NE 795: Advanced Reactor Materials

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Last Time

- Austenitic steels undergo excessive void swelling in fast reactor conditions
- F/M steels have good mechanical properties, are cheap, and their microstructure can be tailored through composition and fabrication
- M23C6 and monocarbide precipitate are prevalent both along grain boundaries and within the grains; M2X metallic precipitates form and can be converted to Laves phases
- F/M steels swell very little due to fundamental nature of defects in ferrite, C-vacancy bonding, and dislocation-solute interactions
- Tailoring of alloying elements has allowed for improved creep strength
- Stress induced preferential nucleation/absorption (SIPN – SIPA)
- Swelling interaction with creep

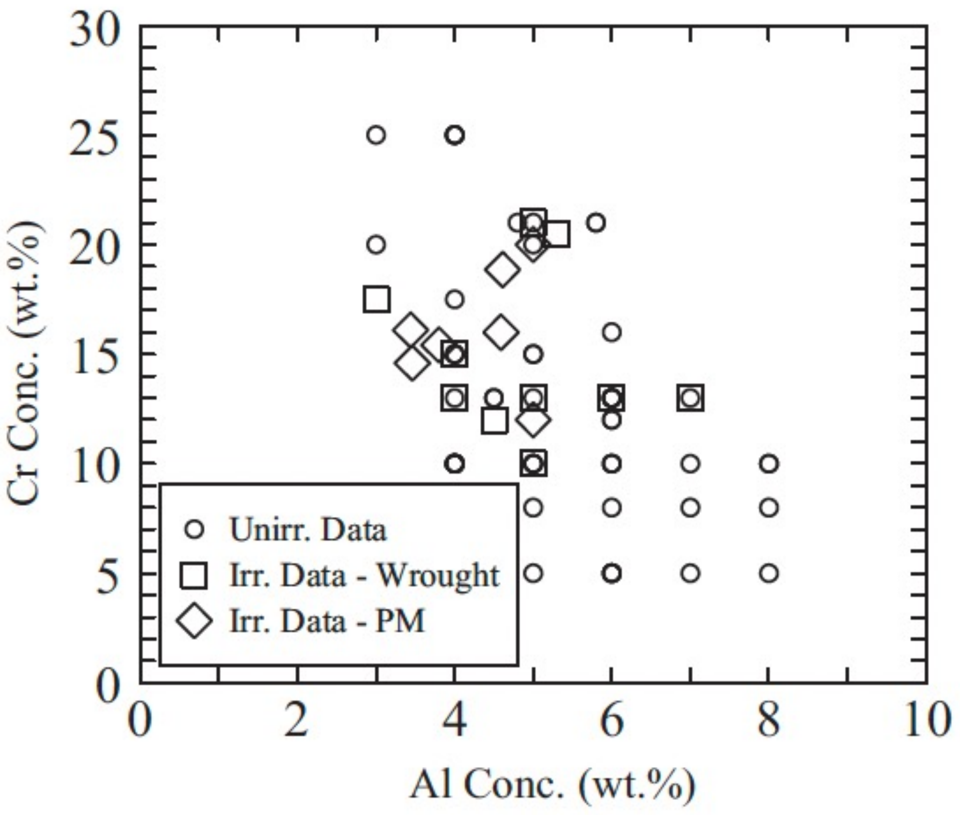
FE-CR-AL STEELS

FeCrAl

- FeCrAl alloys are expected to have excellent high temperature corrosion behavior and very low void swelling, making them viable candidates for both LWR and advanced reactors
- Strong push over the last 10 years to develop FeCrAl after Fukushima, including it as an accident tolerant fuel concept
- Alloying additions are weighed to target properties and microstructure
- Al allows for formation of Al_2O_3, limiting high T steam corrosion
- Too much Cr leads to sigma phase and alpha’ which cause embrittlement, while too much Al leads to the formation of Al intermetallics
- Cr and Al act as bcc stabilizers such that FeCrAl is fully ferritic
- Other alloying species are added to increase strength, modify precipitation, etc.

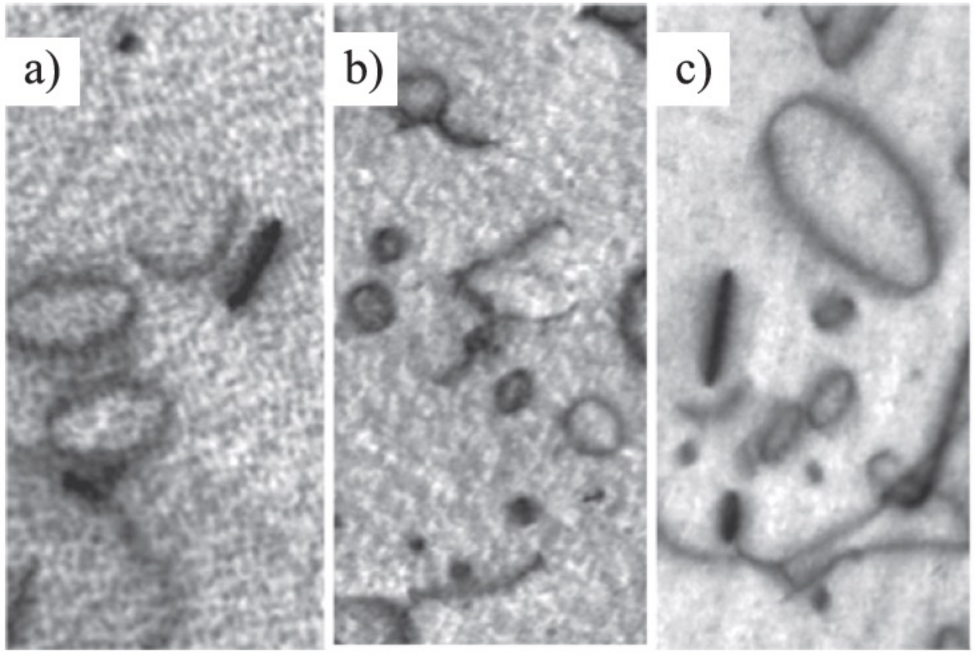
Compositional Limits

- A range of alloys have been studied for radiation tolerance utilizing different fabrication techniques
- Typically operate from 5-25 wt.%Cr and 2-8wt%Al
- If too little Cr/Al is present, get poor high temperature corrosion resistance
- To much Cr/Al, embrittlement and fabrication issues
- To much of either Cr or Al, unfavorable precipitation behavior



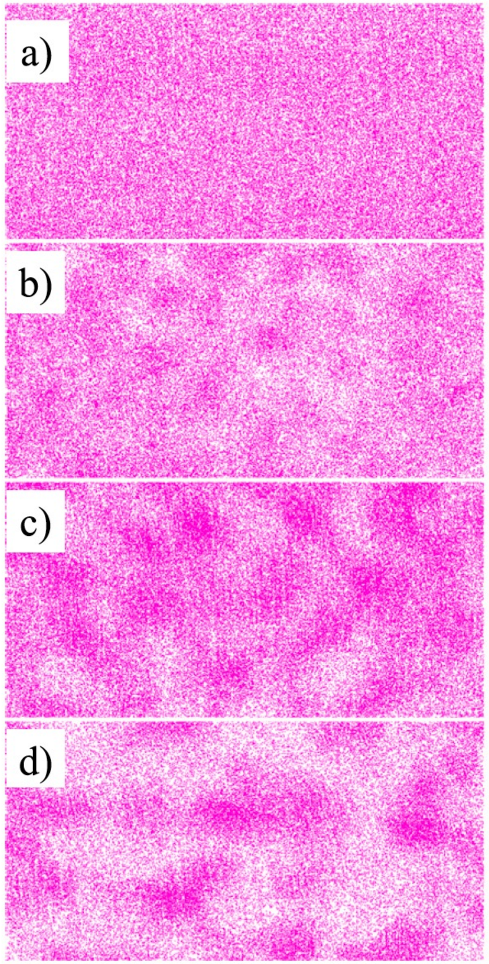
Irradiation Behavior

- Effectively no void swelling has been observed up to 23 dpa and 600C
- These alloys are expected to display excellent void swelling resistance characteristic of ferritic alloys
- Both vacancy and interstitial loops of specific orientations are known to form, regardless of minor compositional variances
- Loop size and density are impacted by composition and as-fabricated microstructure



alpha' Precipitation

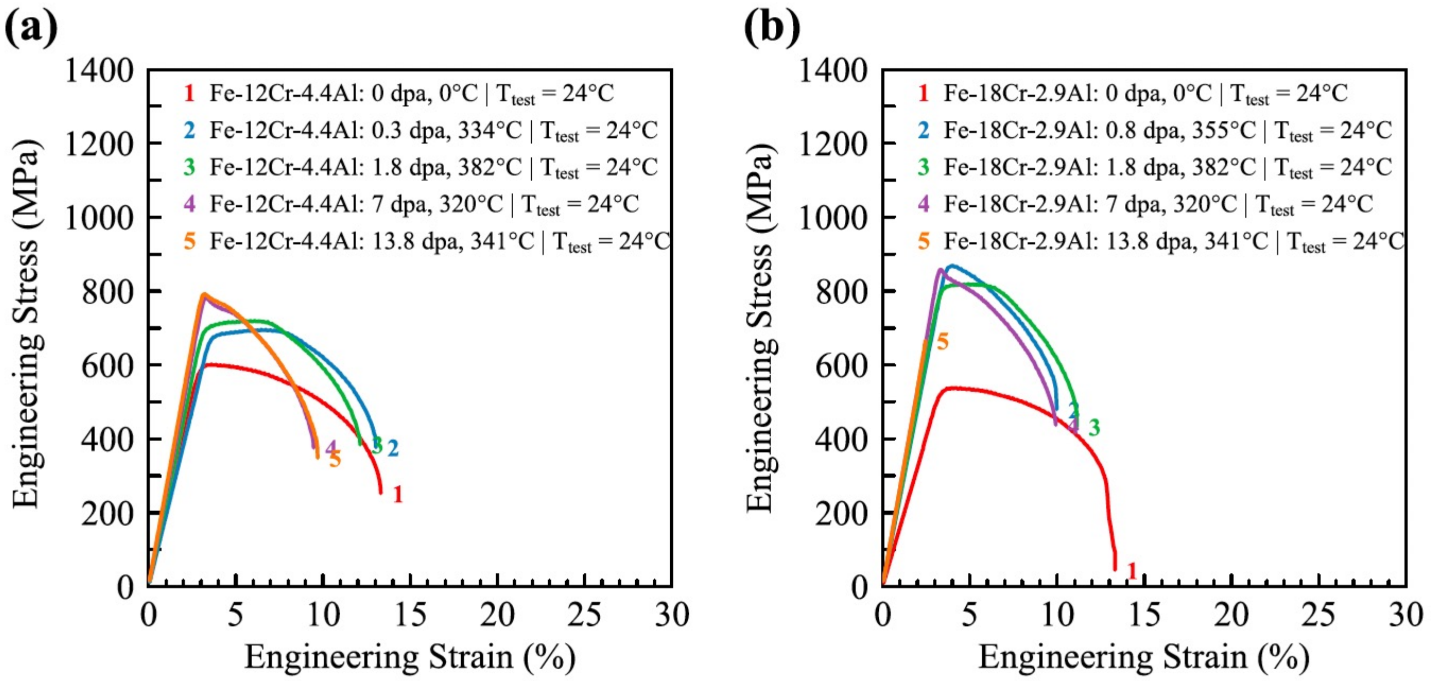
- Like other high-Cr ferritic alloys, FeCrAl alloys have been shown to be susceptible to irradiation-enhanced precipitation of the Cr-rich alpha' phase
- Embrittlement due to alpha' formation has a high likelihood of being the primary factor dictating the useful lifetime of FeCrAl components
- Aluminum is believed to inhibit, but not prevent, alpha' precipitation
- Irradiation enhanced diffusion accelerates the Cr precipitation, reducing the temperature and Cr-content at which alpha' is expected to form



Atom probe tomography Cr atom maps during neutron irradiation

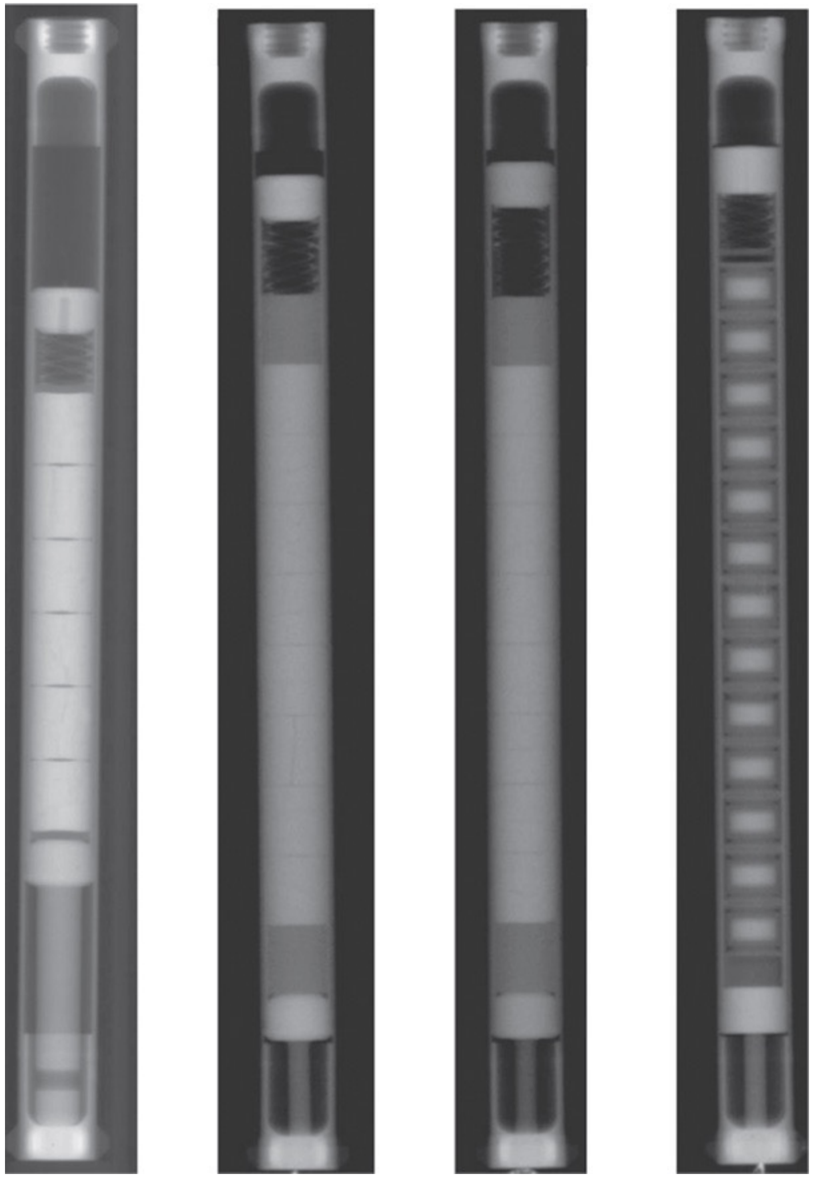
Irradiation Hardening

- FeCrAl shows pronounced increases in yield strength and corresponding decreases in total elongation due to dislocations and alpha’ precipitates
- The general trend is an initial regime where the yield strength steeply increases with increasing dose and then reaches a saturation
- Saturation is typically around 10% elongation
- Some high-Cr alloys have shown a third stage of complete embrittlement



Integral Experiments

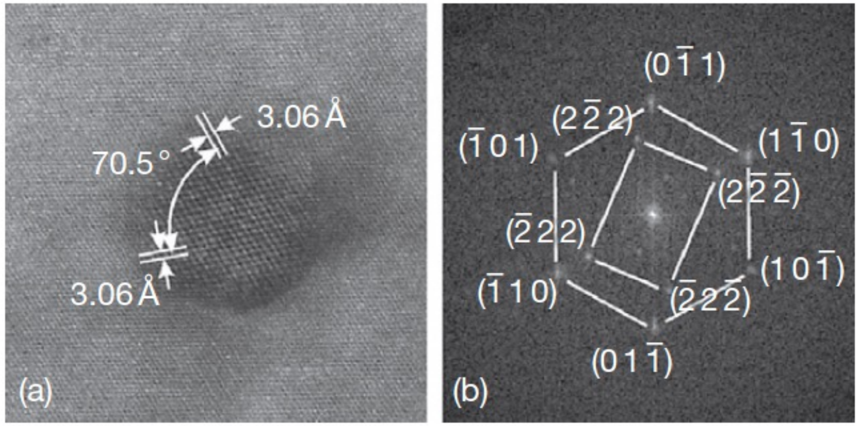
- FeCrAl is still relatively poorly explored in integral expts
- Only a handful of irradiation+corrosion tests; only a handful of fueled cladding tube tests
- No major issues identified, but nothing extended to high burnup or transients
- So, it is a promising material, but still a long way to go to verify its suitability



ODS STEELS

Oxide Dispersion Strengthened

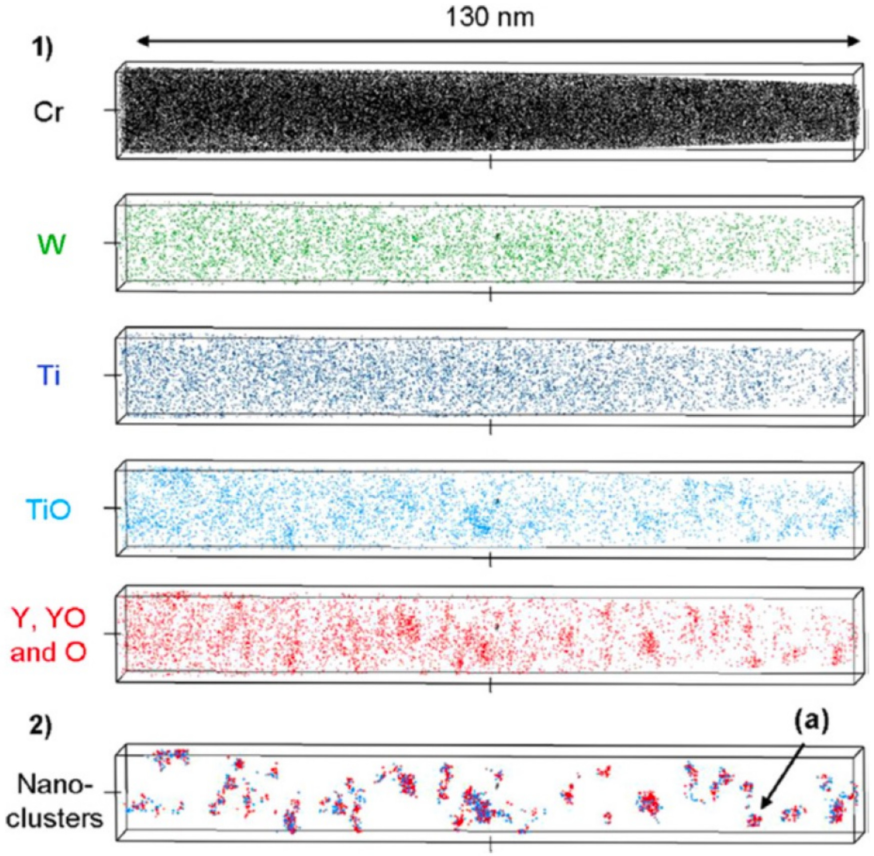
- Thermally stable oxide particles dispersed in the ferritic matrix improve the radiation resistance and creep resistance at high temperature
- ODS steels have a strong potential for high burnup and high temperature applications typical for SFR fuels
- Allow the system to retain essentially a fixed microstructure with irradiation
- Typically, Y2O3 particles or Y2Ti2O7 particles



HRTEM of Y2O3 particle with surrounding matrix

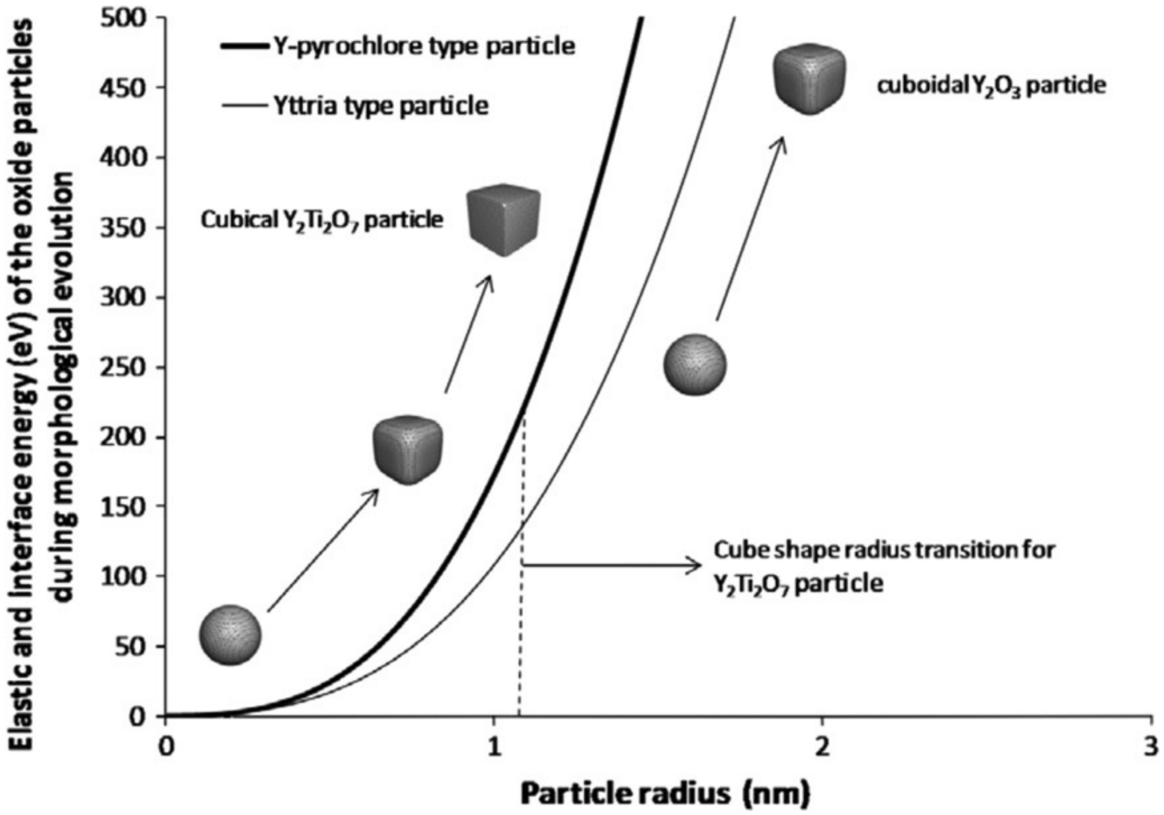
Y2O3 Decomposition

- The fine distribution of Y2O3 particles is attained by the dissociation of stable Y2O3 particles which are forced to decompose into the ferritic steel matrix during the mechanical alloying process
- The lattice structure change of Y2O3 in the ODS steel during MA consists of three stages: (1) destruction of the lattice structure, (2) formation of a blurry lattice structure, (3) appearance of amorphous areas
- Particles precipitate under heat treatment



Oxide Particle Structure

- The structure of the nanoparticles depend on sintering temperature and time, excess oxygen concentration, etc.
- Particles usually evolve from spheroids to cuboids with time/size
- Interfacial energy increases with particle size
- Misfit strain typically increases with particle size

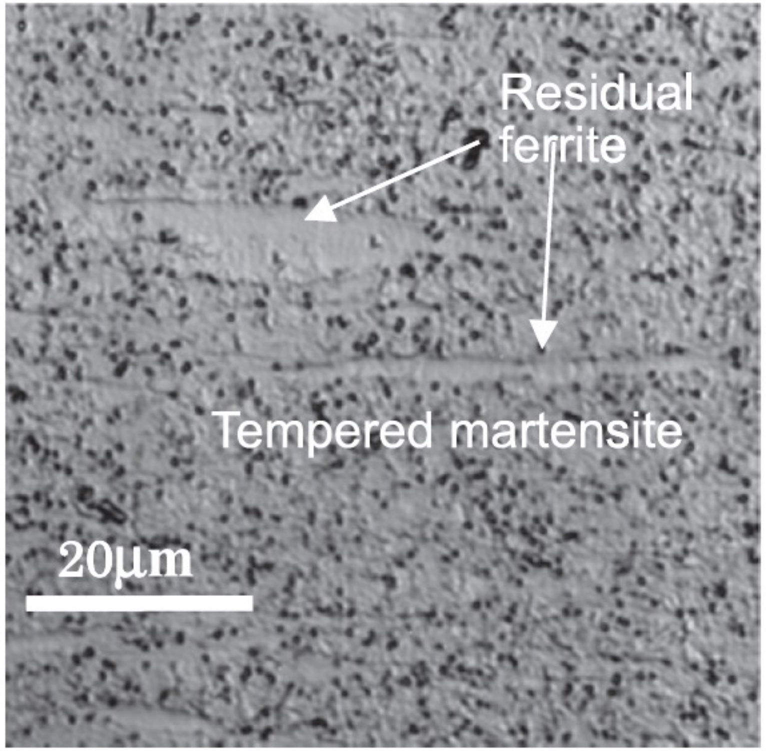


9Cr-ODS

- For nuclear applications, the choice of 9 wt% Cr with a tempered martensitic matrix is preferable to suppress the ductility loss by irradiation hardening and improve the microstructure stability and creep strength at high temperature
- The high-temperature strength of 9Cr is drastically improved by nano-scale oxide particles dispersion in the matrix
- The standard chemical composition of 9Cr-ODS being developed by the JAEA for SFR application is 9Cr–0.13C–0.2Ti–2W– 0.35Y2O3 (wt%)
- The addition of titanium produces the nanoscale dispersion of oxide particles
- Tungsten of 2 wt% is also added to improve high-temperature strength via solid solution hardening

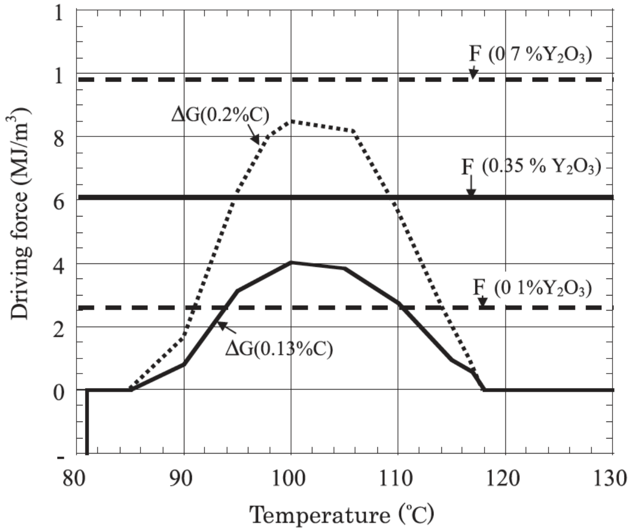
9Cr-ODS microstructure

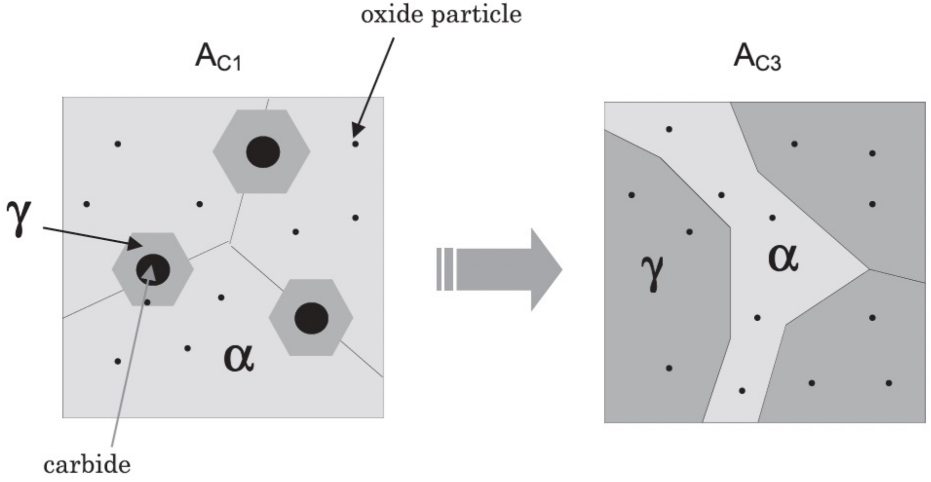
- The microstructure of 9Cr-ODS steel cladding is basically tempered martensite, but includes some residual ferrite phases
- Only the full martensite phase can be expected in 9Cr-ferritic steel without yttria under the same conditions
- The high temperature strength is greatly improved with the ferrite, and thus control of ferrite is key in ODS fabrication



Residual Ferrite

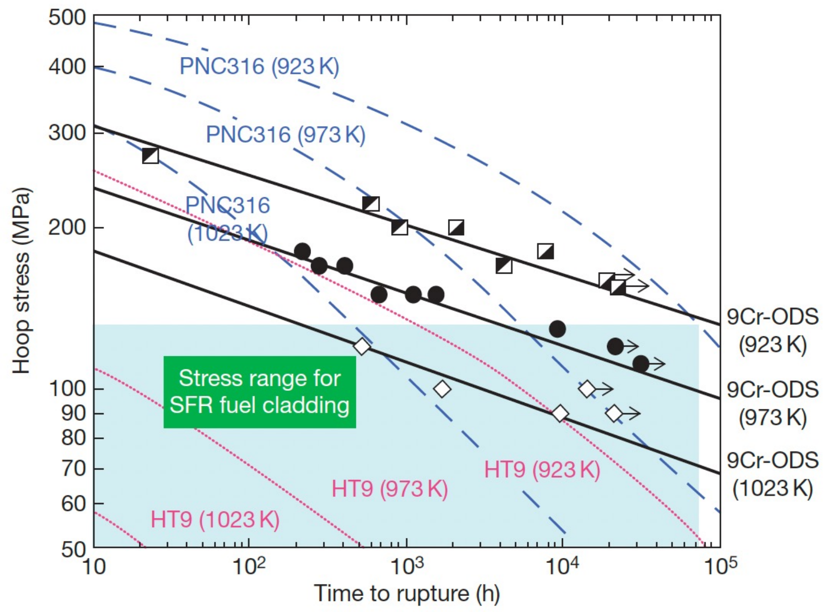
- Annealing results in the formation and precipitation of Y–Ti complex oxide particles
- This heat treatment should convert ferrite into austenite, but when Y2O3 is present, we retain ferrite at high temperature and through quenching
- These oxide particles block the motion of the alpha-gamma interface, there by partly suppressing the reverse transformation from alpha to gamma-phase

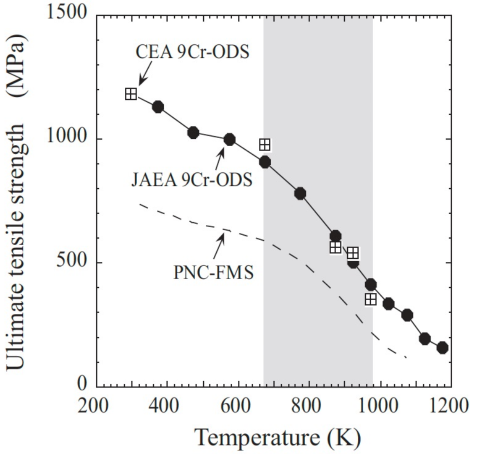


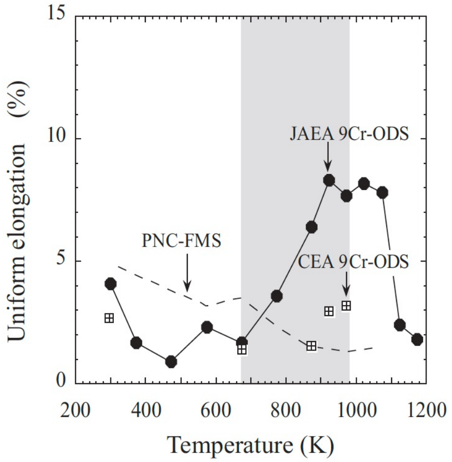


Mechanical Properties

- The lifetime of a SFR cladding is mostly determined by the internal creep rupture strength with the internal pressure of the fission gas at a temperature of ~700C
- PNC316 is austenitic steel used developed by JAEA for fast reactors
- PNC-FMS is a F/M steel
- 9Cr-ODS steels have superior creep resistance and higher tensile strength

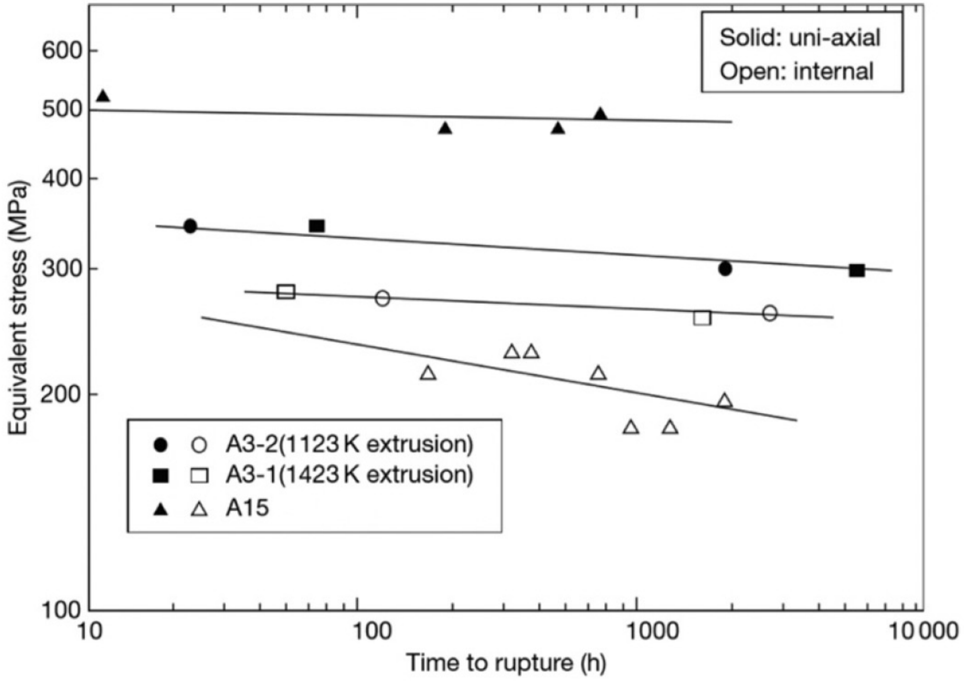






Ferritic 12Cr-ODS Steel

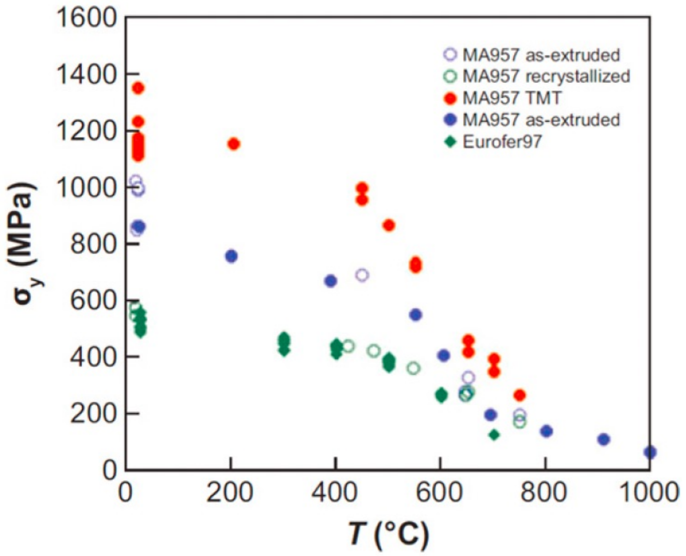
- Development of ODS steels began with purely ferritic types, similar to MA957
- While these types of steel exhibit excellent creep rupture resistance, there is anisotropy of the rupture strength
- Can form elongated grains due to fabrication, weakening cladding in hoop direction
- If the Y2O3 content is kept sufficiently low, an equiaxed grain structure can be maintained, providing more isotropic mechanical properties

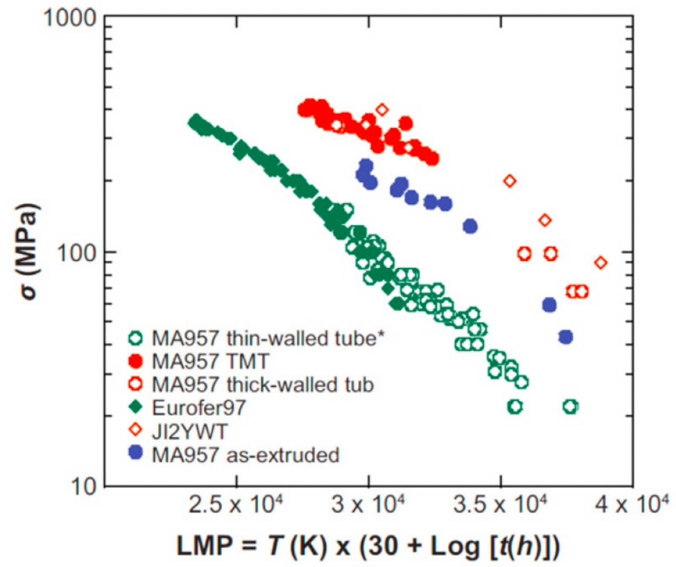


Creep rupture strength of recrystallized (A3) and unrecrystallized (A15) 12Cr-ODS steels at 650C

NFAs

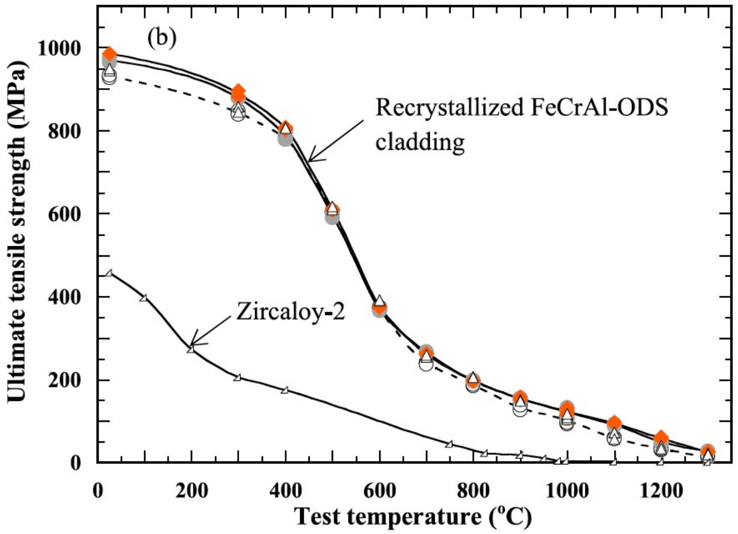
- Nanostructured ferritic alloys (NFAs) are 12%–20% Cr ferritic stainless steels that are dispersion strengthened by a very high density of ultrafine Y-Ti-O nanofeatures
- This high density creates fine grain and dislocation structures
- This can yield excellent strength and radiation resistance, but make fabrication processes very difficult
- MA957 is a NFA, Eurofer is a tempered martensitic steel

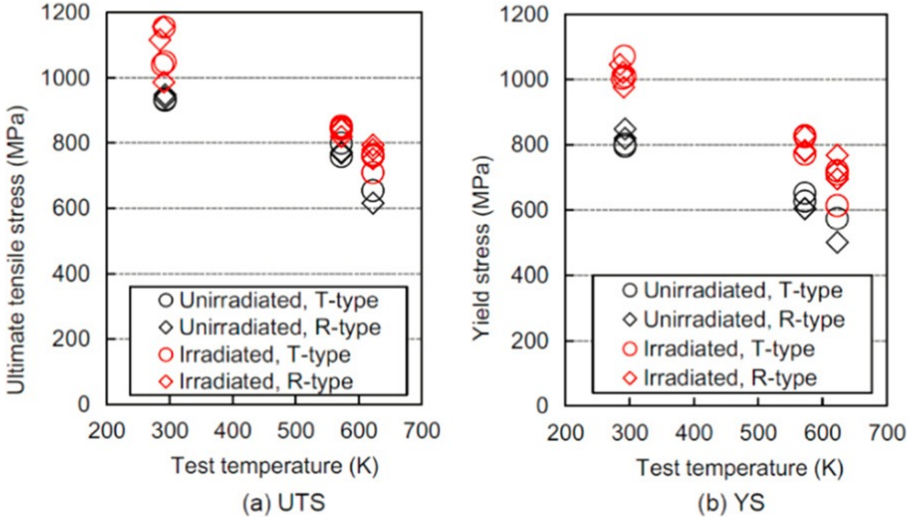




FeCrAl-ODS Steel

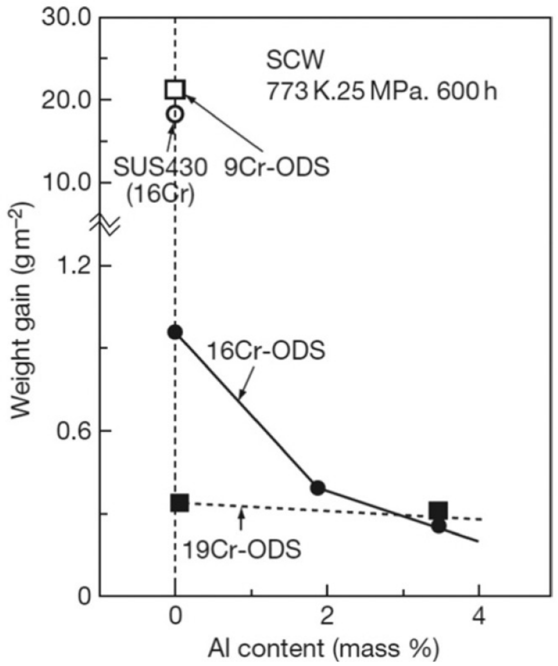
- FeCrAl steels, with and without ODS are of interest since Al-containing steels produce the stable alumina (Al2O3) scale to prevent direct reaction of Fe with steam
- A nominal composition of Fe-10Cr-6.1Al-0.3Zr (wt%) with 0.3wt% Y2O3 has been studied by ORNL, a number of different alloys explored by JAEA program
- Zr is added to prevent 'large' Y-Al oxide particle formation
- The creep rupture strength of Zr-added FeCrAl-ODS cladding is beyond the existing 9CrODS and 12CrODS steel claddings for fast reactors

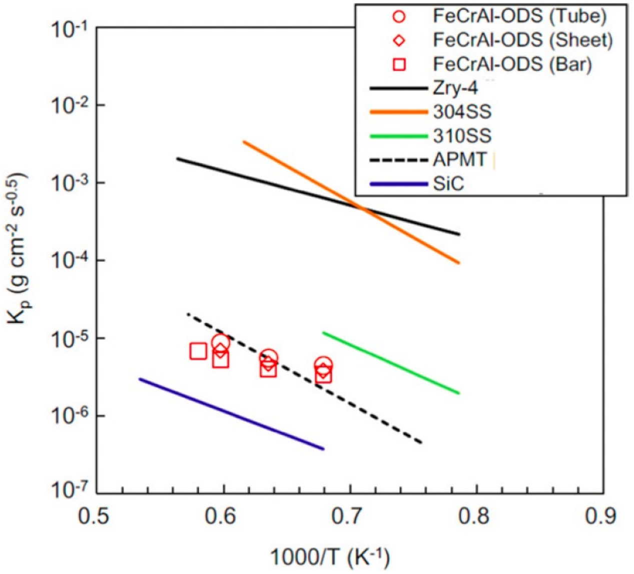




Corrosion

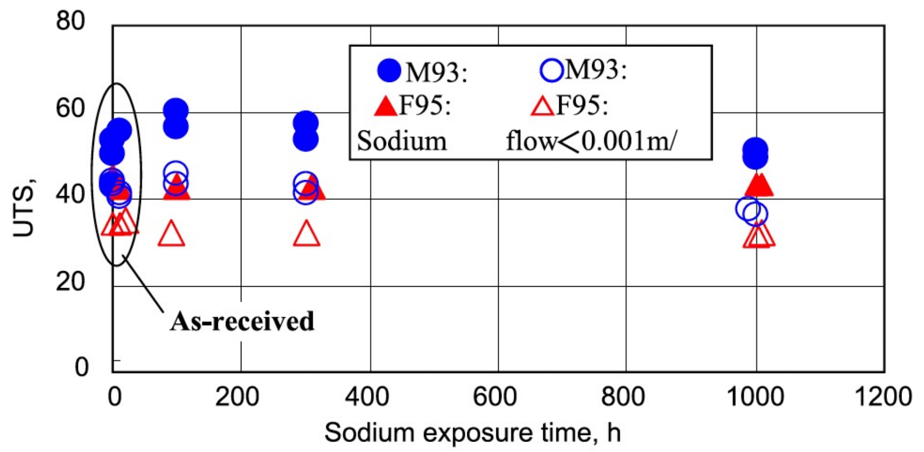
- Hot steam oxidation tests are fairly limited in ODS steels
- Additional Cr improves corrosion resistance, and Al content greater than 2 wt% provides a protective barrier
- Excess oxygen content in the alloys can serve to suppress corrosion
- In systems with high amounts of excess oxygen, Zr content can further aid in corrosion resistance

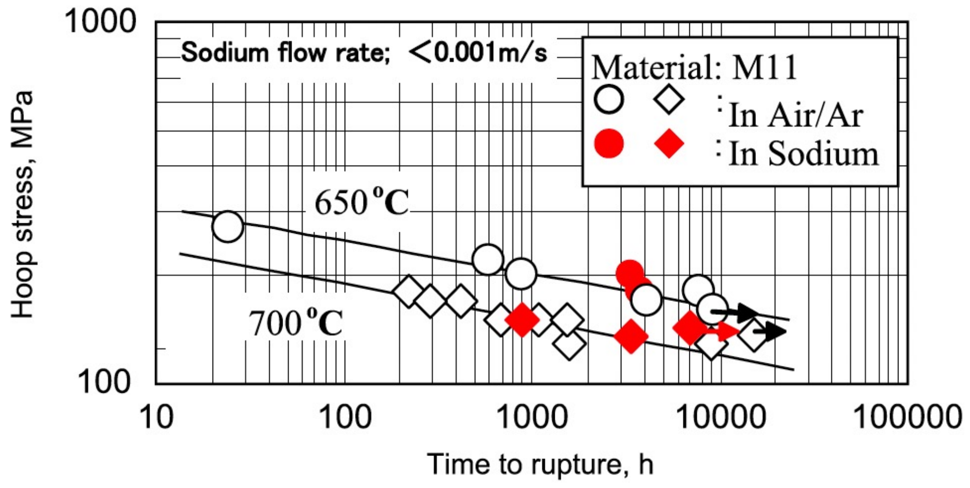




Liquid Na Compatibility

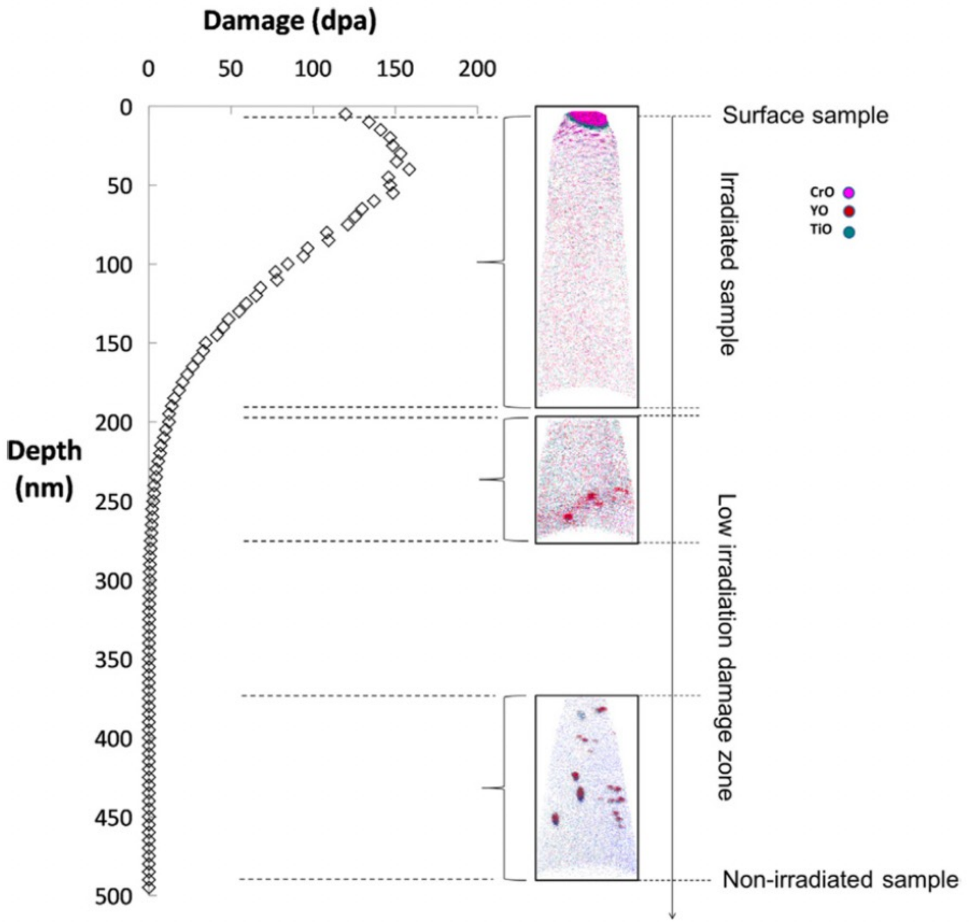
- OSD-steels display excellent compatibility with liquid sodium
- Both 9Cr and 12Cr ODS steels show no degradation in UTS after prolonged exposure to Na
- Creep rupture behavior of ODS steels in air is identical to that in liquid Na
- Under irradiation, this corrosion behavior may change, but has not been thoroughly studied





Irradiation Effects

- The stability of the oxide particles under irradiation is the key factor in these alloys maintaining their advantageous mechanical properties under operation
- Ballistic dissolution-the ejection of atoms from oxide particles due to high energy PKAs and the disordering of the particles-changes the nature of particles under irradiation
- Complete dissolution of particles has been observed via APT

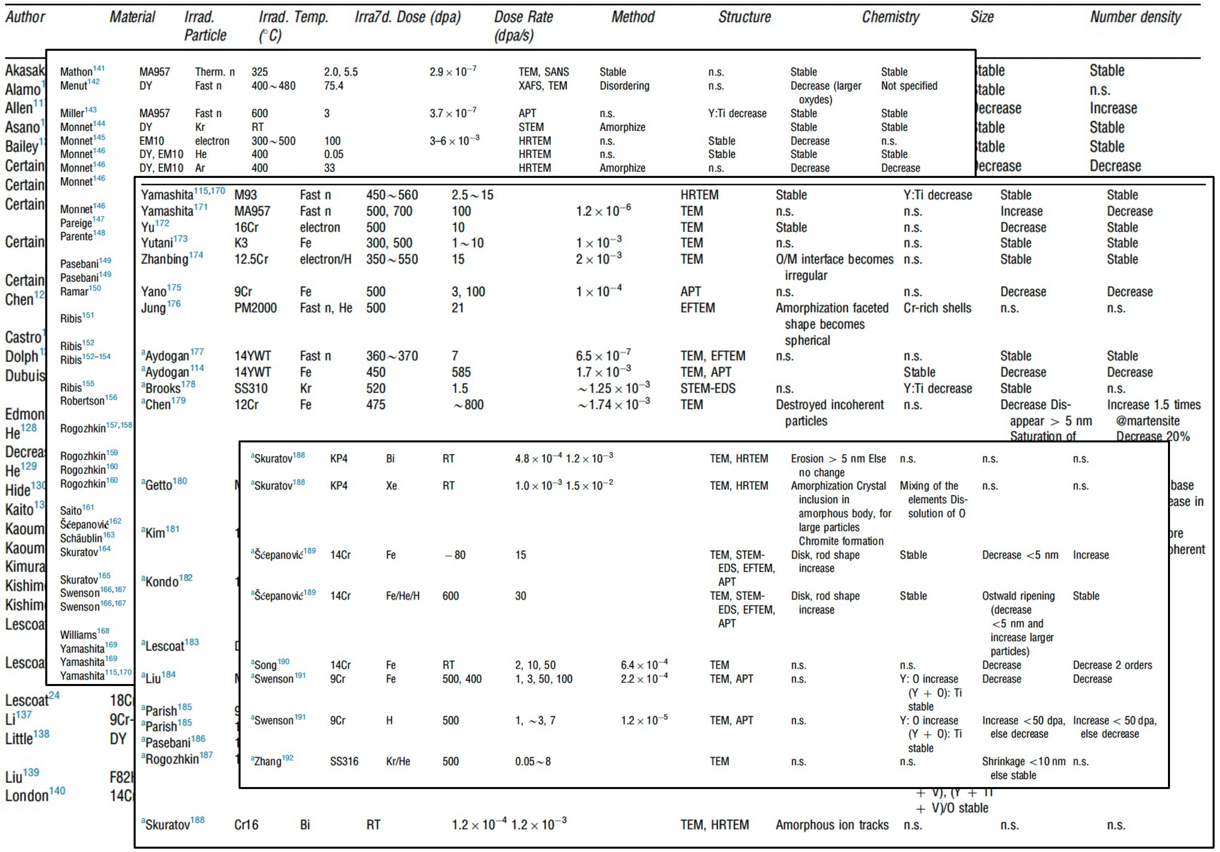


Irradiation Effects

- At higher temperatures where vacancy diffusion is possible, ballistic dissolution works in conjunction with irradiation-assisted diffusion and changes the oxide particles
- The atoms ejected from oxide particles can diffuse back to the original oxide particles, stay in the matrix, or reach other oxide particles
- Most studies have reported that the size and number density of the oxide particles hardly change compared to how they were before irradiation
- The predominant mechanism of of recovery is the back diffusion to the original oxide particles or re-joining to other existing oxide particles

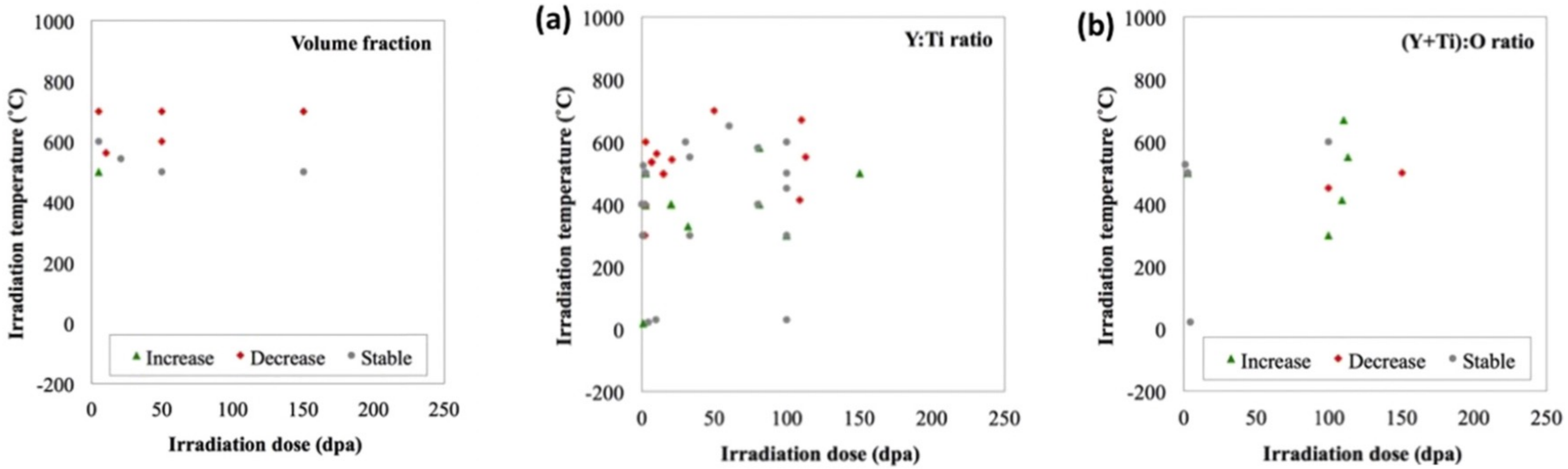
Irradiation Effects

- A large number of irradiation experiments have been performed and analyzed to study the evolution of oxide particles
- It appears that there is no correlation between irradiation dose, irradiation temperature, and the trend of change in size or number density of oxide particles



Irradiation Effects

- There may be critical temperatures at which the stability of particles and their chemistry are affected
- Higher irradiation temperatures may decrease the Y:Ti ratio



Irradiation Effects

- Swelling:
  - ODS steels are very swelling resistant, as the oxide particles trap vacancies and gas atoms, resulting in very small and homogeneously dispersed voids/bubbles
- Hardening:
  - hardness increases due to irradiation in ODS steels are smaller than in non-ODS steels
  - Oxide particles dominate hardness, and act as sinks for generated point defects

Summary

- ODS is fabricated through mechanical alloying and subsequent annealing
- 9Cr-ODS steel has a unique structure consisting of tempered martensite and residual ferrite that induces superior strength through finely dispersed oxide particles
- NFAs have a very high density of oxide particles, producing very high strength and creep resistance, at the cost of workability
- FeCrAl-ODS can provide superior corrosion resistance while retaining the ODS influenced mechanical properties
- Further in-reactor studies on ODS steels need to be performed
- While performance of ODS steels is widely studied, current production is limited to laboratory scale, with prohibitive costs for large scale production

NI ALLOYS

Ni Alloys

- Generally resistant to corrosion and display limited mechanical property degradation at high T
- Stress corrosion cracking (SCC/IASCC) is a key concern in LWR materials
- He embrittlement is of major importance due to the Ni-58 neutron capture cross section which generates He
- In fast reactor systems, Fe and Cr can also undergo n,alpha reactions

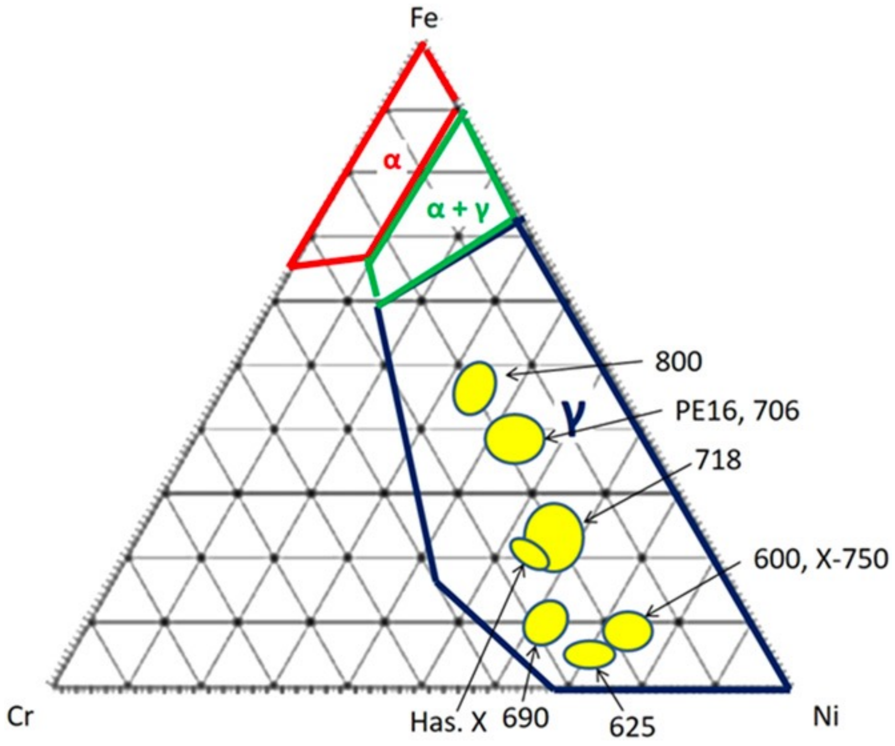
- Ni alloys have been used in LWRs, but mainly in low-dose components, have seen some testing in fast reactors, and are of high interest in advanced reactors

Table 2 Nominal compositions (wt%) of commercial Ni-based alloys

Alloy	*Ni*	*Cr*	*Fe*	*Ti*	*Al*	*Nb*	*Mo*	*Co*	*W*
Nimonic PE16	43	17	33	1.2	1.3		3.7		
Inconel 750	72	15.5	7	2.5	0.7	1			
Inconel 718	53	18	19	0.9	0.6	5	2.5		
Inconel 706	42	16	37	1.7	0.3	2.9	0.1		
Inconel 690	61	29	9	0.5	0.5				
Inconel 625	61	22	5[a]	0.3	0.3	3.5	9		
Inconel 600	75	16	8	0.3	0.2				
Incoloy 800	33	21	39.5[b]	0.4	0.4				
Hastelloy X	47	22	18	0.15[a]	0.5[a]		9	1.5	0.6
Hastelloy N	71	7	4[a]	0.15[a]	0.5[a]		16		0.5[a]

Structures

- All commercial Ni alloys are gamma-phase FCC materials
- Ternary phase diagram at right at 400C
- Ni-alloys by rule have >28 wt% Ni
- Fe and Cr are main alloy constitutents, but Al, Ti, Nb, and Mo all have solubility and can be used to solid solution strengthen or precipitation harden
- Most alloys are precipitation hardened to increased high temperature creep resistance



He generation

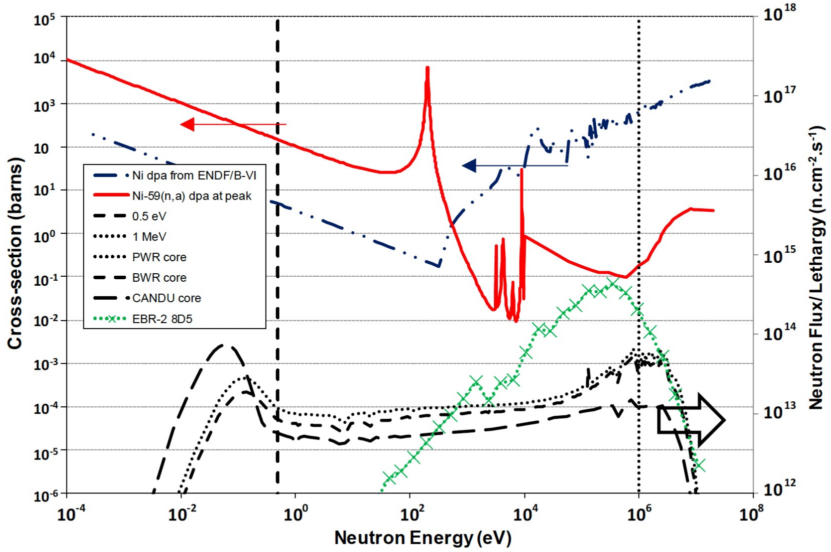
- Large amounts of He and H can be produced due to high neutron dose
- Ni alloys in CANDU reactors have a service lifetime of 20 years and can have >20000 appm He
- The generation of He is also producing high energy PKAs which are introducing further damage into the system

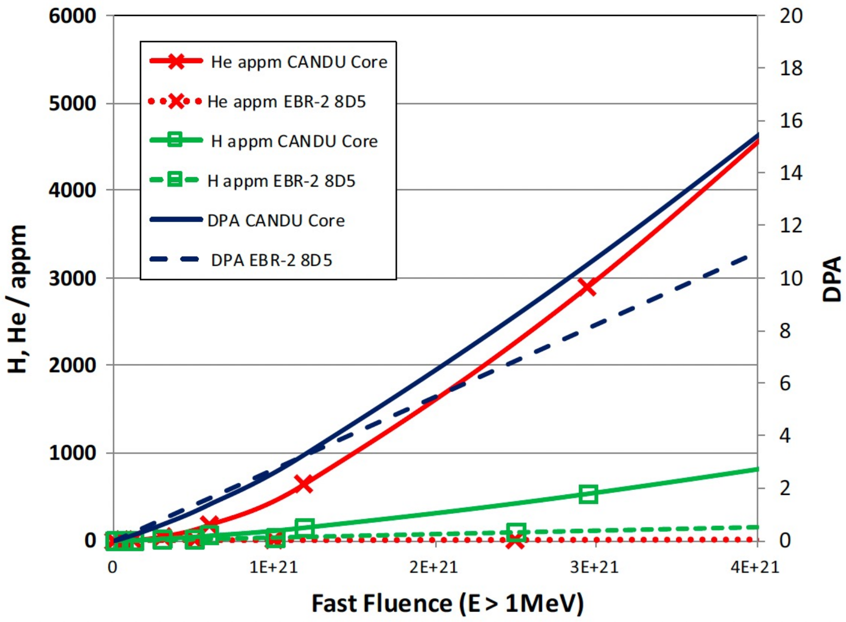
$$^{58}\mathrm{Ni} + \mathrm{n} \rightarrow {}^{59}\mathrm{Ni} + \gamma$$

$$^{59}\mathrm{Ni} + \mathrm{n} \rightarrow {}^{56}\mathrm{Fe} + {}^{4}\mathrm{He}$$

$$^{59}\mathrm{Ni} + \mathrm{n} \rightarrow {}^{59}\mathrm{Co} + \mathrm{H}$$

$$^{59}\mathrm{Ni} + \mathrm{n} \rightarrow {}^{60}\mathrm{Ni} + \gamma$$

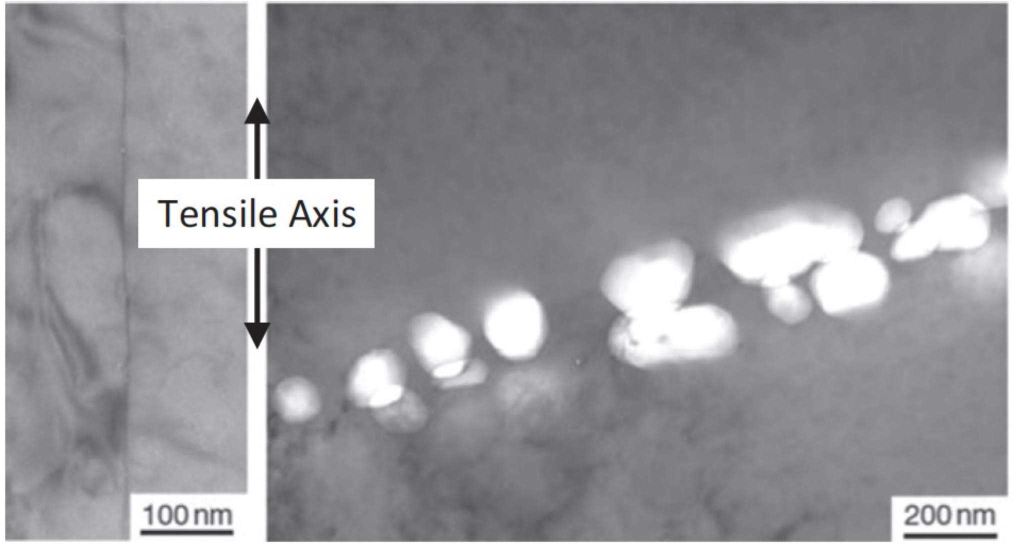




Void Swelling

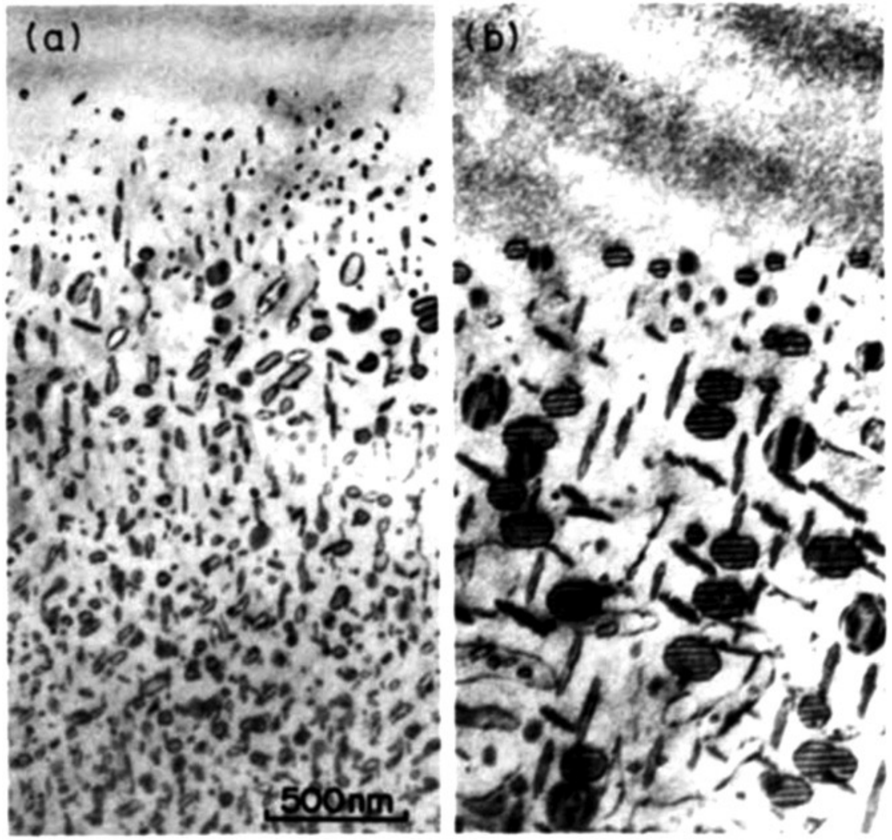
- The concept of void swelling is complicated by the generation of He, in that He bubbles and voids can form separately, or impact each others formation
- In fast reactors, He generation is lower, about 1 appm/dpa, but He impacts on grain boundary bubbles have still been identified
- Often associated with tensile stresses

- Many examples that show high densities of He-stabilized grain boundary cavities in high flux reactors



Dislocations

- Large dislocation loops are observed at high temperatures expected in advanced reactors
- Loop structures have been seen to be very sensitive to temperature controls during irradiation

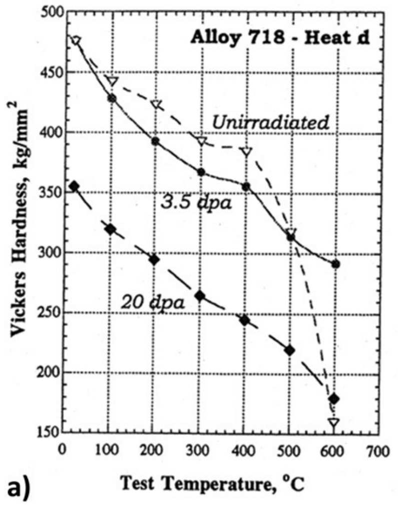


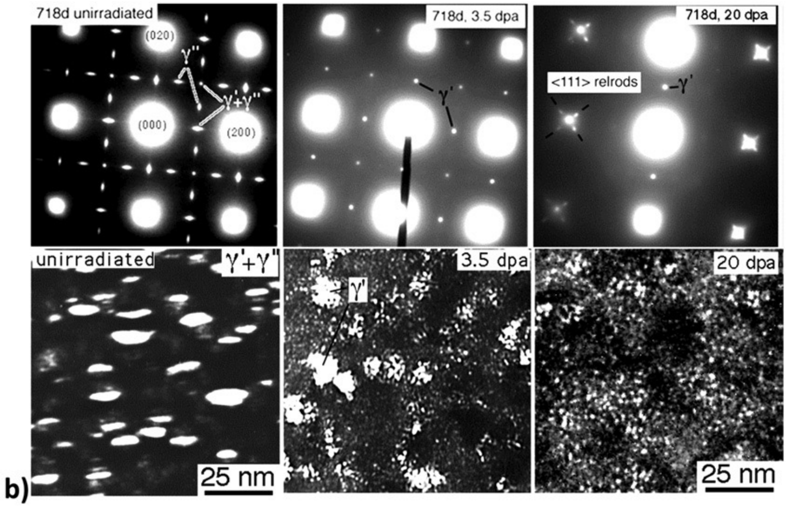
T ramping

Constant T

Precipitation

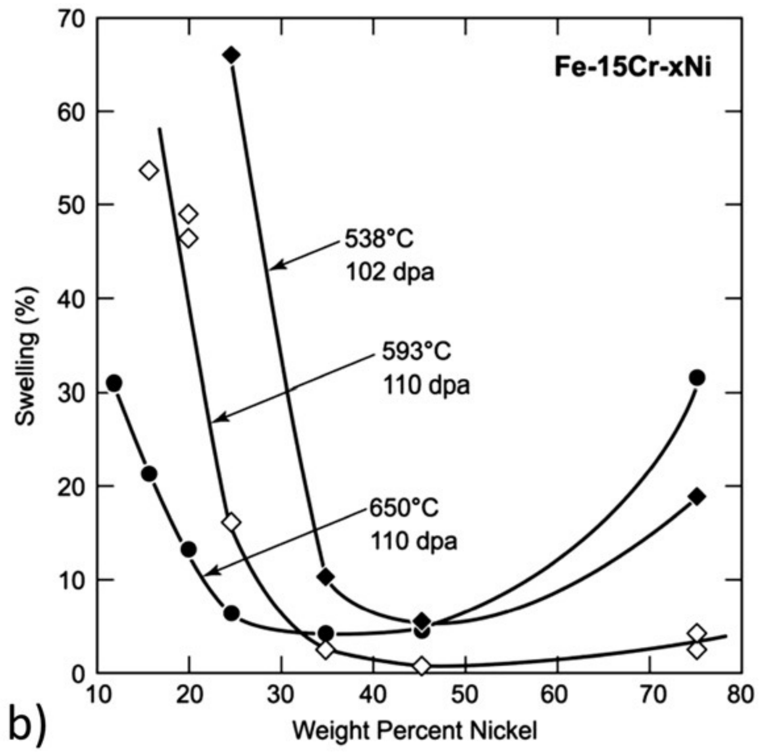
- The primary precipitates that form are gamma’ (Ni3Al) and gamma’’ (Ni3Nb-type), where Ni can be replaced by Fe/Cr
- These precipitates can be dissolved or dispersed during irradiation
- There are competing ballistic and kinetic/thermodynamic factors at play
- Higher temperatures allow more rapid diffusion, and the potential re-precipitation





Swelling

- Ni alloys generally show significantly improved resistance to swelling compared to SS
- The presence of gamma’ precipitates is believed to a factor in the swelling resistance
- Alloying species are expected to have the primary effect on swelling behavior, modifying local strain and vacancy biases via the inverse Kirkendall effect



neutron irradiated in a fast reactor to about 100 dpa