NE 591: Advanced Reactor Materials

Fall 2021

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Last Time

- To remove this (U,Mo)Al phase, we can: 1) coat the particles; 2) modify chemistry (such as by adding Si); 3) substitute the Al matrix with another materials; 4) remove the matrix
- Fuel fabrication specifications can dramatically affect the microstructure and thus the performance of the fuel – this is more critical for monolithic fuels
- The Zr interdiffusion barrier prevents UMo-Al interaction, but creates new interaction layers with a series of phases present
- UMo fuel creeps, creating a bulge just inside the edge of the fuel
- Decomposed regions can accelerate grain refinement and swelling and can be reduced through chemical homogenization and annealing
- Al is ideally suited for the research reactor environment with its excellent corrosion and swelling resistance at applicable temperatures
- Microstructural modeling is attempting to describe the variety of governing phenomena in UMo fuel

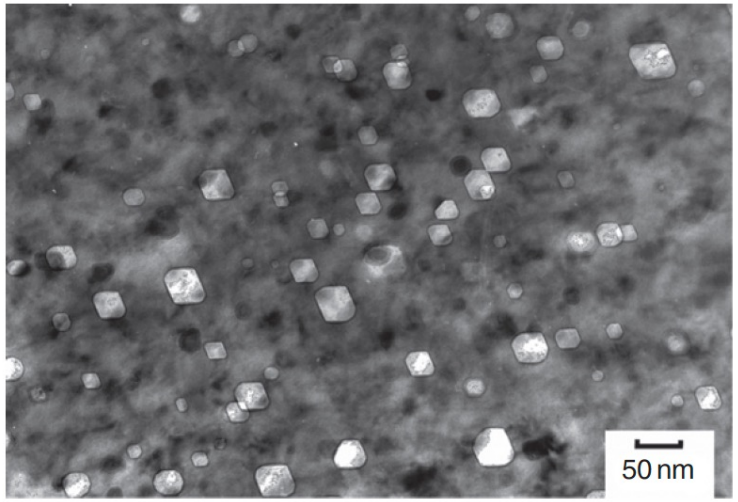
Quantum Espresso Q&A

- What do you got?

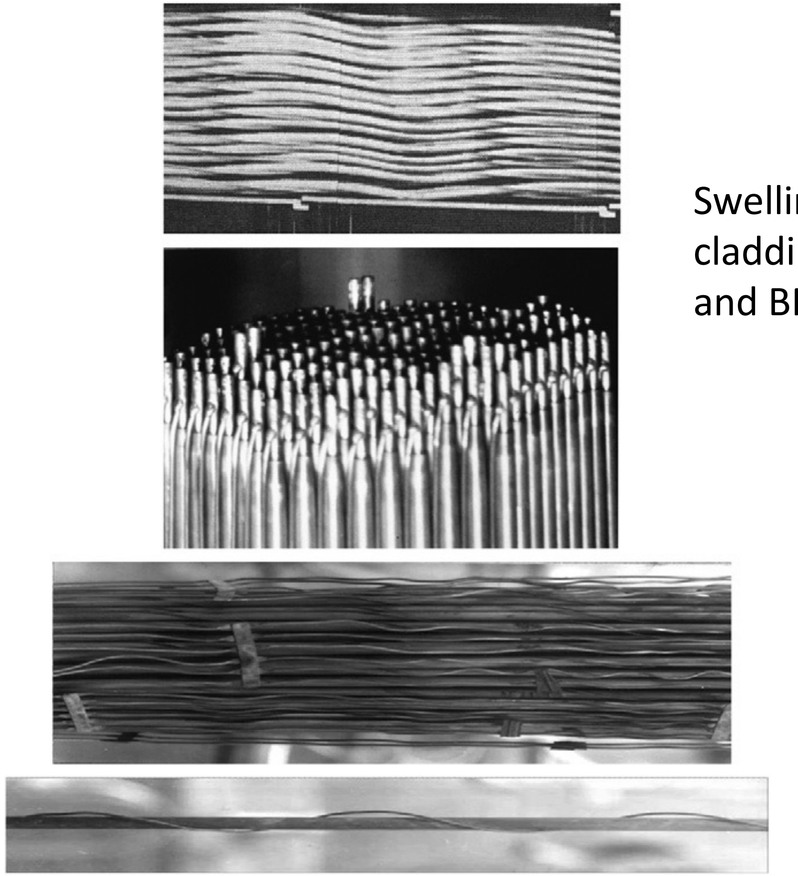
ADVANCED CLADDING

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



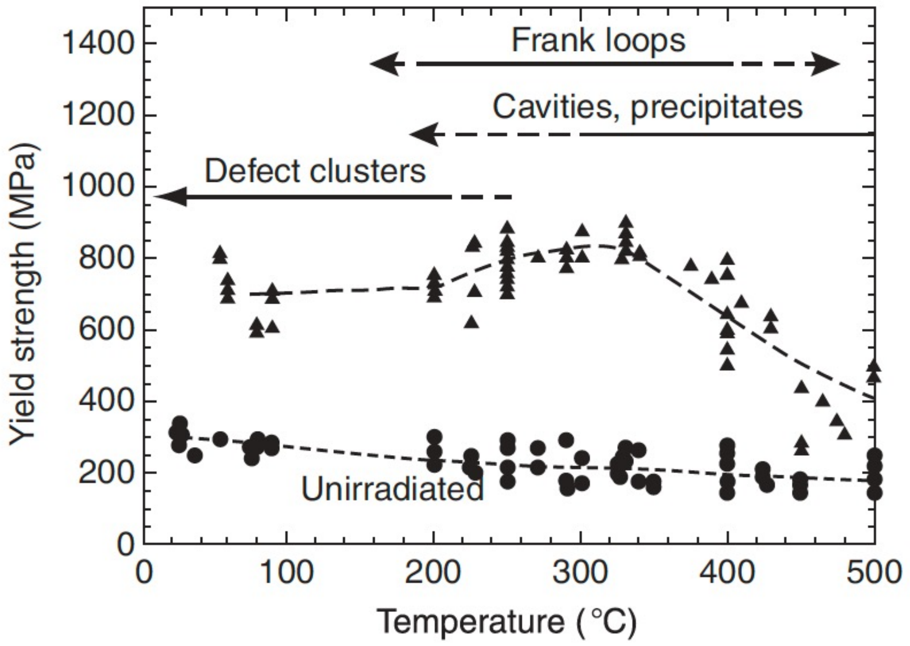
Void swelling in 304SS

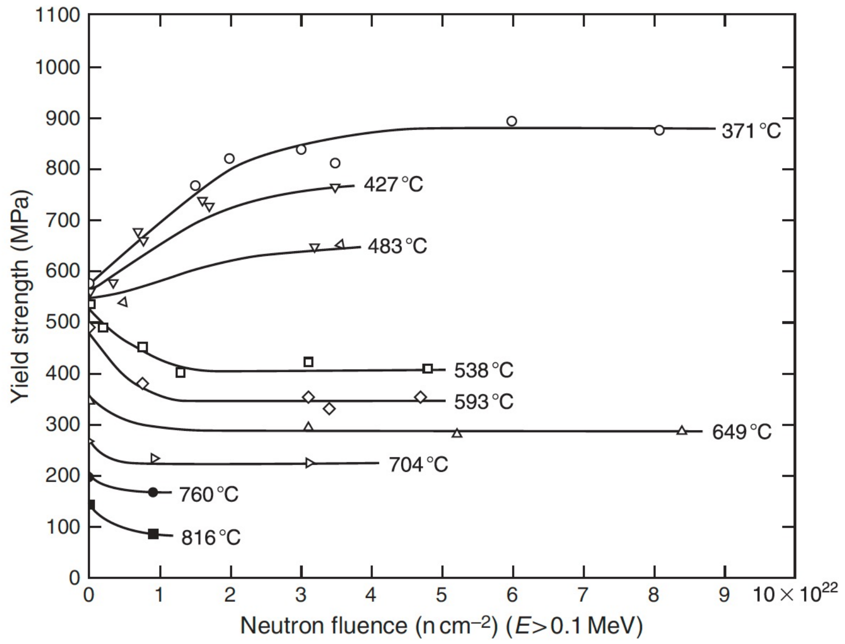


Swelling of cladding in FFTF and BN-600

The need for advanced cladding

- 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





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, irradiation, and helium embrittlement

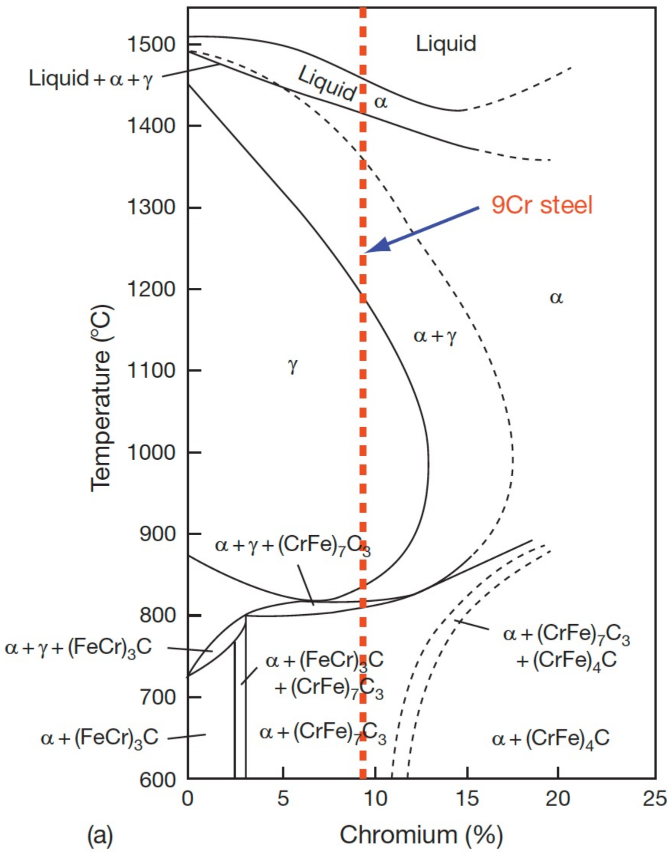
Criterion	*Clad tube*	*Wrapper tube*
Exposure conditions (only trends; exact values depend on core design)	Maximum temperature: 923–973 K Steeper temperature gradient Higher stresses from fission gas pressure Chemical attack from fuel Average neutron energy: 100 keV Neutron flux: 4–7 $\times$ 10^{11}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

Ferritic-Martensitic Steels

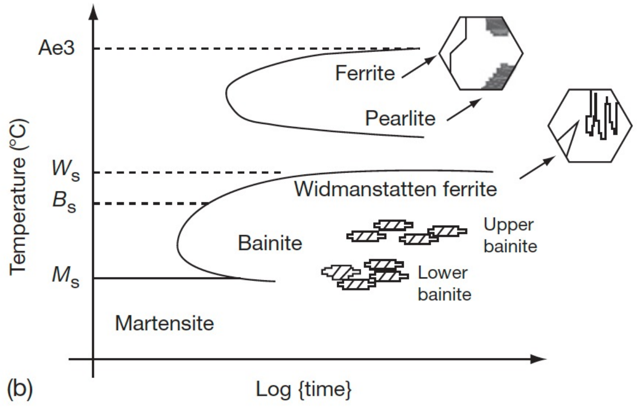
- The advanced ferritic and ferritic–martensitic steels of current interest have evolved from creep-resistant ferritic steels
- Subsequent developments through different levels of Cr and Mo have led to the current ferritic and ferritic–martensitic steels: 9–12% Cr–Mo steels
- F-M steels have advantageous 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

Ferritic-Martensitic Steels

- The ability to retain ferrite (bcc Fe is dependent upon the alloying elements
- In addition to Cr and Mo, the amount of Si, V, and C affect the phase boundaries
- Accordingly, the 9CrMo 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

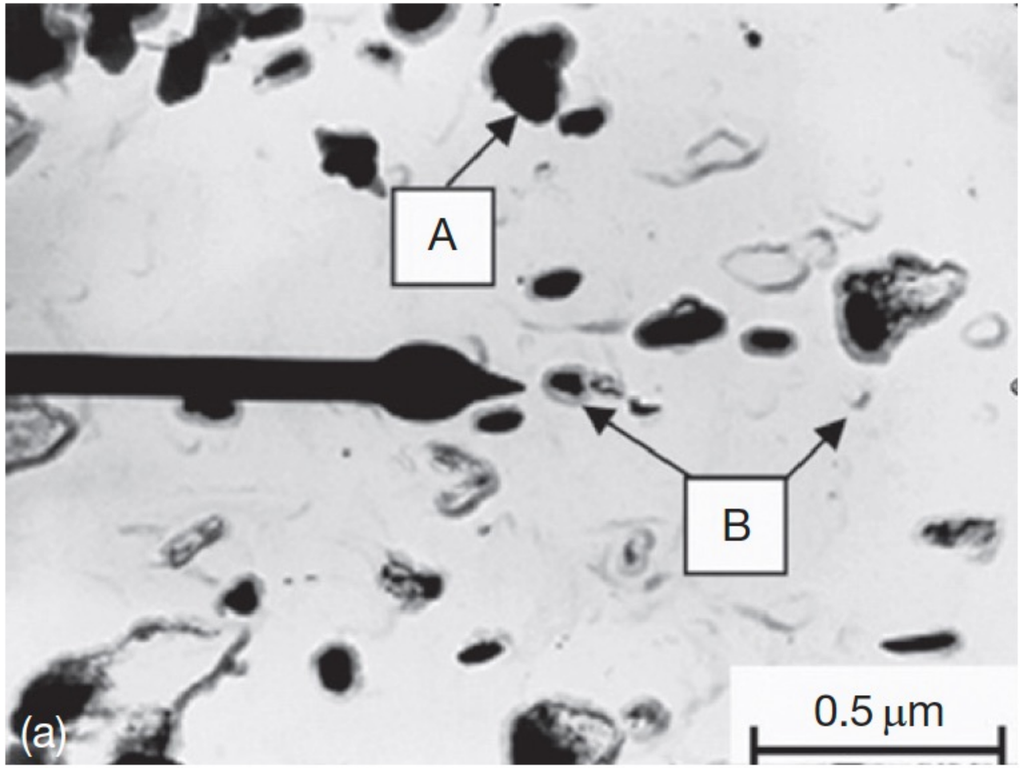
Composition Optimization

- 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

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

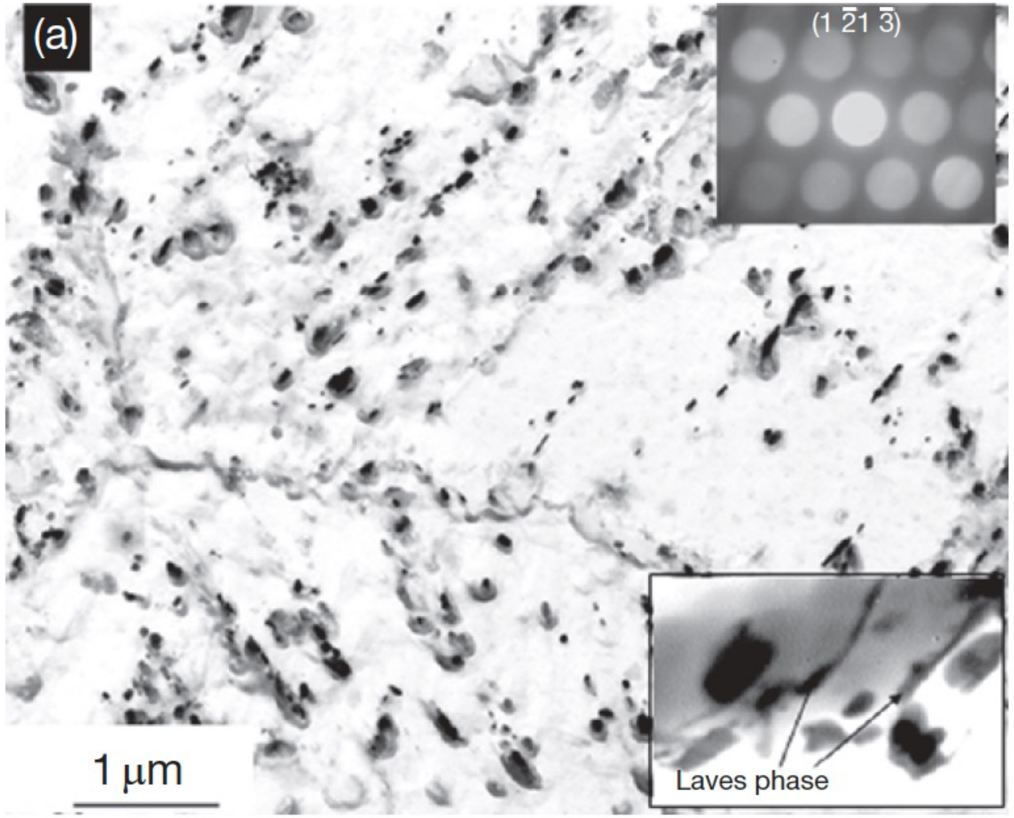
Microstructure

- The microstructure of the steels consists of martensite laths containing dislocations and coarse M23C6 particles located at prior austenite and ferrite grain boundaries
- Finer carbide precipitates are found within the laths and at the lath/subgrain boundaries
- M2X precipitates rich in Cr also form (CrMoWV)2CN



Microstructure

- In reactor, this microstructure will change, with the M2X precipitates being replaced by MX intermetallic and Laves phases
- 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



Void Swelling Resistance

- Ferritic steels were experimentally observed to exhibit superior radiation resistance compared to austenitic steels
- This 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 in contrast 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
- This 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)

Void Swelling

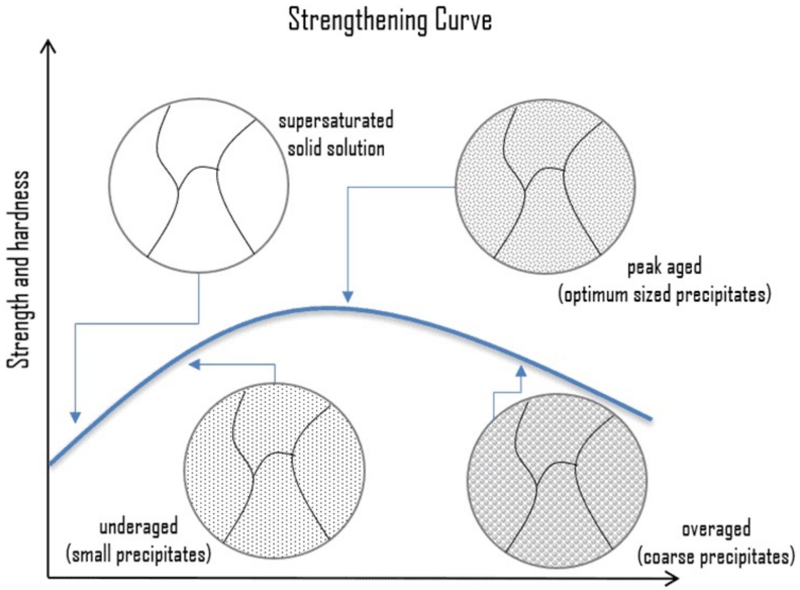
- Since vacancies are more mobile in ferrite, recombination is more likely with the dispersed isolated interstitials
- Additionally, excess vacancies can be trapped at carbide particles
- The C-vacancy binding energy in ferrite is twice that in austenite
- Finally, the way dislocations and solutes interact in ferrite makes them strong sinks
- Given that solutes are oversized substitutionals or interstitials and have a high binding energy with dislocations (often the case), “atmospheres” of solutes can form around dislocations, which are effective sinks for vacancies
- These fundamental differences in the behavior of solutes and point defects make ferritic steel superior to austenitic steels, with respect to void swelling

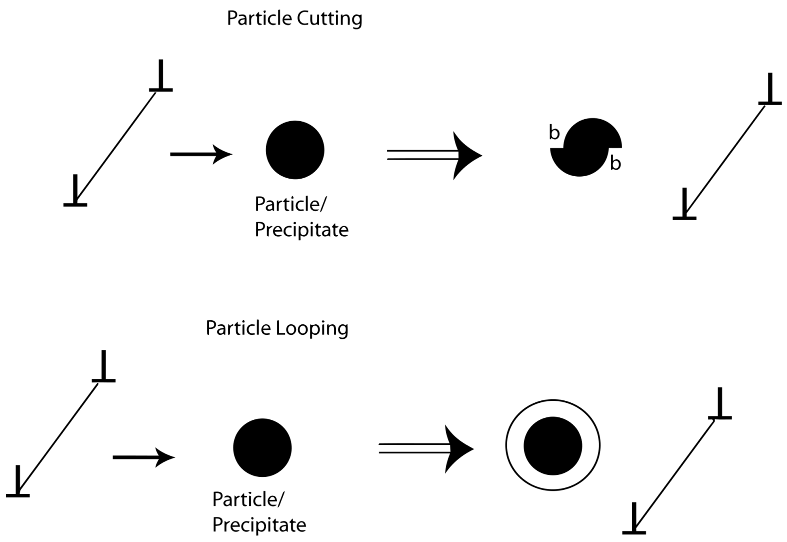
Irradiation Hardening

- Microstructure changes due to irradiation harden 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 to propagate a crack is inversely proportional to the crack length, and crack length at initiation is equal to the diameter of the carbide precipitate, then fracture stress also decreases with increasing precipitate size

Precipitate Hardening

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





Irradiation Hardening

- Cr rich, bcc alpha' precipitates form in the higher chromium steel during thermal exposure and irradiation lead to hardening and embrittlement of the steel
- Delta ferrite can promote the formation of alpha' precipitates
- Fe2Mo type precipitates have also been observed to form in HT9 and T91
- The σ phase (Fe–Cr phase, enriched in Si, Ni, and P) has been observed to form around the M23C6 particles in 9–13% Cr martensitic steels after irradiation
- σ phase formation is considered to be caused by radiation induced segregation

Irradiation Creep Resistance

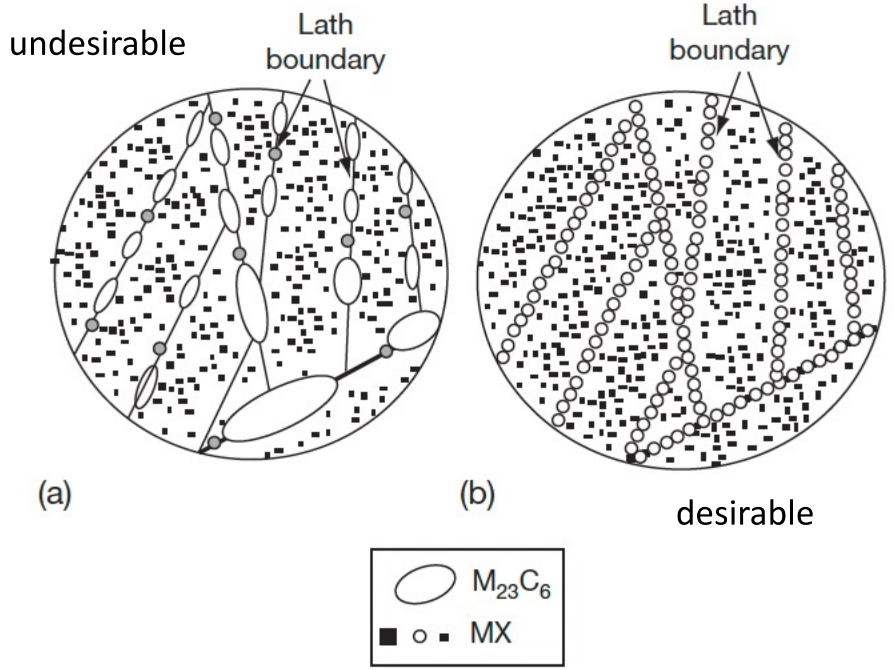
- Irradiation creep resistance needs a good combination of thermal creep behavior and long-term microstructural stability at high temperature
- In order to fabricate creep resistant steels, you design to have a number of microstructural features that are present

- 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

Irradiation Creep Resistance

- 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
- 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



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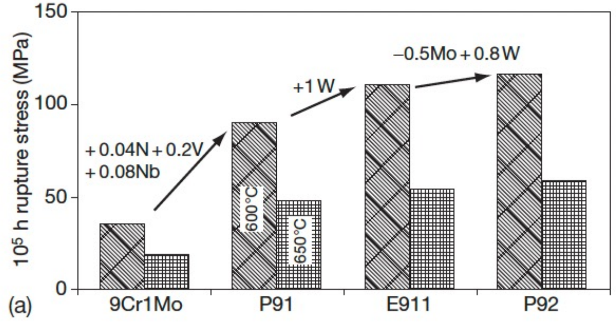
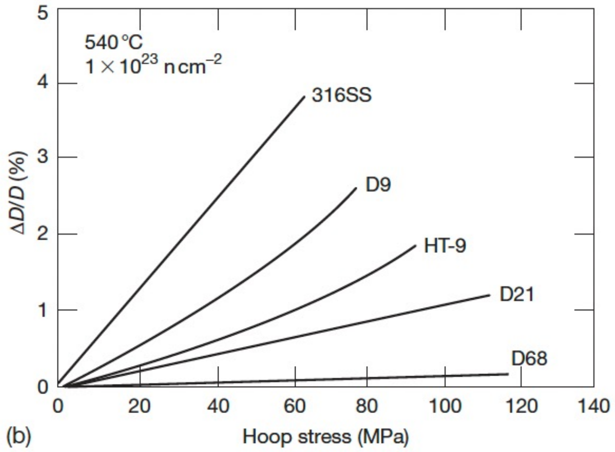
Irradiation Creep Resistance

- This microstructure can only be obtained with very low amounts of C, and we need high amounts of C to have appropriate high temperature behavior
- So careful tailoring of alloying elements has led to improvement of the creep strength

Thermal Creep

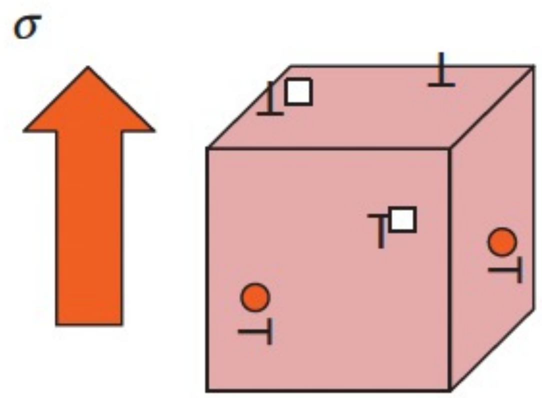


Irradiation Creep



Irradiation Creep Resistance

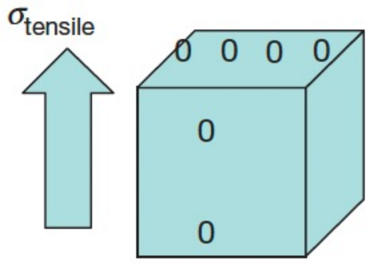
- The excess point defects precipitate into either interstitial or vacancy loops, but not randomly
- The interaction between point defects and stress leads to the precipitation of interstitial loops parallel to the applied stress, while vacancy loops form in planes perpendicular to the stress
- This stress-induced preferential nucleation (SIPN) results in additional creep strain solely due to irradiation



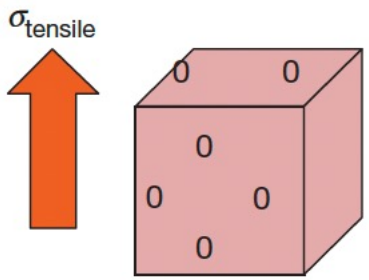
Irradiation Creep Resistance

- Under applied stress, the vacancies migrate preferentially to grain boundaries perpendicular to the applied stress, while the interstitials toward boundaries parallel to the stress
- This is equivalent to removing material from planes parallel to the stress to those which are perpendicular to the applied stress, introducing additional creep strain
- This process is called the stress-induced preferential absorption (SIPA

Interstitial

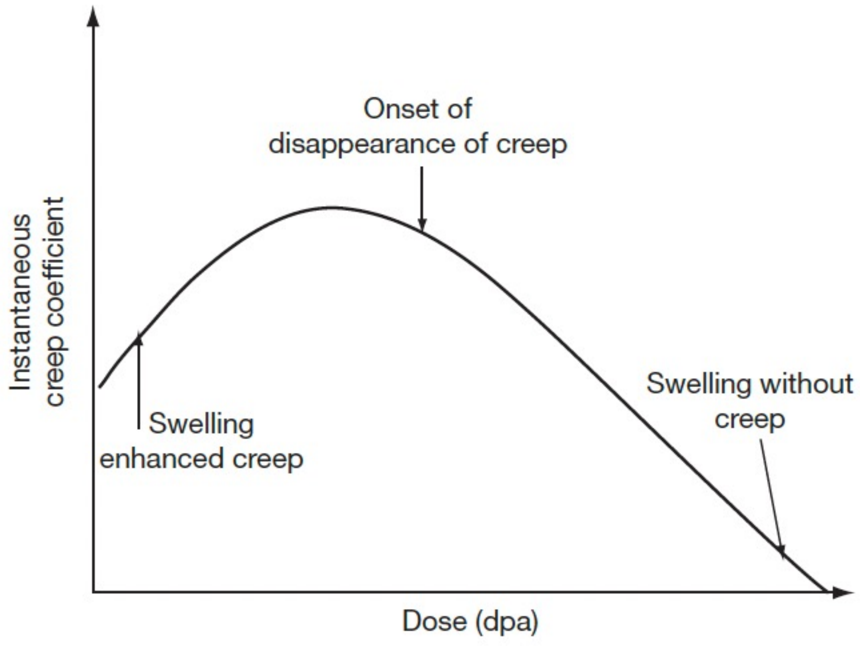


Vacancy



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 sometimes, swelling influences 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 these large of monocarbides, which aid in creep resistance
- The lath boundaries are decorated with Cr rich M23C6 precipitates which increase the thermal stability of the steel
- 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 clad, which are subjected to high temperature and pressure with a residence time of a few years, creep embrittlement is the issue which decides their design and performance
- 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

Irradiation Embrittlement

- Extensive evaluation of the embrittlement behavior of the ferritic steels for different chemistry has been performed