NE 795: Advanced Reactor Materials

Fall 2023

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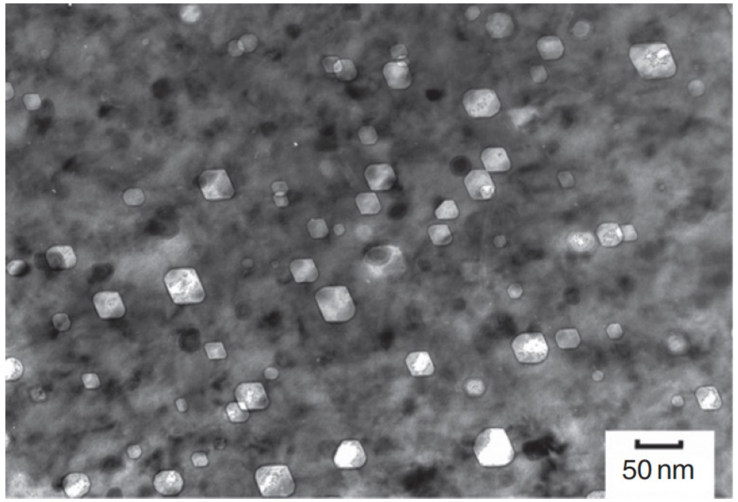
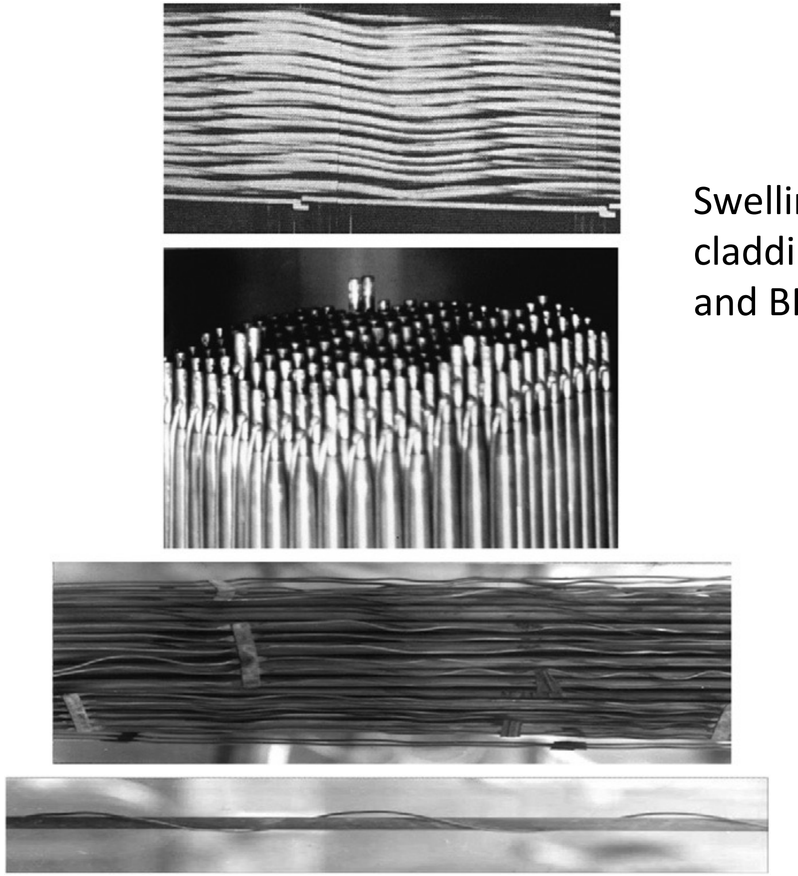
ADVANCED CLADDING

The need for advanced cladding

- Austenitic stainless steels are widely used as structural components in nuclear service
- At high dose, the microstructure develops a high concentration of voids, leading to dramatic swelling



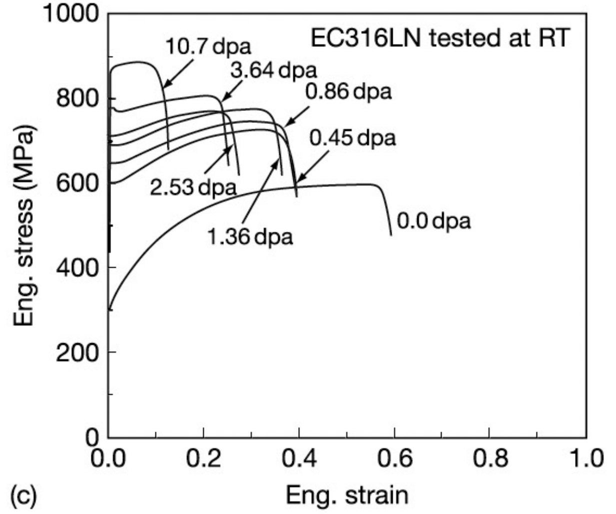
Void swelling in 304SS

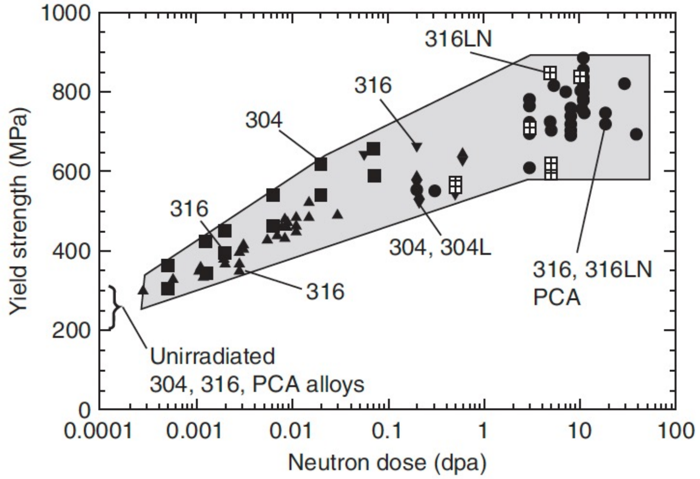


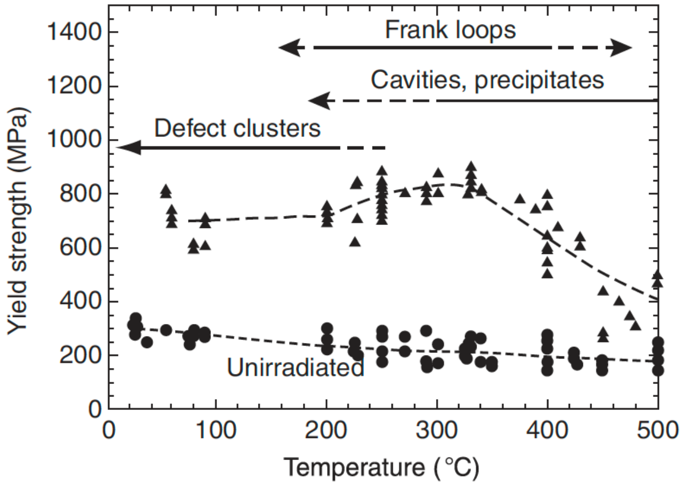
Swelling of cladding in FFTF and BN-600

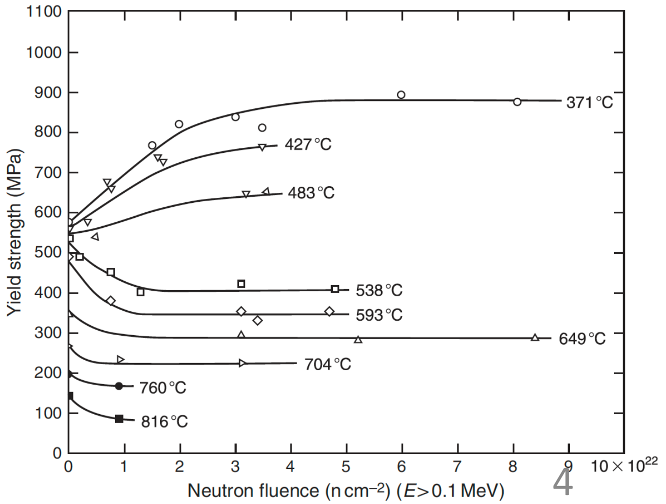
The need for advanced cladding

- High fluence can also provide significant radiation hardening, coupled with severe losses in ductility
- In addition to high fluence, high temperature contributes to void swelling
- SS significantly weakens with increasing temperature
- Thus, their applicability is limited in advanced reactor systems where high dose and high temperature are present









Fast Reactor Conditions

- The structural components experience a different environment in advanced fast reactors than those in commercial LWRs
- Key phenomena include void swelling, irradiation growth, irradiation hardening, irradiation creep, and helium embrittlement

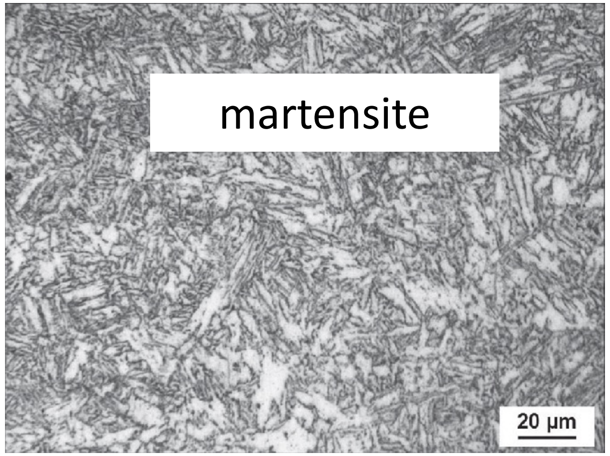
Criterion	*Clad tube*	*Wrapper tube*
Exposure conditions (only trends; exact values depend on core design)	Maximum temperature: 923–973 K	Lower temperature range than clad: 823 K
	Steeper temperature gradient	Lower temperature gradient
	Higher stresses from fission gas pressure	Moderate stresses from coolant pressure
	Chemical attack from fuel	Flowing sodium environment
	Average neutron energy: 100 keV	Neutron environment similar
	Neutron flux: 4–7 $\times$ 10^{11} n m^{-2} s	
	Neutron fluence: 2–4 $\times$ 10^{19} n m^{-2}	
Major damage mechanisms	Void swelling	Void swelling
	Irradiation creep at higher temperatures	Irradiation creep
	Irradiation embrittlement	Irradiation embrittlement
	Interactions with fuel and fission products	Interaction with sodium
Selection criteria: mechanical properties	Tensile strength	Tensile strength
	Tensile ductility	Tensile ductility
	Creep strength	
	Creep ductility	
Corrosion criteria	Compatibility with sodium	Compatibility with sodium
	Compatibility with fuel	
	Compatibility with fission products	
General common selection criteria		
Good workability		
International neutron irradiation experience as driver or experimental fuel subassembly		
Availability		

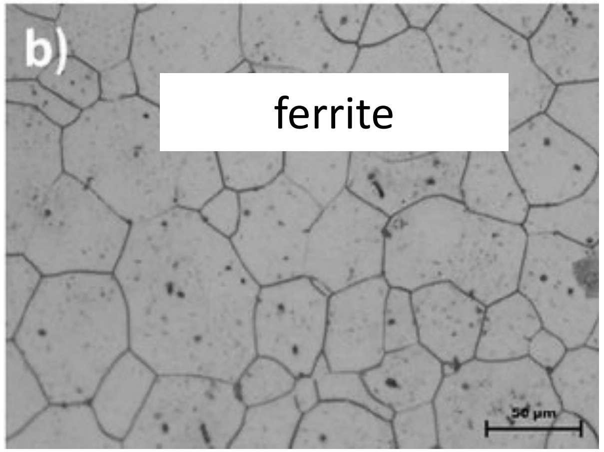
Ferritic and Ferritic-Martensitic Steels

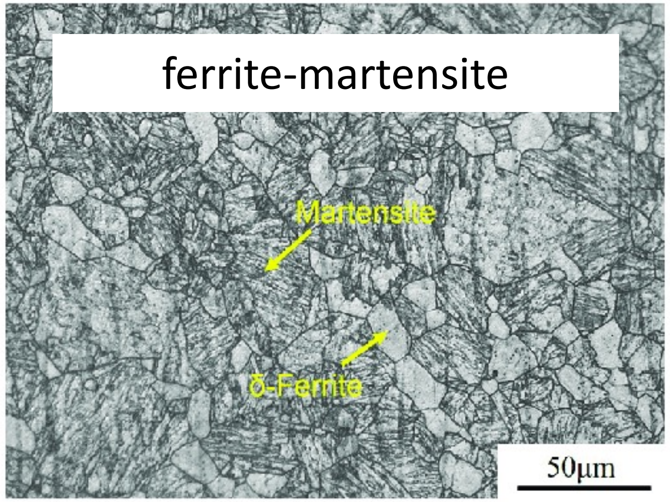
- The advanced ferritic and ferritic–martensitic steels of current interest have evolved from creep-resistant ferritic steels
- Subsequent developments through different levels of Cr and Mo have led to the current ferritic and ferritic–martensitic steels: 9–12% Cr–Mo steels
- F-M steels have advantageous mechanical properties, are relatively cheap, and control of their microstructure can be performed with heat treatments
- F-M steels generally have worse high T mechanical properties than austenitic steels, especially creep life and irradiation creep resistance

Crystal and Micro Structures

- alpha-Fe: ferrite, bcc
- gamma-Fe: austenite, fcc
- delta-Fe: high temperature ferrite, bcc
- martensite: C-rich bct
- pearlite: lamellar combination of ferrite and cementite (Fe3C)
- also upper and lower bainite: don't worry about it
- alpha': Cr rich ferrite (mainly induced via thermal aging)

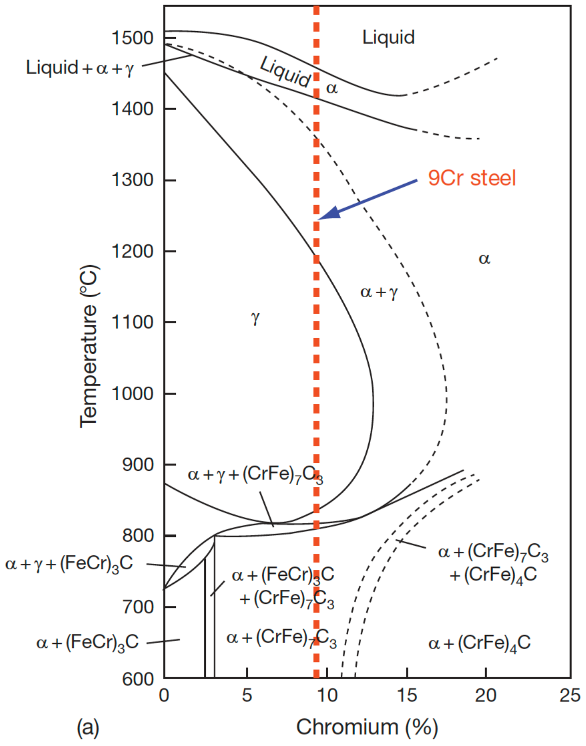




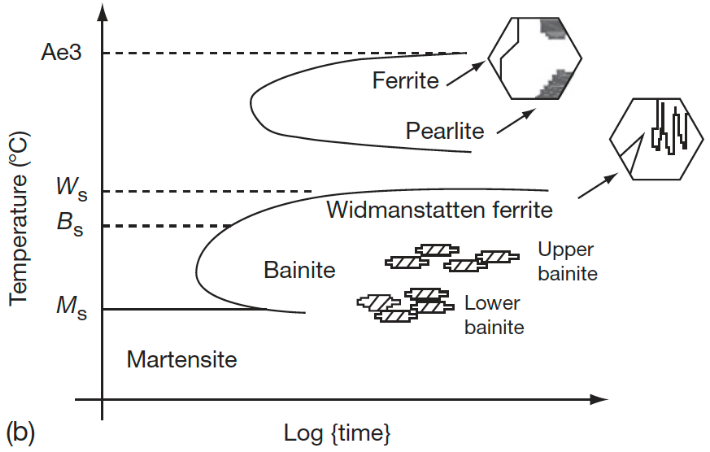


Ferritic-Martensitic Steels

- The ability to retain ferrite is dependent upon the alloying elements and the heat treatments
- In addition to Cr and Mo, the amount of Si, V, and C affect the phase boundaries
- Accordingly, the 9-12% Cr/Mo family of steels can either be martensitic (9Cr–1MoVNb (T91)), ferritic (12Cr–1MoVW (HT9)) or ferritic–martensitic (9Cr–2Mo–V–Nb (EM12)) steel



Pseudo-binary phase diagram with Cr equivalent



TTT diagram of austenite

Composition Effects

- The developed of 9Cr-Mo steels was initially focused on oxidation resistance and creep strength
- The optimized initial alloy composition considered was 9Cr, 2Mo, 1W, 0.5Si, with C, B, V, Nb, and Ta in small amounts
- A reduction in Cr content lowers the oxidation resistance
- Higher Cr content has two effects, 1) it increases the hardenability leading to the formation of martensite, and 2) promotes the formation of δ-ferrite, reducing the toughness
- If the W+Mo concentration is kept <3%, creep strength will reduce, while higher amount promotes the formation of δ-ferrite and brittle Fe2Mo Laves phase

Composition Optimization

- The addition or replacement of Mo with W and B increases the stability of M23C6
- Lower Ni content introduces δ-ferrite, while its increase reduces creep strength
- Lower Si reduces oxidation resistance, while higher Si content leads to agglomeration of carbides
- The composition of all other elements can be optimized, based on structure–property correlation studies

Table 2 Optimizing the constitution in the development of ferritic steels

Element	*Function*
Cr	Basic alloying element, corrosion resistance, hardenability
Mo, W, Re, Co	Solid solution strengthening
V, Nb, Ti, Ta	Strengthening by formation of MX-carbonitride
C, N	Austenite stabilizer, solid solution strengthening, carbonitride formers
B	Grain boundary strengthening, stabilization of carbide
Ni, Cu, Co	Austenite former, inhibits δ-ferrite formation

Composition Optimization

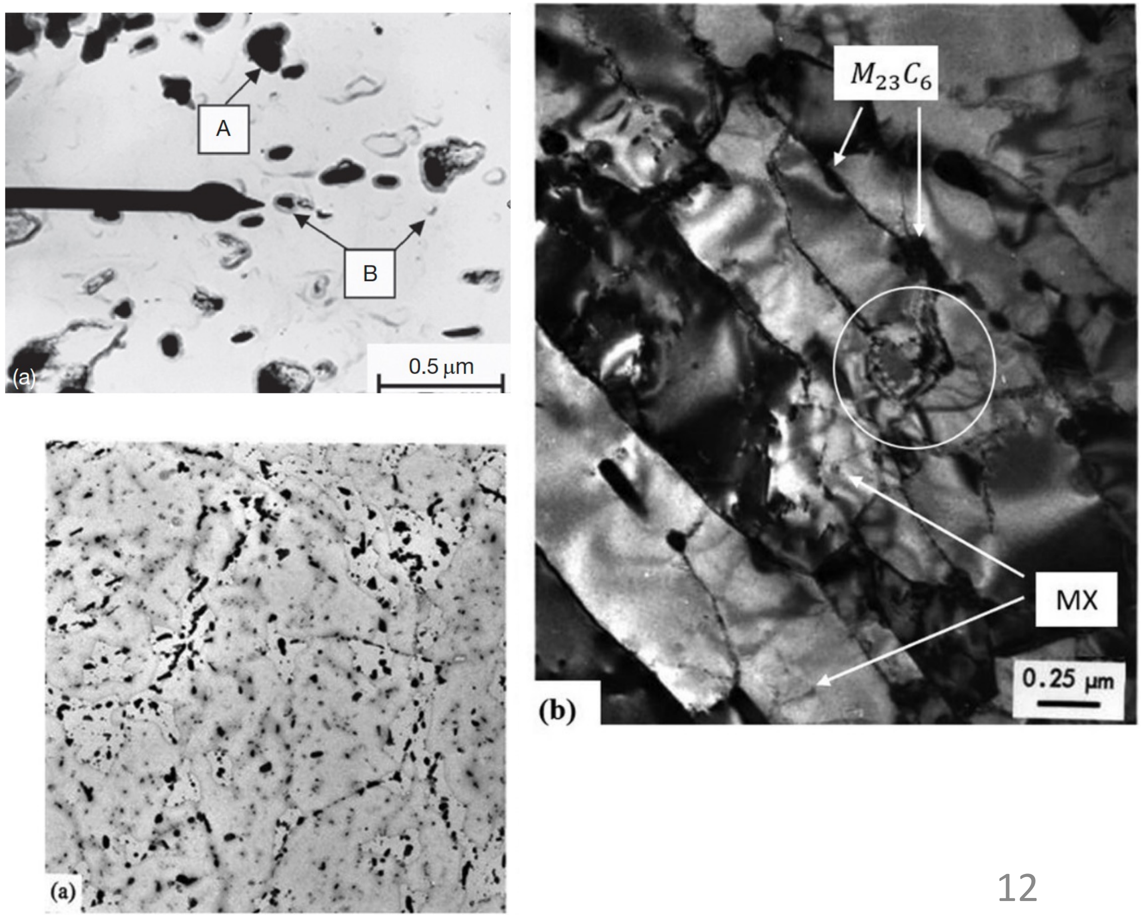
- The development of high creep-rupture strength steels is based on optimizing the composition, δ-ferrite content, increasing the stability of the martensite, dislocation structure, and maximizing the solid solution and precipitation hardening
- Based upon this property tailoring, a large number of alloys have been developed over the last 75 years
- Reduced activation ferritic-martensitic (RAFM) steels steels have been developed in order to make concentrations of high activation residual elements lower

Commercial name	*Chemistry*	*10^5 h creep strength at 873 K MPa^{-1}*
T22	2.25Cr1Mo	35
Stab. T22	2.25Cr1MoV	60–80
HCM2S	2.25Cr1MoWNb	100
T9	9Cr1Mo	35
EM12	9Cr2MoVNb	60–80
F9	9Cr1MoVNb	60–80
T91	9Cr1MoVNb (optimized)	100
T92	9Cr(MoW)VNb	120
Eurofer	9CrWTiV	~120
HT91	12Cr1MoV	60–80
HT9	12Cr1MoWV	60–80
HCM12A	12CrMoWVNbCu	120
SAVE12	12CrWVNbCo	180

Microstructure

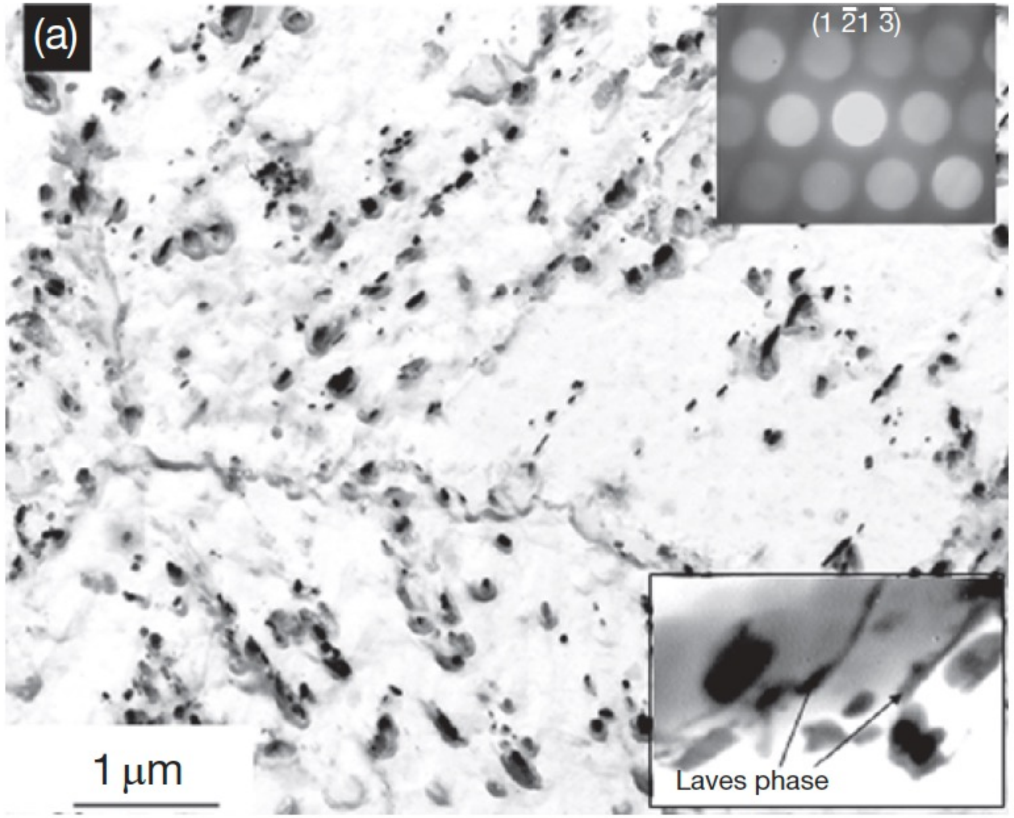
- The microstructure of the steels consists of a) martensite laths containing dislocations; b) coarse M23C6 particles located at prior austenite and ferrite grain boundaries; c) finer carbide precipitates found within the laths and at the lath/subgrain boundaries
- M2X precipitates rich in Cr also form

HT-9 initial microstructures



Microstructure

- In reactor, this microstructure will change, with the M2X precipitates being replaced by MX intermetallic and Laves phases due to long exposure to high temperature
- There are three types of processes with respect to evolution of secondary phases: irradiation-induced precipitation, irradiation-enhanced transformations, and the irradiation modified phases
- The evolution of these phases depends on the composition and structure of the steel and the irradiation parameters like the temperature and fluence



Fe2Mo Laves intermetallic phase around the M23C6

Radiation Damage

- Dislocation loops are the primary defect species observed
- Loops are typically larger and with a lower number density as the irradiation temperature is increased
- Loop size and density are increased as a function of dose, with loop density potentially saturating at 10 dpa
- Voids can also form above 400C

- Radiation-induced segregation can occur in these steels, but has been significantly less studied than in austenitic steels
- General consensus that Cr is depleted at interfaces, and Ni, Si , and P are enriched at sinks
- RIS appears to be dependent on both irradiation dose and temperature

Phase Precipitation

- Thermal processing will lead to precipitation, which affects the mechanical properties
- Most of the carbon forms in M23C6 precipitates, which increase strength and reduce ductility
- RIS leading to Cr depletion increases the matrix composition and can lead to alpha' formation, which embrittles the material
- Chi, G, and sigma phases are enriched in Si and Ni and can nucleate at interfaces

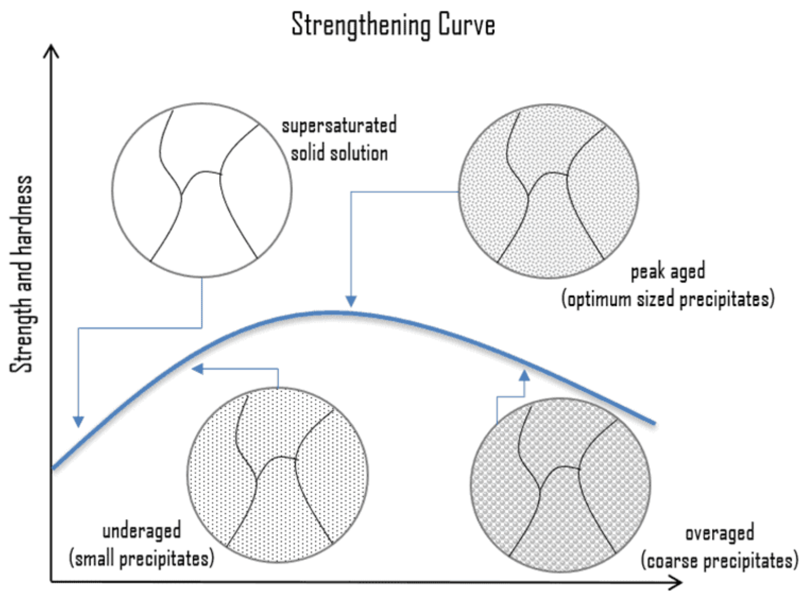
Table 4 Phases precipitated in high-chromium steels during tempering and subsequent aging at temperatures in the range 400–750°C

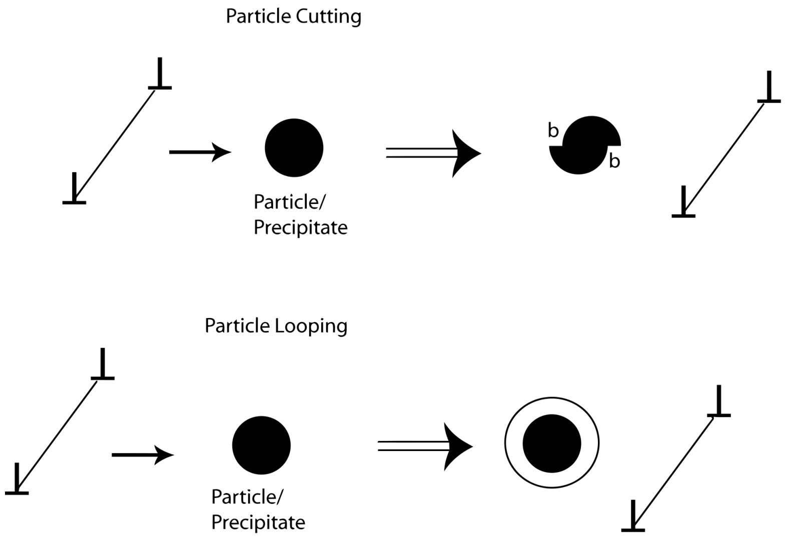
Phase	*Crystal Structure*	*Typical Composition*	*Distribution*	*Radiation-induced*
$M_{23}C_6$	FCC	$(Cr_{16}Fe_6Mo)C_6$ $(Cr_4Fe_{12}Mo_4Si_2WV)C_6$	Coarse particles at prior austenite grain and martensite lath boundaries and fine intra-lath particles	No
MX	FCC	NbC, NbN, VN, (CrV)N, Nb(CN), (NbV)C	Undissolved particles and fine precipitates at martensite lath boundaries	No
M_2X	Hexagonal	Cr_2N, Mo_2C, W_2C	Martensite lath boundaries (Cr_2N, Mo_2C); prior austenite grain boundaries (Mo_2C); intra-lath (Mo_2C, W_2C); δ-ferrite in duplex [$Cr_2(CN)$], $(CrMo)_2(CN)$	No
Z	Tetragonal	(CrVNb)N	Large plate-like particles in the matrix after creep straining at 600°C	No
η-carbides	Diamond Cubic	M_6C $(Fe_{39}Cr_6Mo_4Si_{10})C$	Prior austenite grain and martensite lath boundaries and intra-lath	No
Vanadium carbide	FCC	V_4C_3	Low number density	No
Laves	Hexagonal	Fe_2Mo, Fe_2W, $Fe_2(MoW)$	Prior austenite grain and martensite lath boundaries and intra-lath; δ-ferrite in duplex steel	Yes
Chi (χ)	BCC	$M_{18}C$, $Fe_{35}Cr_{12}Mo_{10}C$	Intra-martensite lath; δ-ferrite in duplex steels	Yes
α'	BCC	Cr-rich ferrite	High density of fine particles in tempered martensite	Yes
η	Diamond Cubic	M_6X (X: Si, Cr, Ni, Si)		Yes
G	FCC	$Mn_7Ni_{16}Si_7$		Yes
Sigma (σ)		Fe-Cr enriched in Si, Ni, and P	Thin ribbons surrounding $M_{23}C_6$ particles	Yes
Cr_3P			Needle shape	Yes

Note: Klueh, R.L., Harries, D.R., 2001. High Chromium Ferritic and Martensitic Steels for Nuclear Applications. USA: ASTM.

Precipitate Hardening

- Precipitation hardening relies on changes in solid solubility with temperature to produce fine particles of an impurity phase which impedes the movement of dislocations
- Since dislocations are often the dominant carriers of plasticity, this serves to harden the material

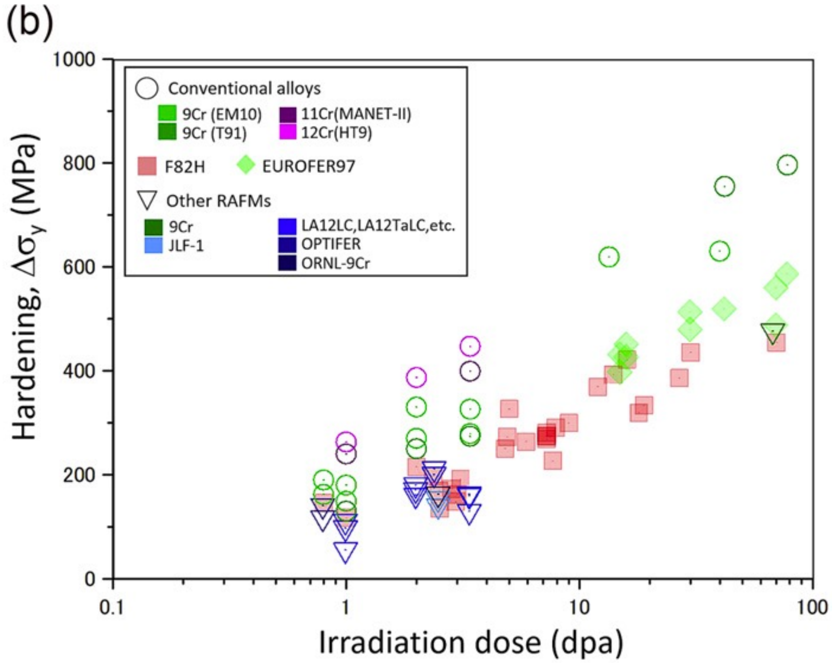




Irradiation Hardening

- Microstructure changes lead to irradiation hardening of the steel
- High amounts of carbon in 12% Cr steels leads to a large amount of precipitation, up to twice as much as 9% Cr steels
- This high carbon content is needed to use steels as martensite
- Both the steels have mainly M23C6 carbides with a small fraction of monocarbides
- This high concentration of precipitates can eventually lead to brittle failure

- The critical stress is inversely proportional to the crack length, crack length is equal to the diameter of the carbide precipitate, thus fracture stress also decreases with increasing precipitate size

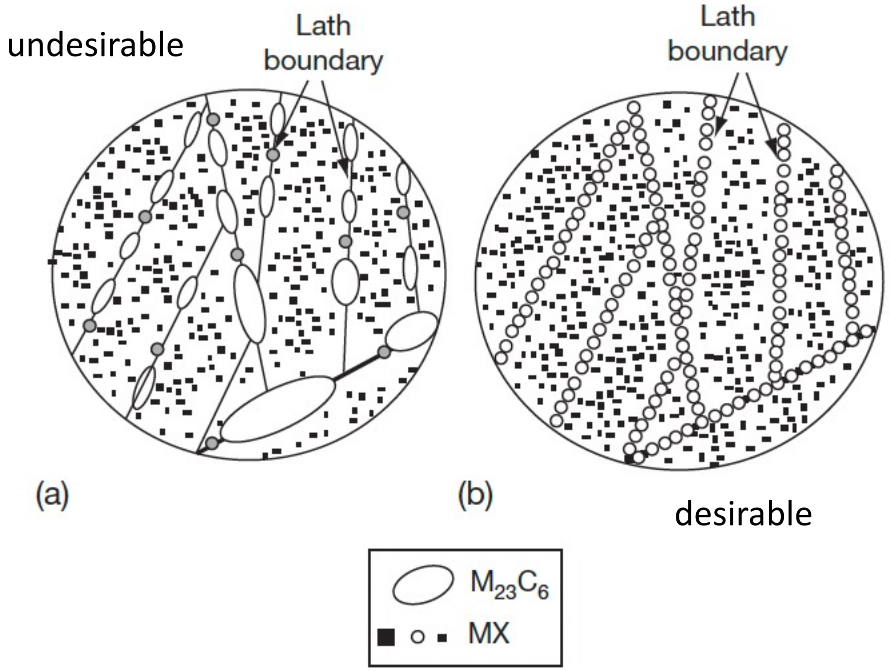


Irradiation Creep Resistance

- Irradiation creep resistance needs a good combination of thermal creep behavior and long-term microstructural stability at high temperature
- In order to fabricate creep resistant steels, you design to have a number of microstructural features that are present
- Introduce high dislocation density to increase the strength of the basic lattice
- Strengthen the host lattice by solid solution strengtheners or defects
- Stabilize the boundaries created by phase transformations by precipitating carbides along the boundaries
- Arrest dislocation glide and climb by selection of crystal structure, solid solution, interfaces, dislocation interactions
- Resist sliding of grain boundaries by introducing special types of boundaries and anchoring the boundaries with precipitates

Irradiation Creep Resistance

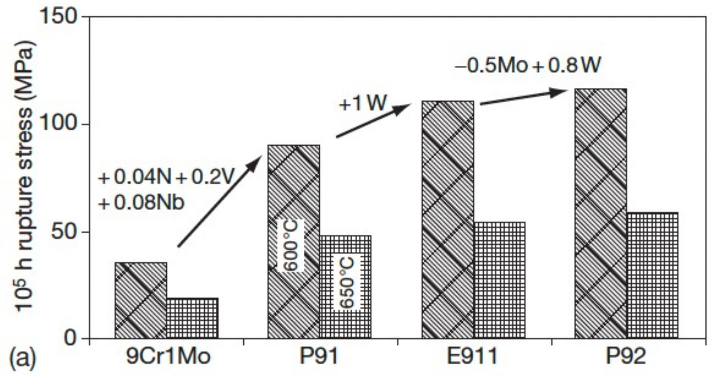
- Ensure long-term stability of the microstructure, especially against recovery and coarsening of the fine second phase particles
- In the case of 9–12 Cr steels, the martensitic lath structure decorated with only MX which should be stable over long-term service life is the most desired structure
- MX can be stabilized over M23C6 by reducing the carbon content, but we need high amounts of C to have appropriate high temperature behavior



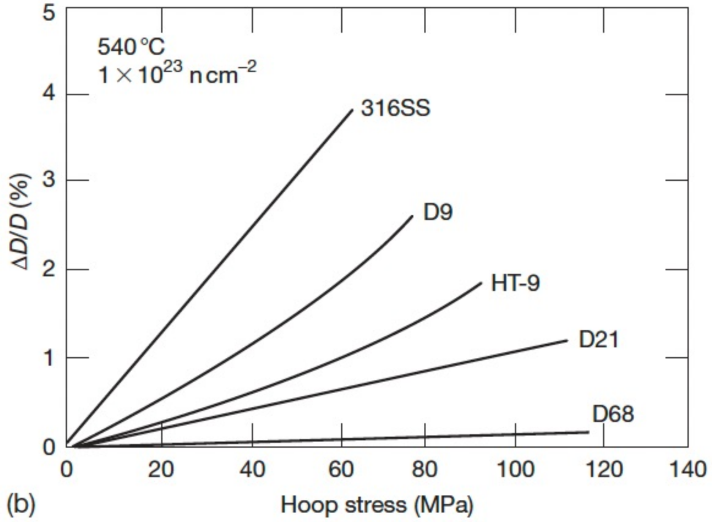
Irradiation Creep Resistance

- So careful tailoring of alloying elements has led to improvement of the creep strength
- Thermal creep behavior provides a starting point, which can then be refined by studying creep under irradiation
- The irradiation creep depends on the stress level, the temperature, and the dose

Thermal Creep

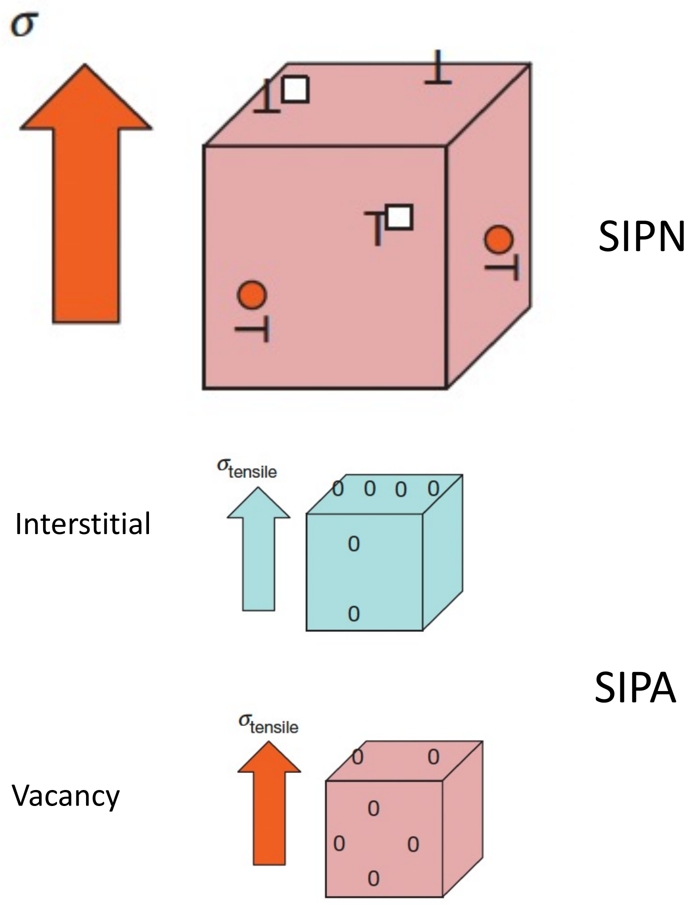


Irradiation Creep



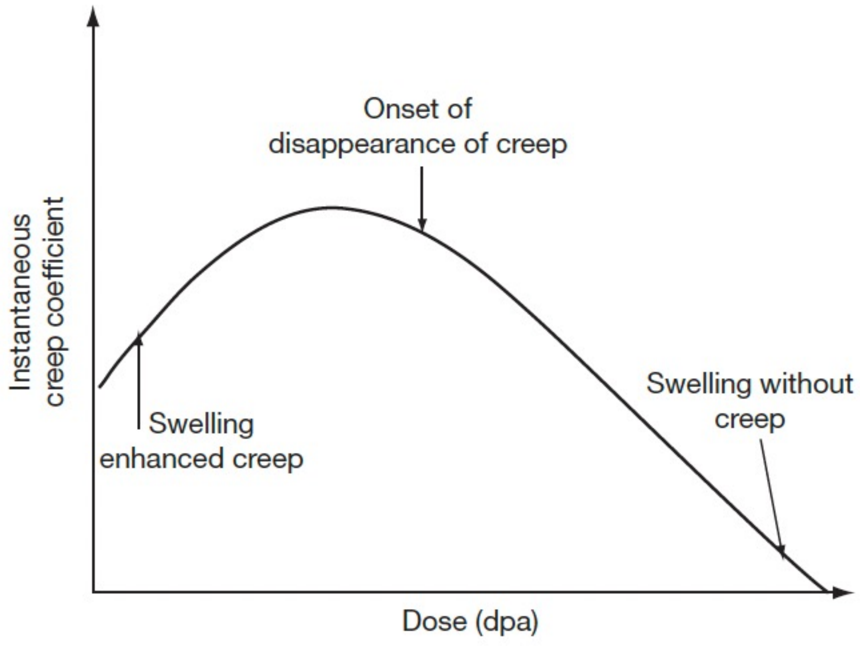
Irradiation Creep Resistance

- The excess point defects precipitate into either interstitial or vacancy loops, but not randomly
- The interaction between point defects and stress leads to the precipitation of interstitial loops parallel to the applied stress, while vacancy loops form in planes perpendicular to the stress: stress-induced preferential nucleation (SIPN)
- Under applied stress, the vacancies migrate preferentially to grain boundaries perpendicular to the applied stress, while the interstitials toward boundaries parallel to the stress: stress-induced preferential absorption (SIPA)



Creep Evolution

- The radiation-induced defects also evolve from isolated point defect to loops and voids, which have different types of influence on irradiation creep
- Irradiation creep occurs simultaneously with swelling and swelling can influence irradiation creep
- At very small dose levels, swelling enhances creep rates; beyond a certain dose level the creep component reduces; at high dose levels creep disappears, while swelling continues



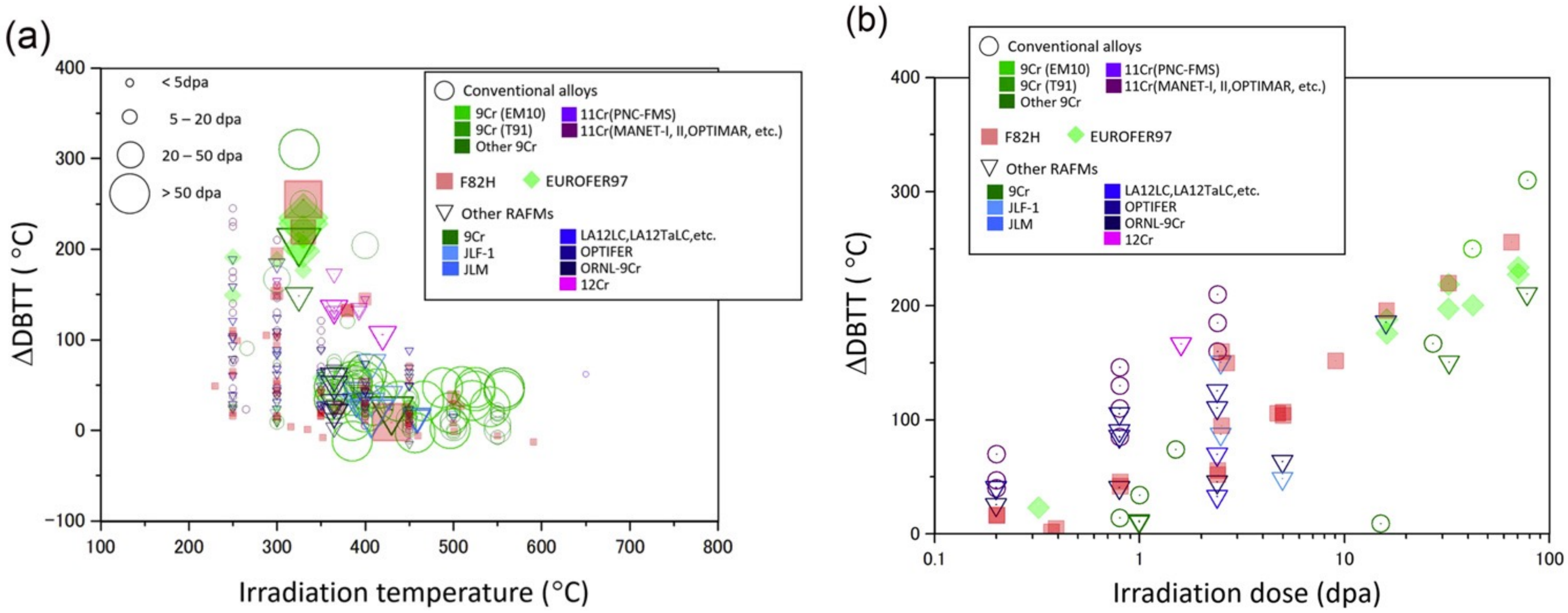
Irradiation Embrittlement

- Ferritic steels have a large number of monocarbides which aid in creep resistance
- The lath boundaries are decorated with Cr rich M23C6 precipitates which increase the thermal stability
- Embrittlement is caused by 1) segregation of elements to lath boundaries which make the grain boundaries decohesive, and 2) evolution of carbides and intermetallic phases
- For removable components such as cladding, which are subjected to high temperature and pressure with a residence time of a few years, creep is the issue which decides their design and performance
- For permanent support structures increase in hardening and loss in fracture toughness on irradiation are major issues

Irradiation Embrittlement

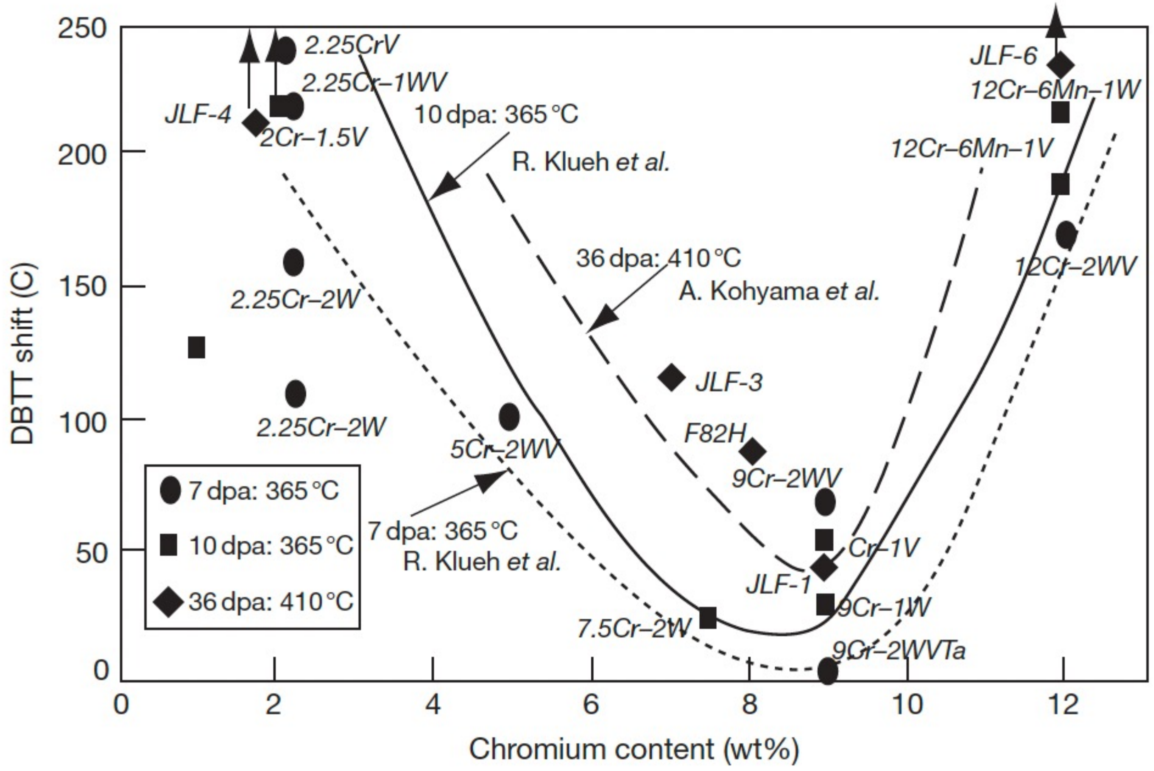
- The increase in the ductile to brittle transition temperature, DBTT, is known to be related to irradiation hardening, which is generally observed to saturate with fluence
- Evidence for a possible maximum in DBTT was observed for the 12Cr steel irradiated in the range of 35–100 dpa in the FFTF
- High fluence and/or high temperature are required before a maximum is observed
- Thus, these properties are a balance between the point defect production and irradiation-induced precipitation
- The precipitation during irradiation hardens the steel and irradiation accelerated recovery and aging soften the steel
- The high temperature recovery produces an observable saturation in hardening above ~720K

DBTT Changes



DBTT

- BCC materials can undergo significant increase in the DBTT at low T for even 1 dpa
- The minimum operating temperature to avoid embrittlement F/M steels is ~500 K
- Extensive evaluation of the embrittlement behavior of the ferritic steels for different compositions has been performed
- Compositions around 9Cr show the least change in the DBTT, and addition of phosphorous, copper, vanadium, aluminum, and silicon increase the DBTT



- The 12Cr steels, like HT9, show a larger shift in DBTT as compared to modified 9Cr–1Mo steel, balancing between swelling resistant 12Cr steels and 9Cr steel which is less prone to embrittlement than 12Cr steels

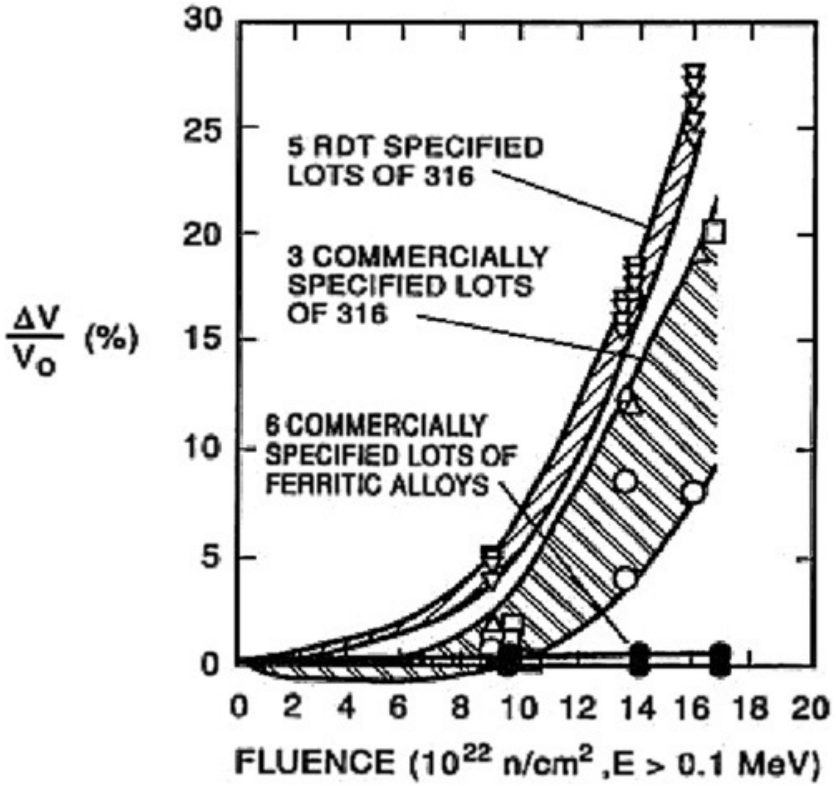
Features affecting Embrittlement

- There are a number of microstructural features that can impact the embrittlement of F/M steels
- Prior austenite grain size (PAGS)
- The size of martensitic lath and packet (which is sensitive to austenitization temperature)
- Tempering/annealing, which can increase carbide precipitate size
- The generation of helium through (n,alpha) reaction

Void Swelling Resistance

- Ferritic steels were experimentally observed to exhibit superior radiation resistance compared to austenitic steels, which is largely based on their low swelling behavior
- The 9Cr–1Mo steel, modified 9Cr–1Mo (Grade 91), 9Cr–2Mo, and 12Cr–1MoVW (HT9) have low swelling rates at doses as high as 200 dpa
- The threshold dose for swelling in ferritic steels is as high as nearly 200 dpa, compared to 80 dpa for the present generation austenitic stainless steel

- HT9 shows 1% swelling at 693 K for 200 dpa

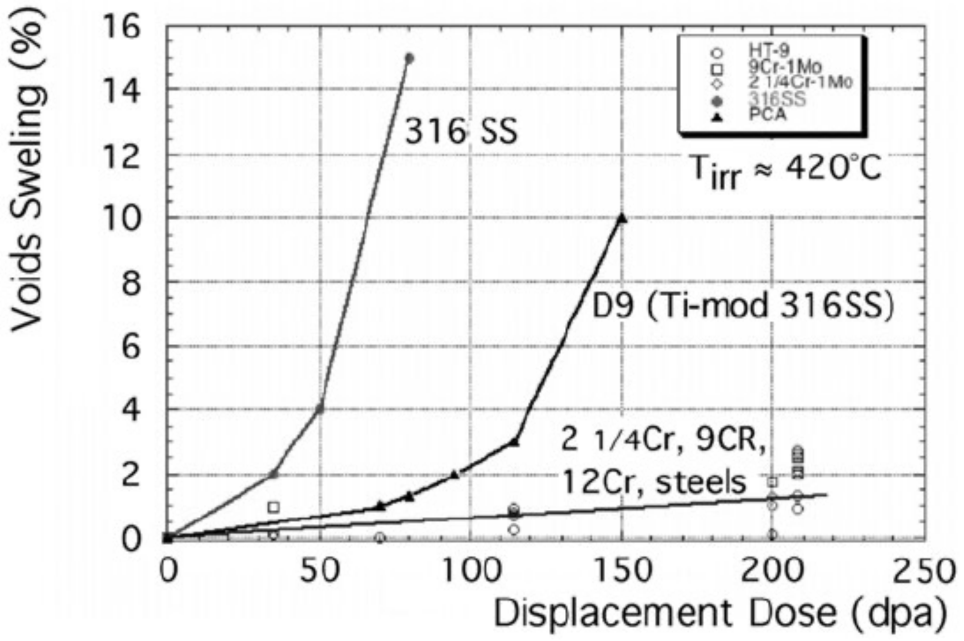


Void Swelling

- Void swelling depends crucially on the structure of the matrix lattice, in which irradiation produces the excess defects
- There are several reasons why the swelling resistance in ferritic steels is lower than austenitic steels
- First, the relaxation volume for interstitials is large in ferrite than in austenite
- Thus, for a given interstitial, the strain field is larger in ferrite, which has the impact of more strongly repelling other interstitials, and more strongly attracting vacancies
- Second, the migration barrier of vacancies in ferrite is much lower than in austenite (0.55 eV to 1.4 eV)
- Since vacancies are more mobile in ferrite, recombination is more likely with the dispersed isolated interstitials
- Third, excess vacancies can be trapped at carbide particles, of which there is a high number density, as the C-vacancy binding energy in ferrite is twice that in austenite

Void Swelling

- Fourth, the way dislocations and solutes interact in ferrite makes them strong sinks, generating strain fields that attract vacancies and provide a high sink density
- Finally, the complex microstructure of martensite laths and a ferrite matrix inherently produces a very high density of sinks, with some arguing the fundamental microstructure of F-M steels governs the improved swelling behavior
- Some combination of all of these factors likely contribute



Ferritic/Martensitic Steels Summary

- 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
- Tailoring of alloying elements has allowed for improved creep strength
- Embrittlement is caused by segregation of elements to lath boundaries and evolution of precipitates
- DBTT shift is minimized for 9Cr steels
- F/M steels swell very little, one of the key features making them suitable for application