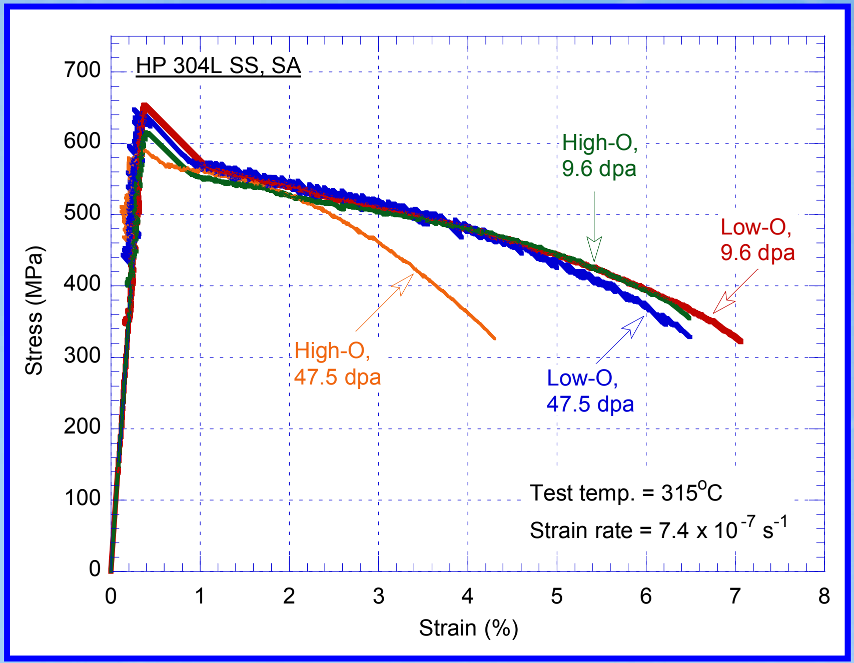

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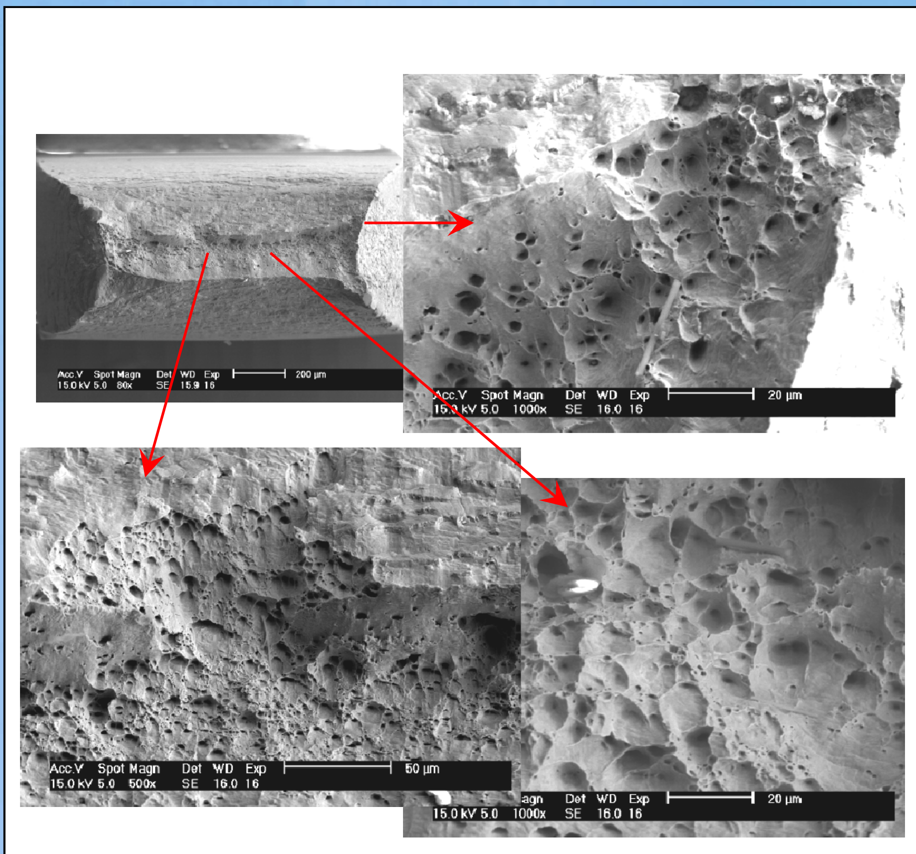
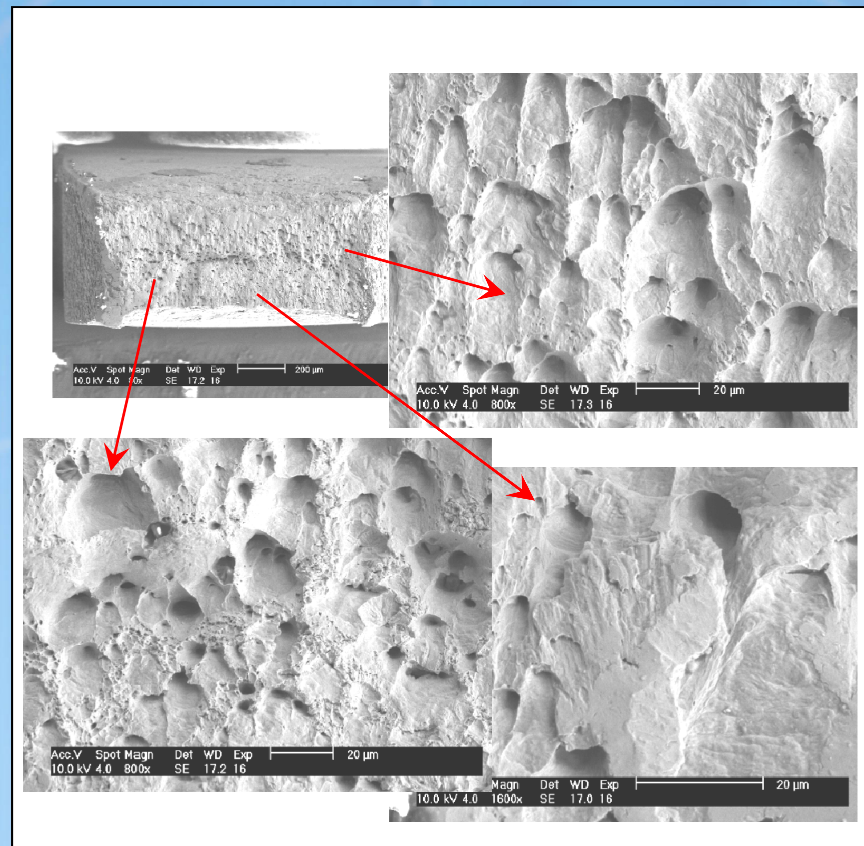
HP 304L SS – 10 dpa, low-O vs. high-O

Low-O 10 dpa,
RA=82%, dimples



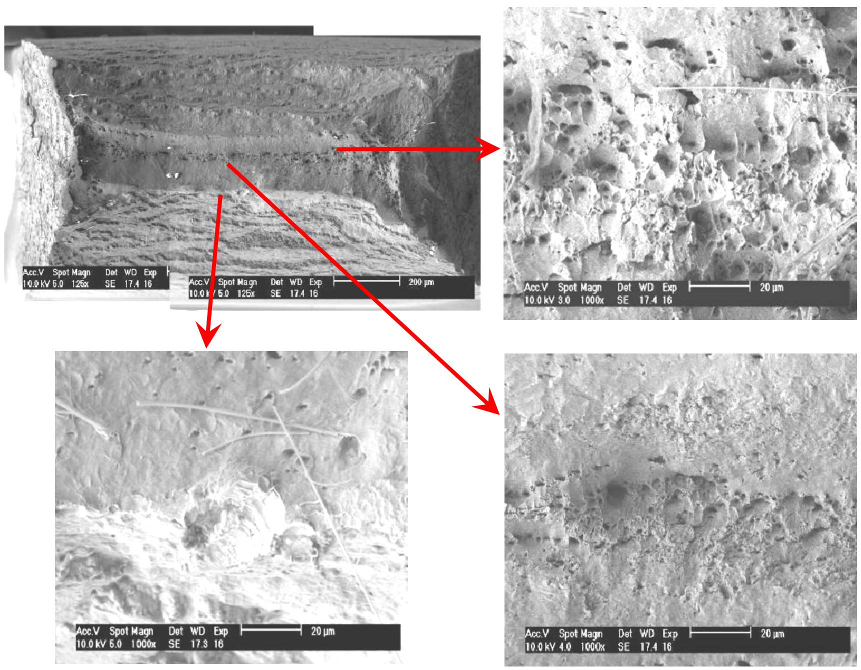
High-O 10 dpa,
RA=60%, dimples



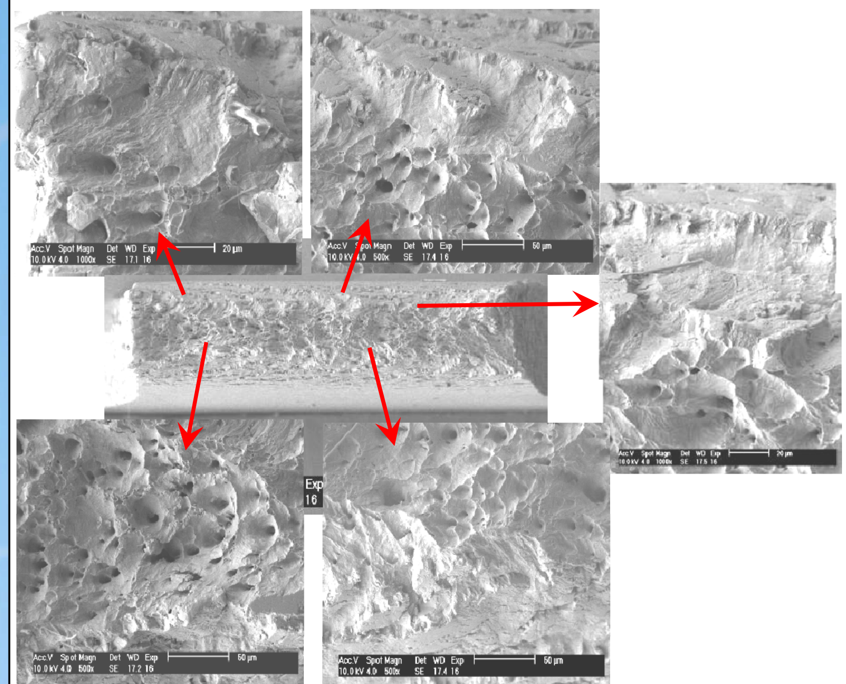
RA - reduction of area

HP 304L SS – 48 dpa, low-O vs. high-O

RA≈76%, dimples   48 dpa, <u>Low-O</u>



RA≈58%, dimples   48 dpa, <u>High-O</u>



- **Fracture morphology was unchanged with increasing dose from 10 to 48 dpa. Dimples remain the dominant features on failure surface.**
- **Reduction of area (RA) was similar to that of 10-dpa, ~60% for high-O, and ~80% for low-O specimens.**

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Crack Growth Rate (CGR) Testing

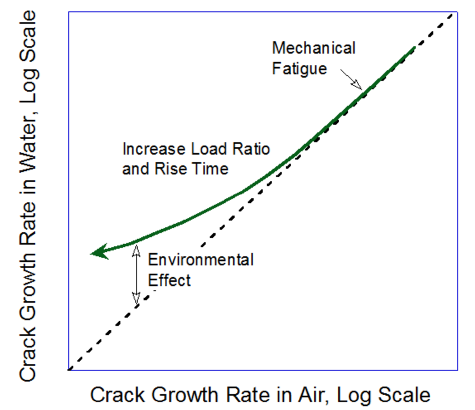
Crack Growth Rate (CGR) Tests

- **Fatigue cyclic loading with triangle waveform at 1-2 Hz and load ratio 0.2-0.3 are used to obtained a *sharp* crack.**
- **Cyclic loading with saw tooth waveform of increasing load ratio and rise time.**

– **The obtained CGR is compared with CGR in air to evaluate environmental enhancement for each step.**

– **If the observed CGR is higher than CGR in air, then we continue to increase the *rise time, load ratio (R)* up to 1000 s rise time and R=0.5-0.7. Load ratio ® = (Minimum load/Maximum load)**

– **If the observed CGR fall back to CGR in air, we *repeat* the cyclic loading steps until we observe the environmental enhancement again.**

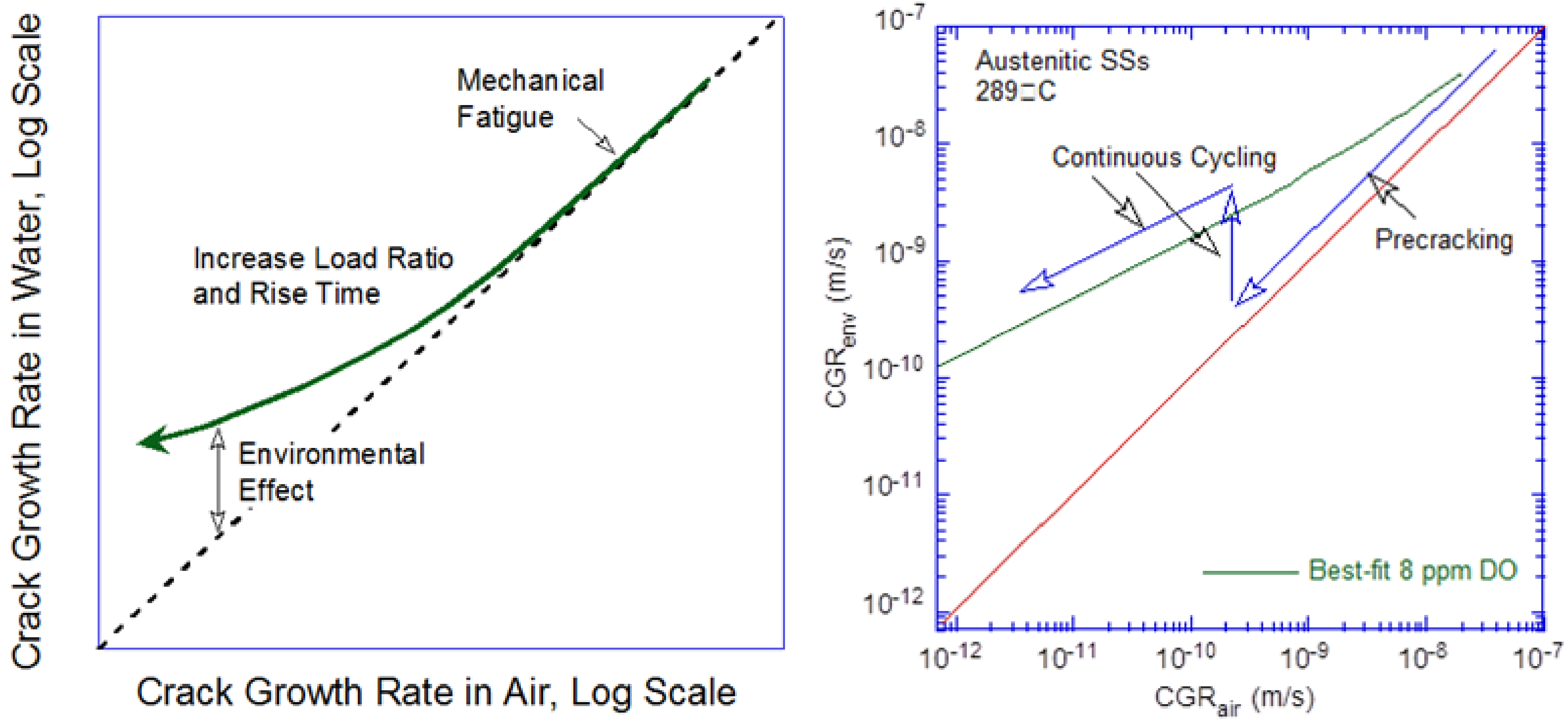


- **Set the test in a constant load *with* or *without* periodic partial unloading (PPU)**

– **Eg. CASS is known to be difficult to crack, especially in low-corrosion-potential environments. Therefore PPU is applied for CASS sample testing.**

– **PPU is done every 1 to 2 hours depending upon the situation (whether crack is initiated or not).**

Effect of Environment on Crack Growth Rate



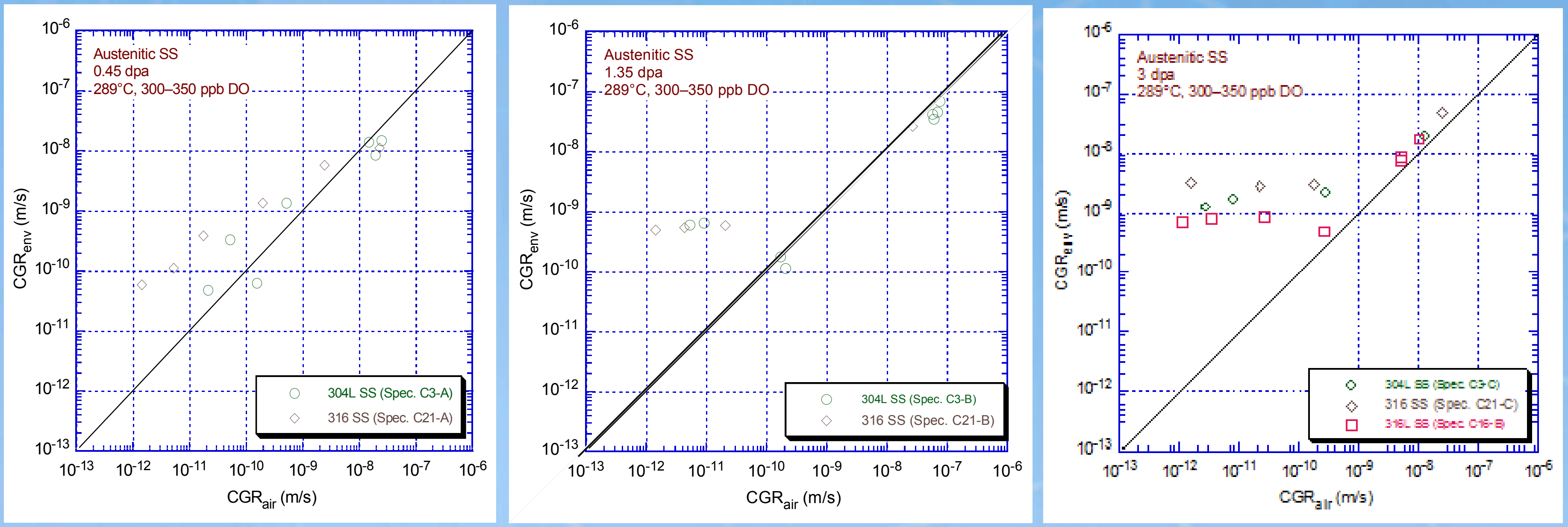
Schematic diagram for EAC in test environment

- **Under more rapid cycling loading condition ➔ pre-cracking occurs &**
  crack growth will be dominated by mechanical fatigue

Note: ➢ **For stress intensity K_{max} 15-18 MPa $m^{1/2}$**
- **environmental enhancement typically occurs at R ≥ 0.5 & rise time ≥ 30 s;**
- **fracture morphology changes from transgranular (TG) to intergranular(IG)**

Note: ➢ **To transition TG fatigue crack to IG SCC fracture**
- **Change ➔ rise time from 30 ➔1000 seconds & loading conditions (R) to R = 0.5 ➔ 0.7.**

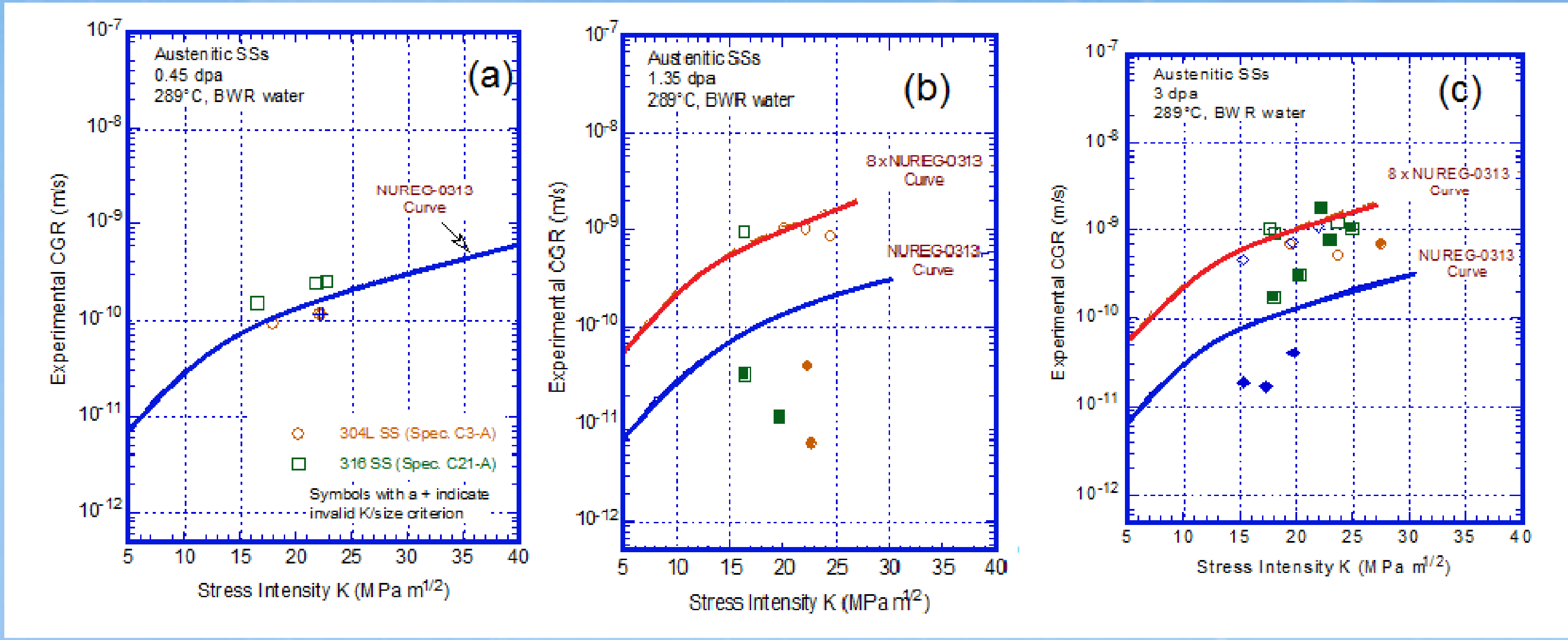
Cyclic CGR on austenitic stainless steels in 300-335 ppb DO environment



Cyclic CGRs for austenitic SSs irradiated to (a) 0.45 dpa, (b) 1.35 dpa, and (c) 3 dpa.

- ➔ **At 0.45 dpa no environmental enhancement was detected for Type 304L SS.**
- ➔ **Moderate enhancement was observed for Type 316 SS (specimen C21-A).**
- ➔ **With increasing dose, environmentally enhanced cracking also increases.**
- ➔ **The difference in cyclic CGRs for different austenitic SSs tend to decrease.**
  - **At 1.35 and 3 dpa the cyclic CGRs for Type 304L and 316 SS are nearly identical.**
- ➔ **The low-carbon Type 316 SS (specimen C16-B) showed slightly lower cyclic CGRs than the normal-carbon-content Type 316 SS (specimen C21-C) at 3 dpa**

Dose dependence of constant load CGR for austenitic stainless steels in BWR (NWC) environment



Constant-load CGRs versus stress intensity for austenitic SSs irradiated to (a) 0.45 dpa, (b) 1.35 dpa, and (c) 3 dpa.

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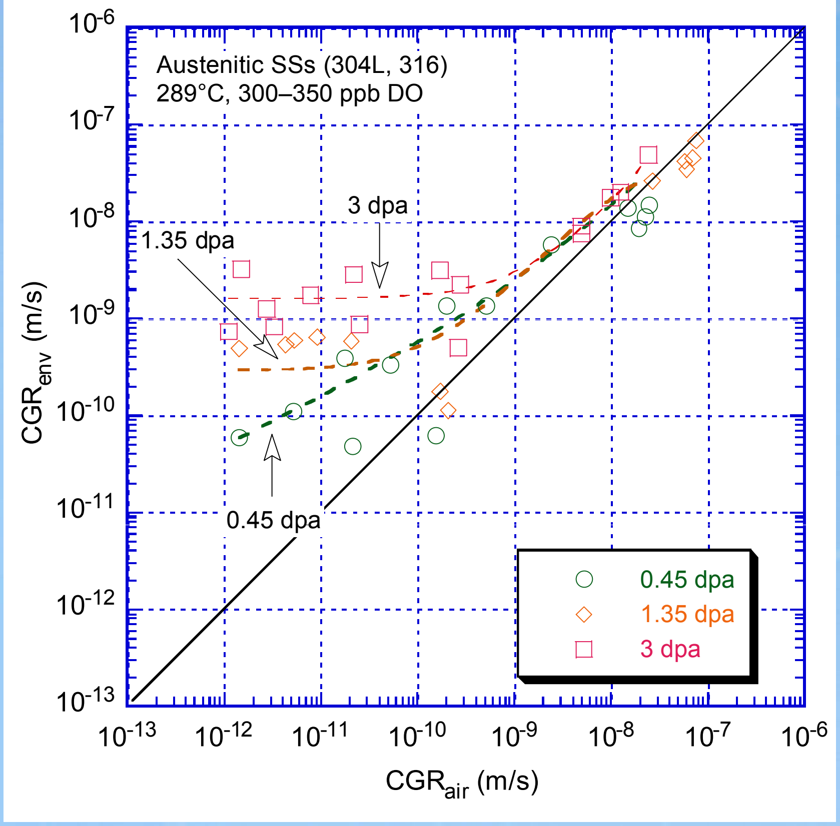
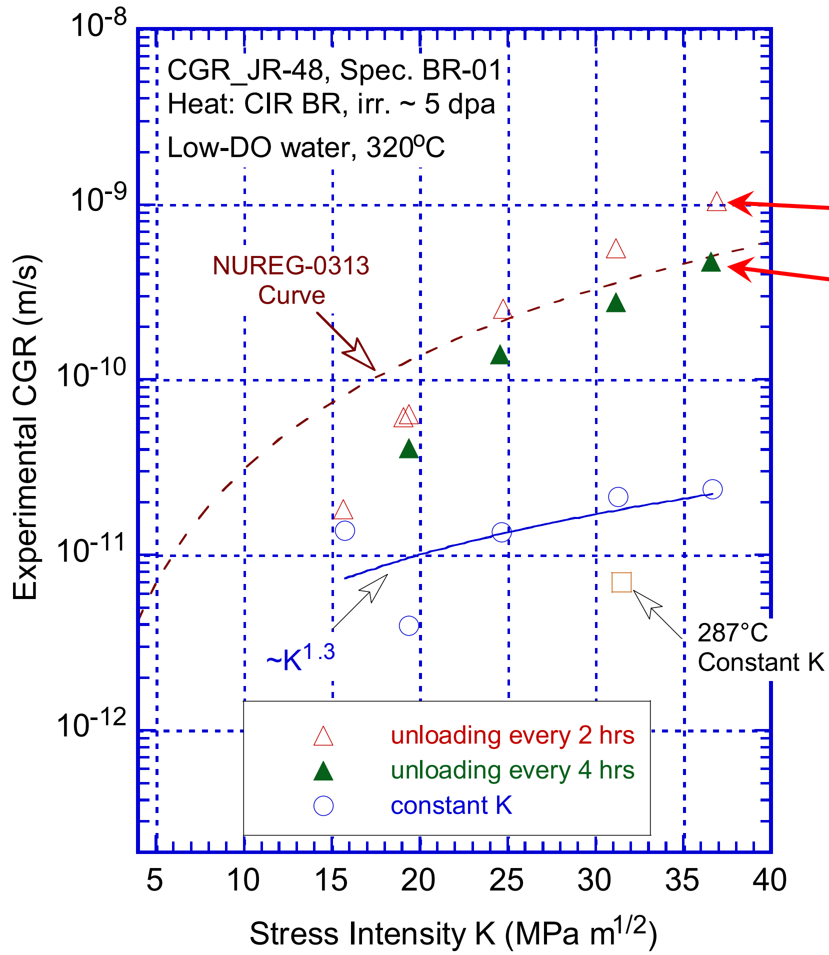
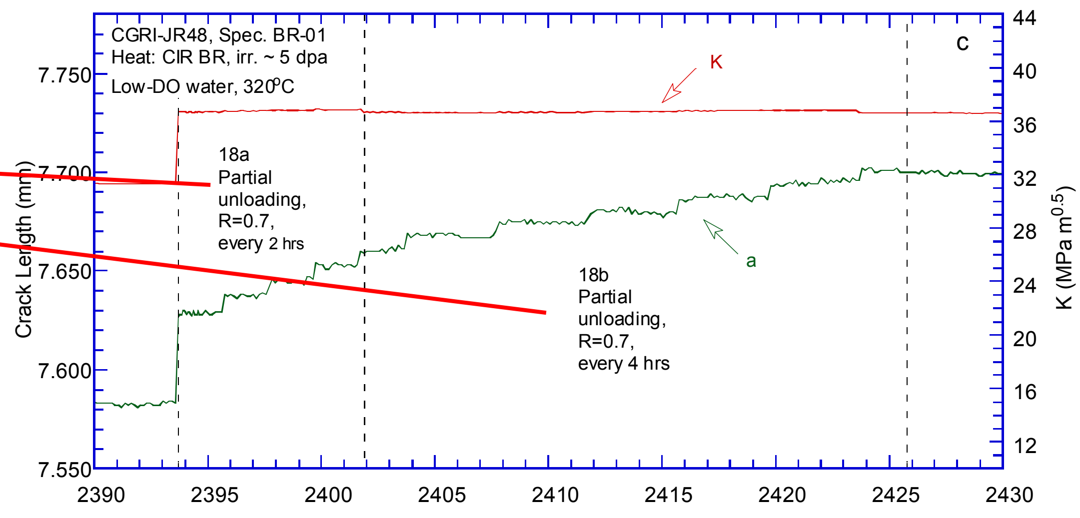
Dose dependence of cyclic CGRs for Type 304L and 316 SSs.



- **The IASCC susceptibility is observed to increase with an increase in neutron dose**





- **CGRs for a 2-hour hold time are about a factor of two greater than the CGRs of a 4-hour hold time, suggesting the stepped crack growth also occurred at lower stress intensity levels.**
- **The ligaments are being broken to support additional crack growth and or**
- **The passive layer is broken with unloading to result in higher CGR.**

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Summary

- Microstructural changes vary with irradiation condition, i.e., temperature, fluence, dose rate, & spectrum, and material condition & composition
- Below 300°C: black spot defect clusters & faulted dislocation loops
- Above 300°C: large faulted loops, network dislocations, cavities/voids, & precipitates
- RIS results in GB depletion of Cr, Mn, Mo & enrichment of Ni, Si, P, C, B
- Segregation depends strongly on irradiation temperature, dose, & dose rate
- In LWRs, RIS increases with neutron dose, peaks at intermediate temp, & increases at lower dose rates
- Defect structure & precipitates act as obstacles to dislocation motion that lead to matrix strengthening (work hardening) - increase in yield strength & decrease in ductility
- Yield stress is higher and elongation is lower for CW SS than that of SA SS

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Summary Cont.

- The increase of yield stress of either SA or CW is not affected by neutron irradiation beyond 10 dpa, however the total elongation and reduction of area tends to continuously decrease with increasing dose up to 48 dpa.
- SA samples possess fully ductile features while brittle features are seen in CW samples.
- While some inter granular (IG) cracking is observed in SA samples, predominant trans granular (TG) cracking is noticed in CW samples.
- With an increase in the neutron dose, the environmentally enhanced cracking increases in both 304 and 316 steels.
- IG cracking is severe in the high-S Type 304 SS, but not in the low-S 304 SS
- The low-O specimens are more ductile than the high-O steels.
- At 0.45 dpa no environmental enhancement was detected for Type 304L SS.
- Moderate enhancement was observed for Type 316 SS (specimen C21-A).
- With an increase in the neutron dose, the environmentally enhanced cracking increases in both 304 and 316 steels.
- The IASCC susceptibility of both 304 and 316 steels increase with an increase in neutron dose up to 5 dpa.