

NE 591: Advanced Reactor Materials

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Dr. Benjamin Beeler

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
- $M_{23}C_6$ and monocarbide precipitate are prevalent both along grain boundaries and within the grains; $M_{23}C_6$ 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

ADVANCED CLADDING

Irradiation Embrittlement

- Ferritic steels have these large monocarbides which aid in creep resistance
- The lath boundaries are decorated with Cr rich $M_{23}C_6$ 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 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
- For permanent support structures increase in hardening and loss in fracture toughness on irradiation are major issues

Irradiation Embrittlement

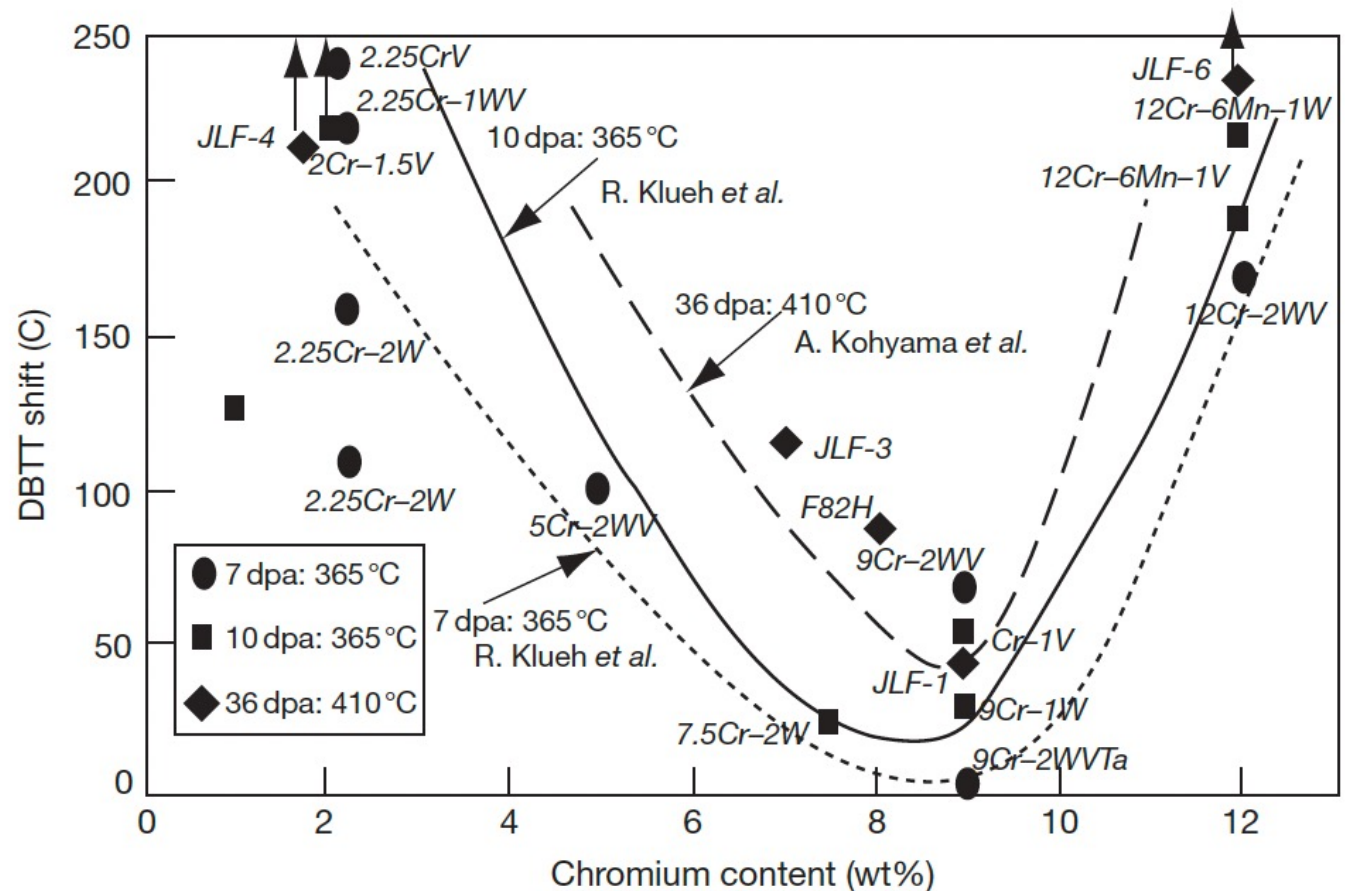
- The increase in the ductile to brittle transition temperature, DBTT, is known to be related to irradiation hardening, which is generally observed to saturate with fluence
- Evidence for a possible maximum in DBTT was observed for the 12Cr steel irradiated in the range of 35–100 dpa in the FFTF
- High 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 $\sim 720\text{K}$

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 chemistry has been performed
- Compositions around 9Cr show the least change in the DBTT
- Chemical variation affects on DBTT changes has been thoroughly studied
- Addition of phosphorous, copper, vanadium, aluminum, and silicon increase the DBTT

DBTT

- The 12Cr steels, HT9, show a larger shift in DBTT as compared to modified 9Cr–1Mo steel
- The balance is always between nearly nil 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,α) reaction
- For low thickness components, the triaxial stress necessary for the embrittlement does not develop, which reduces the intensity of this otherwise serious problem of embrittlement in ferritic steels

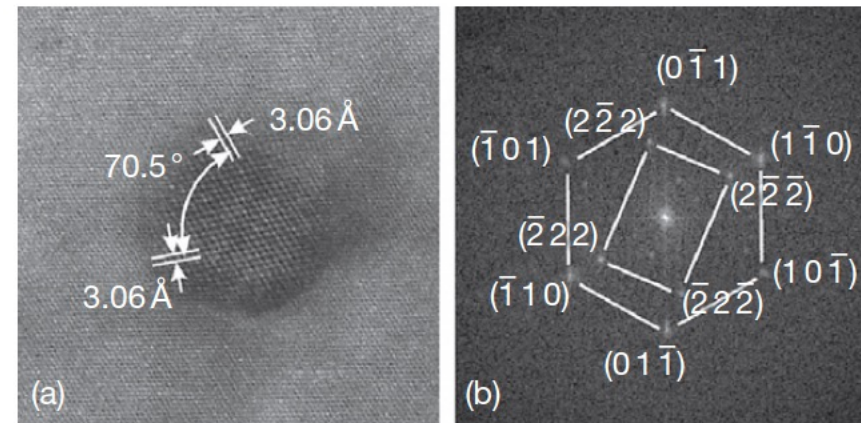
Ferritic/Martensitic Steels Summary

- Refer to “last time” slide...
- Embrittlement is caused by segregation of elements to lath boundaries and evolution of precipitates
- Maximum DBTT shift occurs in F/M steels for high T or fluence
- DBTT shift is minimized for 9Cr steels
- Microstructure can impact the embrittlement behavior
- In thin-walled materials, such as cladding, the stress state that leads to cladding embrittlement is typically not prevalent

ODS STEELS

Oxide Dispersion Strengthened

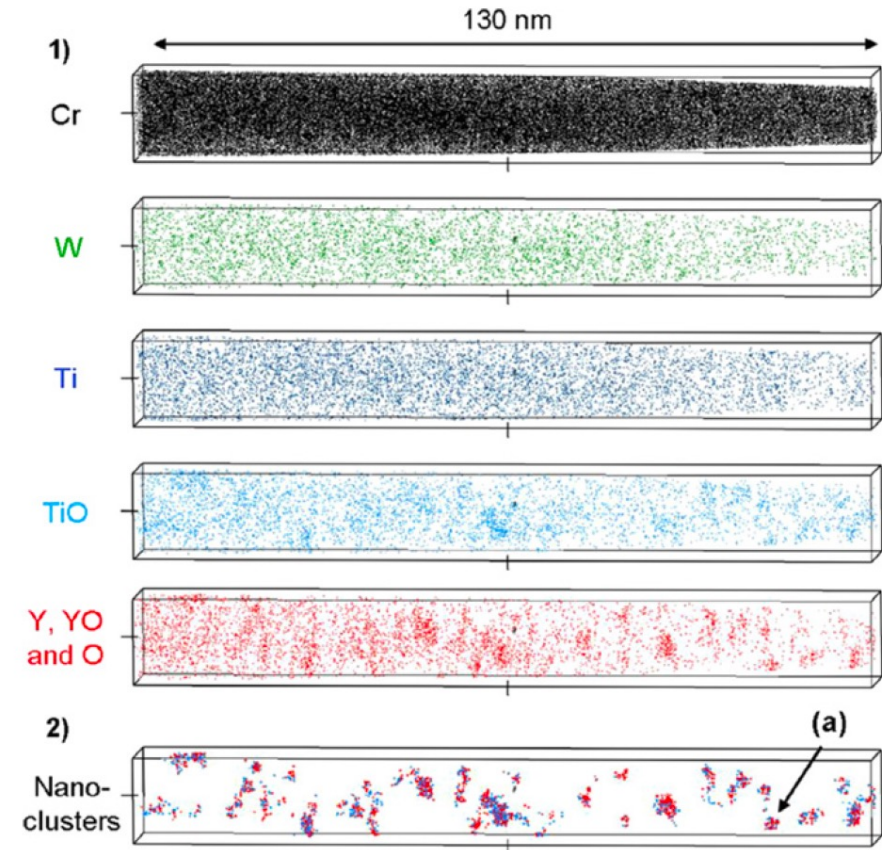
- Thermally stable oxide particles dispersed in the ferritic matrix improve the radiation resistance and creep resistance at high temperature
- ODS steels have a strong potential for high burnup (long-life) and high temperature applications typical for SFR fuels
- Typically, Y_2O_3 particles or $\text{Y}_2\text{Ti}_2\text{O}_7$ particles



Y_2O_3 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 decomposed 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

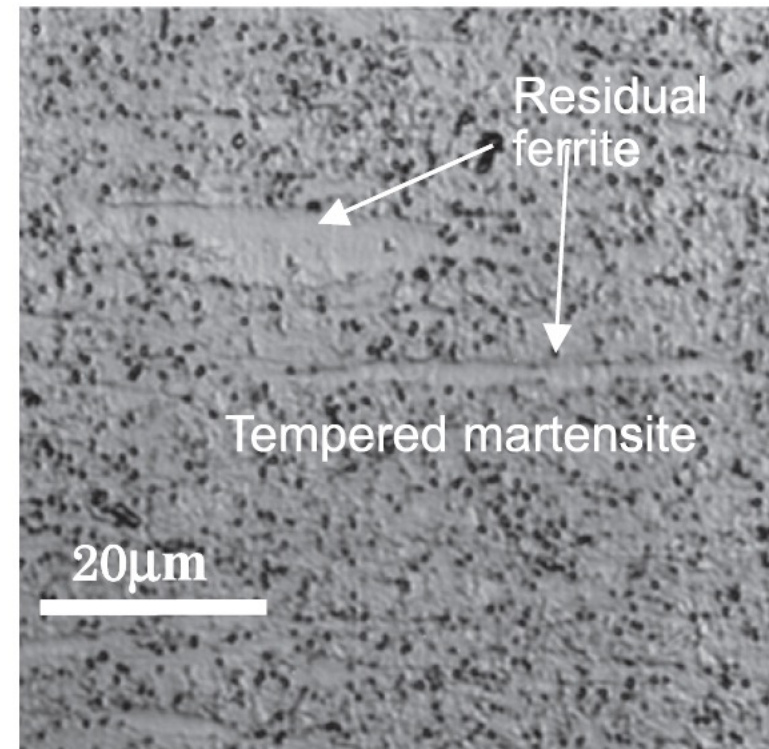


9Cr-ODS

- 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-ODS 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 in order to improve high-temperature strength by means of solid solution hardening

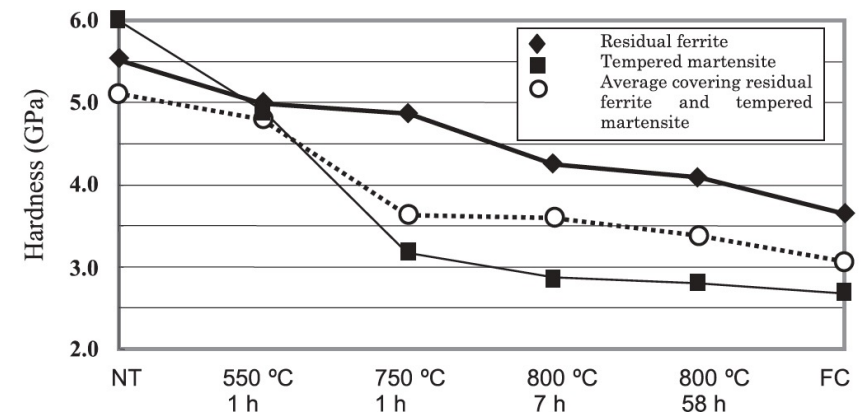
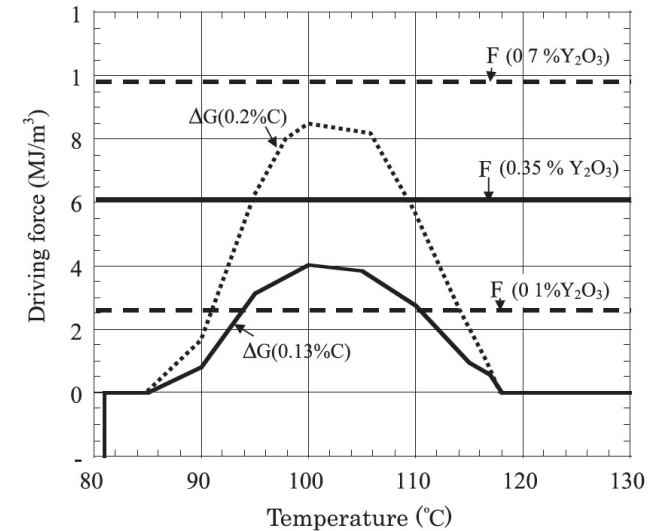
9Cr-ODS microstructure

- 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



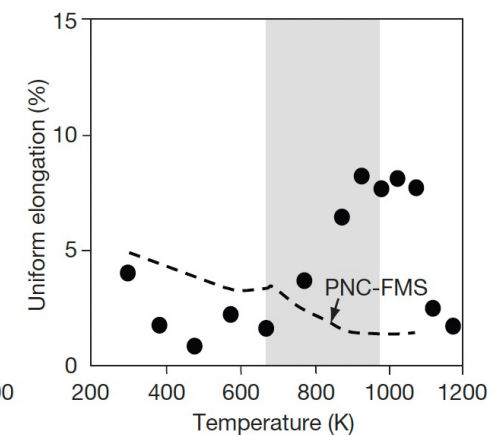
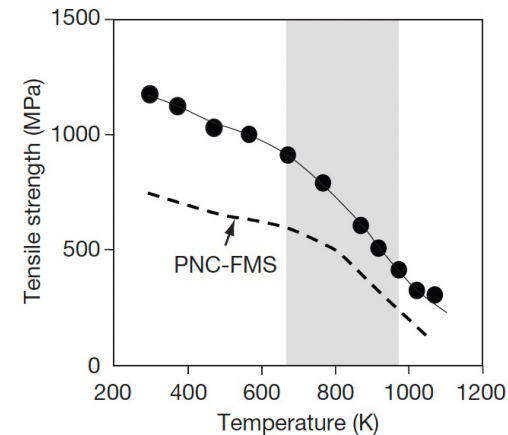
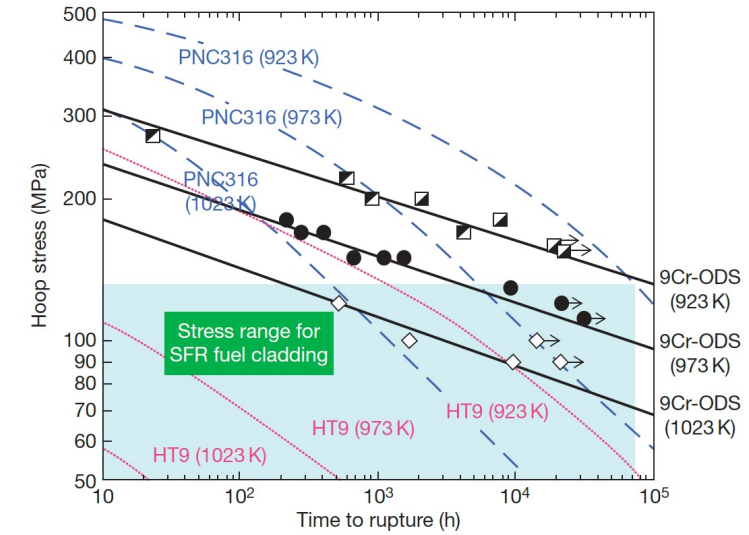
Residual Ferrite

- Annealing results in the formation and precipitation of Y–Ti complex oxide particles at elevated temperatures of 700C or higher
- Since the reverse transformation of alpha (ferrite) to gamma (austenite) takes place at a temperature over 850C, alpha ferrite is attributed to the presence of the Y-Ti-O particles
- These particles block the motion of the alpha-gamma interface, thereby partly suppressing the reverse transformation from alpha to gamma-phase



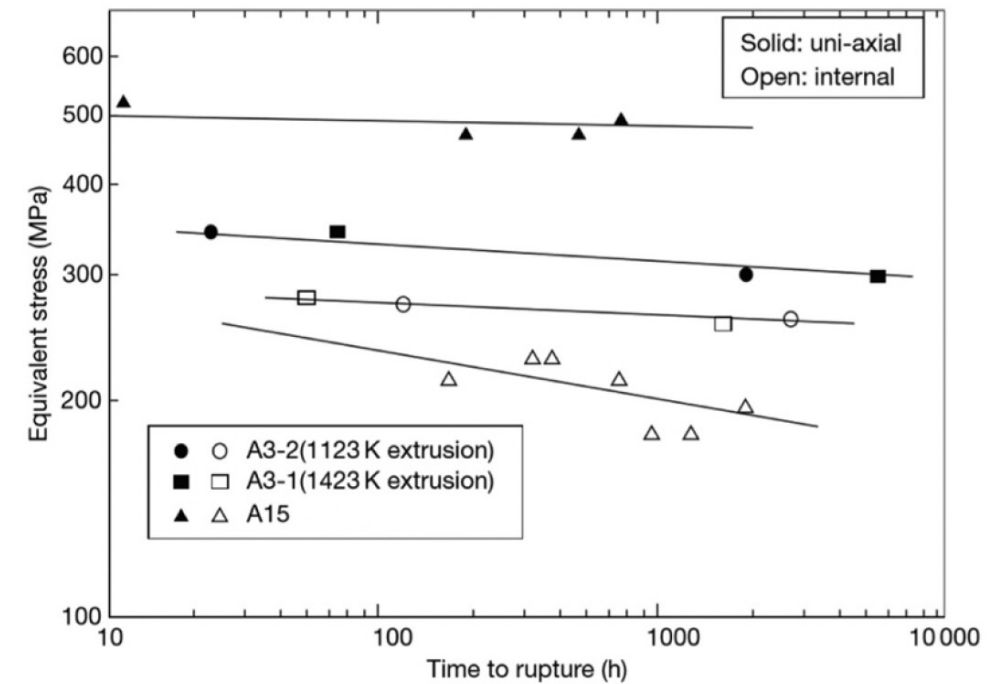
Mechanical Properties

- 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 $\sim 700^\circ\text{C}$
- 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



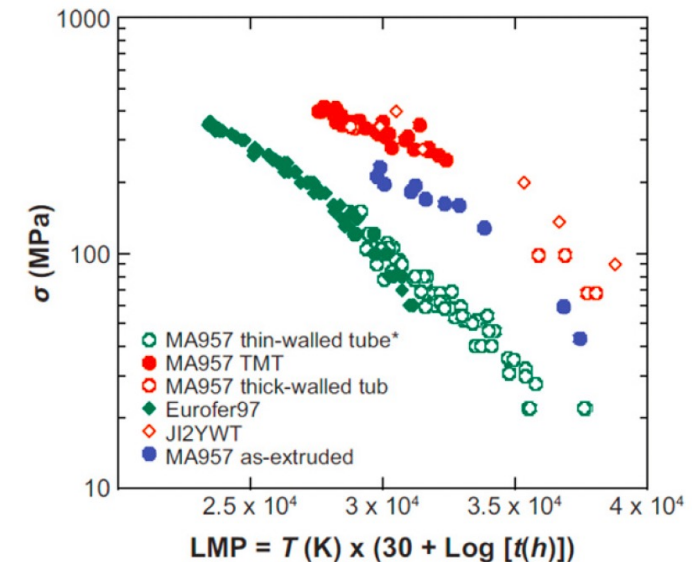
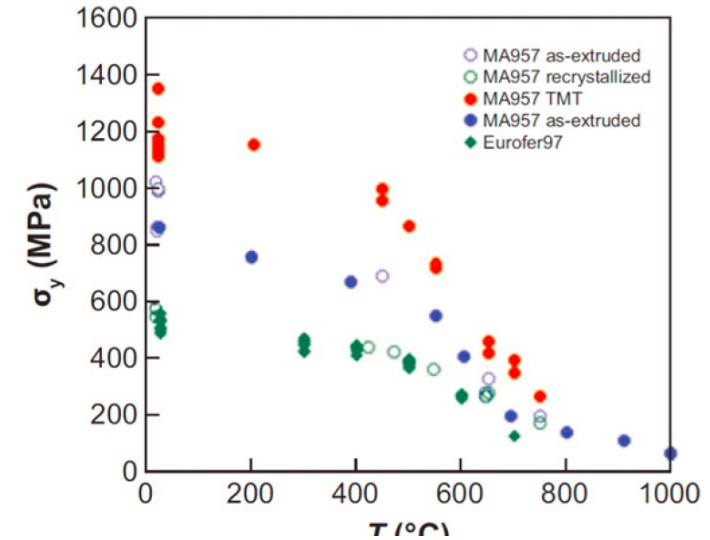
Ferritic 12Cr-ODS Steel

- 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
- If the Y_2O_3 content is kept sufficiently low, an equiaxed grain structure can be maintained, providing more isotropic mechanical properties



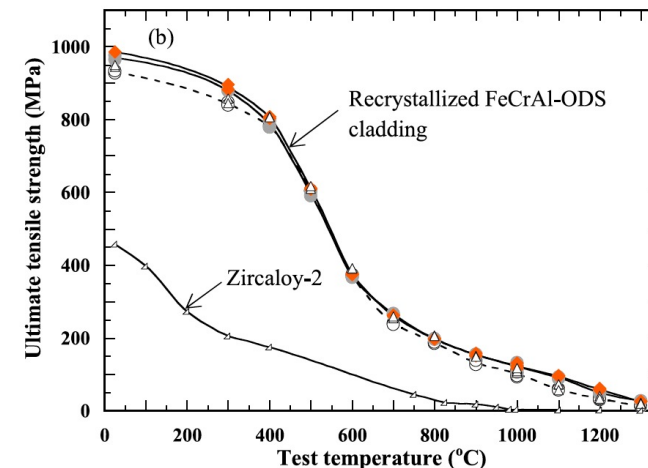
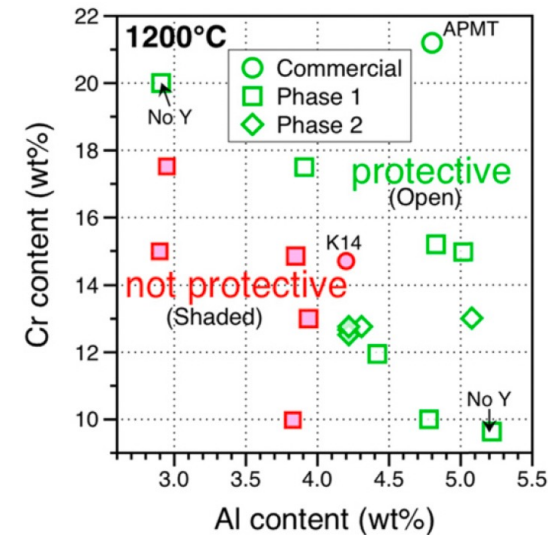
NFAs

- 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 can yield excellent strength and radiation resistance, but make fabrication processes very difficult
- MA957 and Eurofer are examples of NFAs



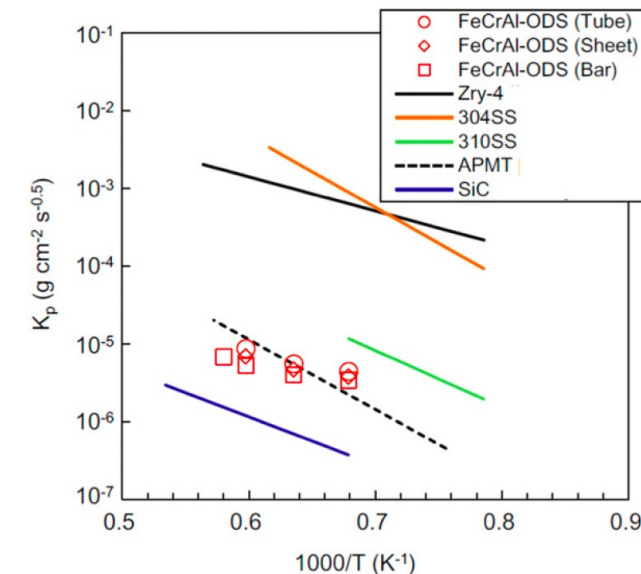
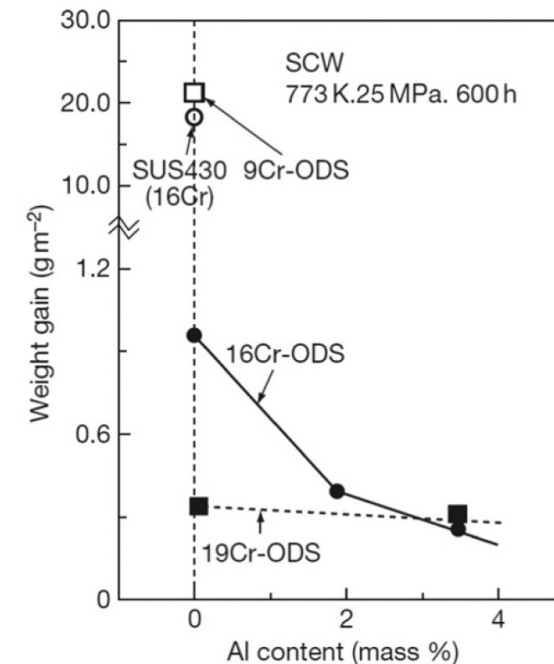
FeCrAl-ODS Steel

- FeCrAl steels, with and without ODS are of interest since Al-containing steels produce the stable alumina (Al_2O_3) scale to prevent direct reaction of Fe with steam
- A nominal composition of Fe-10Cr-6.1Al-0.3Zr (wt%) with 0.3wt% Y_2O_3 has been studied by ORNL
- Zr is added to prevent Y-Al oxide particle formation



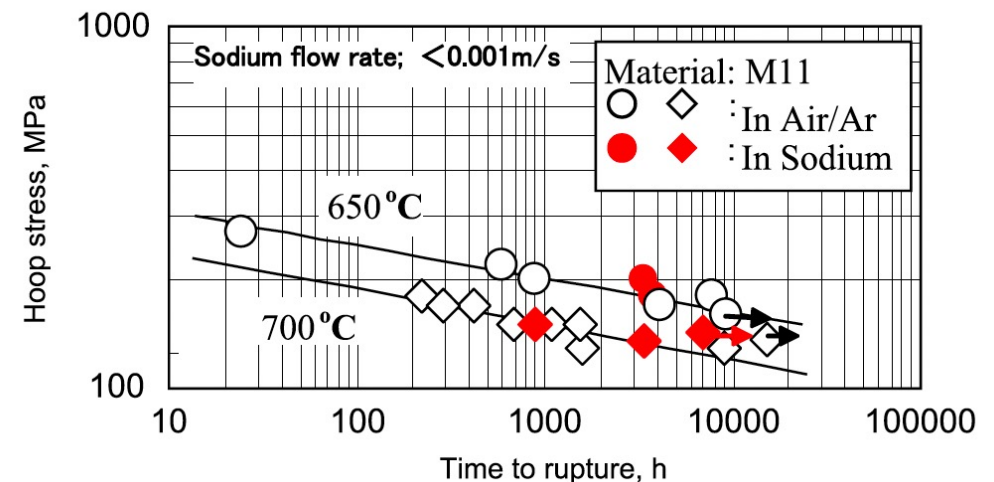
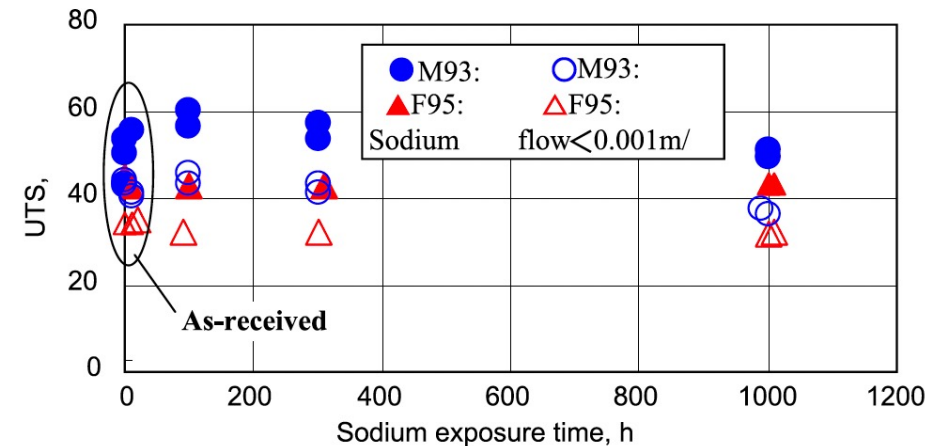
Corrosion

- 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



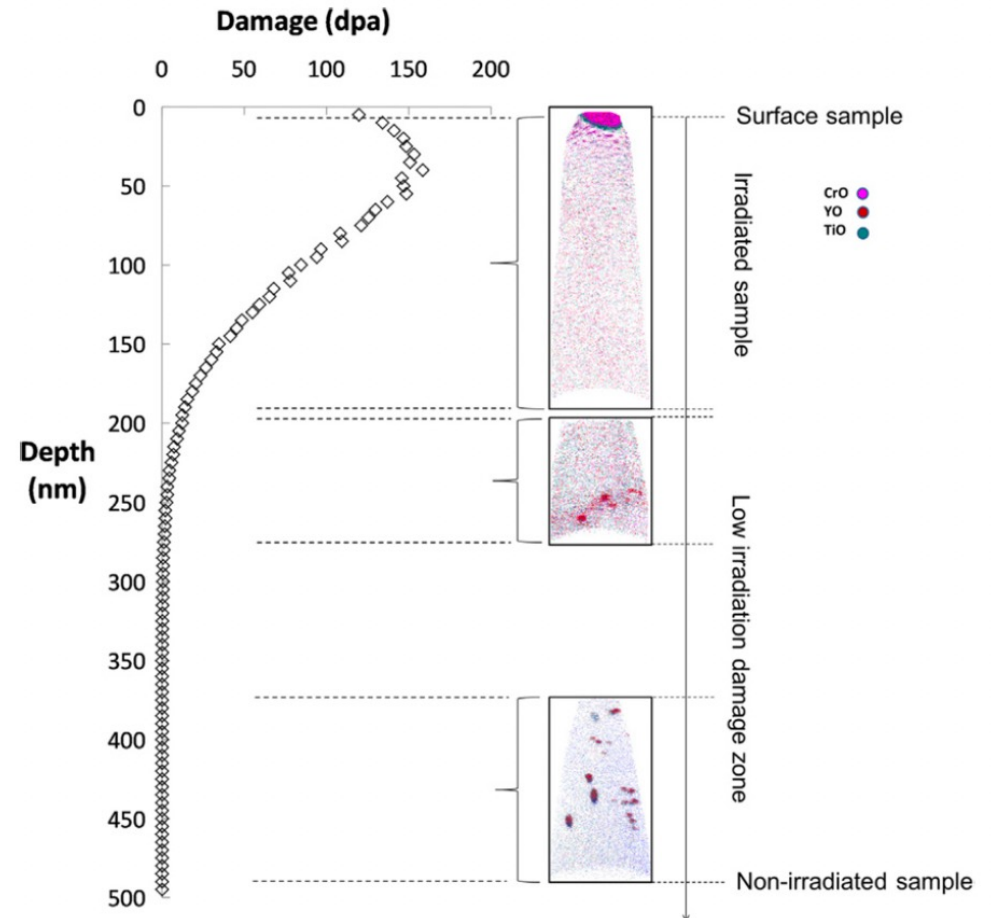
Liquid Na Compatibility

- 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 is the ejection of atoms from oxide particles due to high energy PKAs and the disordering of the particles



Irradiation Effects

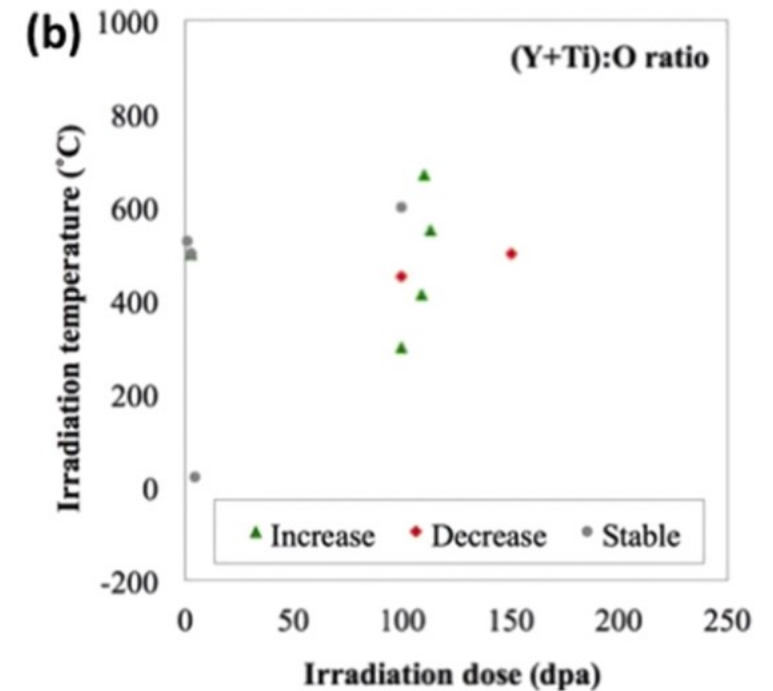
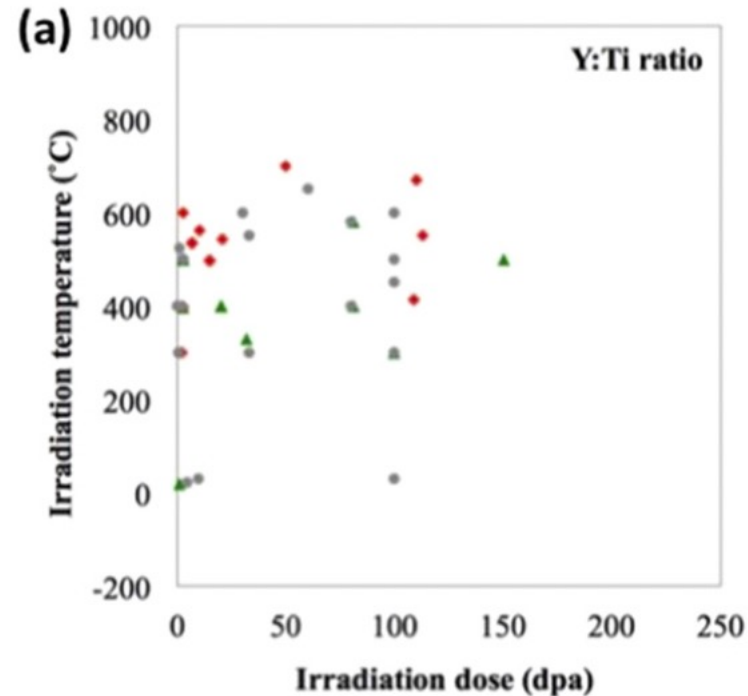
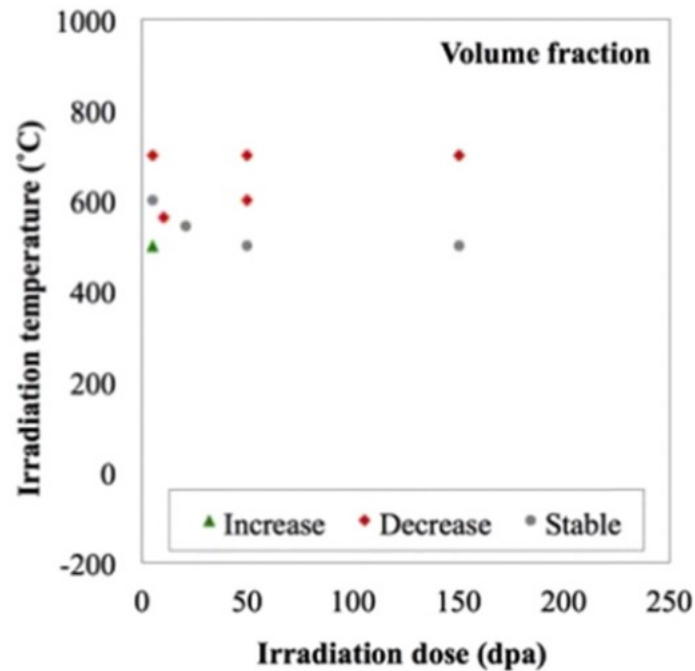
- At higher temperatures where vacancy diffusion is possible, ballistic dissolution works in conjunction with irradiation-assisted diffusion and changes the dispersion of oxide particles
- The atoms ejected from oxide particles can diffuse back to the original oxide particles, stay in the matrix, or reach other oxide particles
- Most research groups 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 these results are the recovery arising from back diffusion to the original oxide particles or re-join 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

Author	Material	Irrad. Particle	Irrad. Temp. (°C)	Irrad. Dose (dpa)	Irrad. Dose Rate (dpa/s)	Method	Structure	Chemistry	Size	Number density
Akasaka ¹⁴¹	MA957	Therm. n	325	2.0, 5.5	2.9×10^{-7}	TEM, SANS	Stable	n.s.	Stable	Stable
Alamo ¹⁴²	Menat	DY	400 ~ 480	75.4		XAFS, TEM	Disordering	n.s.	Decrease (larger oxides)	Not specified
Allen ¹⁴³	MA957	Fast n	600	3	3.7×10^{-7}	APT	n.s.	Y:Ti decrease	Stable	Stable
Asano ¹⁴⁴	Monnet ¹⁴⁴	DY	RT	Kr		STEM	Amorphize	n.s.	Stable	Stable
Bailey ¹⁴⁵	Monnet ¹⁴⁵	EM10	electron	300 ~ 500	100	HRTEM	n.s.	Stable	Decrease	n.s.
Certain ¹⁴⁶	Monnet ¹⁴⁶	DY, EM10	He	400	0.05	HRTEM	Stable	Stable	Decrease	Stable
Certain ¹⁴⁶	Monnet ¹⁴⁶	DY, EM10	Ar	400	33	HRTEM	Amorphize	n.s.	Decrease	Decrease
Yamashita ^{115,170}	M93	Fast n	450 ~ 560	2.5 ~ 15		HRTEM	Stable	Y:Ti decrease	Stable	Stable
Monnet ¹⁴⁶	Yamashita ¹⁷¹	Fast n	500, 700	100		TEM	n.s.	n.s.	Increase	Decrease
Pareige ¹⁴⁷	16Cr	electron	500	10	1.2×10^{-6}	TEM	Stable	n.s.	Decrease	Stable
Parente ¹⁴⁸	Yutani ¹⁷³	K3	Fe	300, 500	1 ~ 10	TEM	n.s.	n.s.	Stable	Stable
Pasebani ¹⁴⁹	Zhanbing ¹⁷⁴	12.5Cr	electron/H	350 ~ 550	15	TEM	O/M interface becomes irregular	n.s.	Stable	Stable
Pasebani ¹⁴⁹	Yano ¹⁷⁵	9Cr	Fe	500	3, 100	APT	n.s.	n.s.	Decrease	Decrease
Ramar ¹⁵⁰	Jung ¹⁷⁶	PM2000	Fast n, He	500	21	EFTEM	Amorphization faceted shape becomes spherical	Cr-rich shells	n.s.	n.s.
Ribis ¹⁵¹										
Ribis ¹⁵²	³ Aydogan ¹⁷⁷	14YWT	Fast n	360 ~ 370	7	TEM, EFTEM	n.s.	n.s.	Stable	Stable
Dolph ¹⁵³	³ Aydogan ¹¹⁴	14YWT	Fe	450	585	TEM, APT	n.s.	Stable	Decrease	Decrease
Dubuis ¹⁵⁴	³ Brooks ¹⁷⁸	SS310	Kr	520	1.5	STEM-EDS	n.s.	Y:Ti decrease	Stable	n.s.
Edmon ¹⁵⁵	³ Robertson ¹⁵⁶	12Cr	Fe	475	~ 800	TEM	Destroyed incoherent particles	n.s.	Decrease Dis-appear > 5 nm	Increase 1.5 times @martensite
Rogozhkin ^{157,158}									Saturation of	Decrease 20%
Skuratov ¹⁵⁹	KP4	Bi	RT	4.8×10^{-4} 1.2×10^{-3}		TEM, HRTEM	Erosion > 5 nm	n.s.	n.s.	n.s.
Skuratov ¹⁶⁰	KP4	Xe	RT	1.0×10^{-3} 1.5×10^{-2}		TEM, HRTEM	Amorphization Crystal inclusion in amorphous body, for large particles Chromite formation	Mixing of the elements Dis-solution of O	n.s.	n.s.
Getto ¹⁸⁰										
Saito ¹⁶¹	Šćepanović ¹⁶²	14Cr	Fe	~ 80	15	TEM, STEM-EDS, EFTEM, APT	Disk, rod shape increase	Stable	Decrease < 5 nm	Increase
Kim ¹⁶¹										
Šćepanović ¹⁶⁹	14Cr	Fe/He/H	600	30		TEM, STEM-EDS, EFTEM, APT	Disk, rod shape increase	Stable	Ostwald ripening (decrease < 5 nm and increase larger particles)	Stable
Kondo ¹⁸²										
Williams ¹⁶⁸	³ Lescoat ¹⁸³	14Cr	Fe	RT	2, 10, 50	TEM	n.s.	n.s.	Decrease	Decrease 2 orders
Yamashita ¹⁶⁹	³ Li ¹⁸⁴	9Cr	Fe	500, 400	1, 3, 50, 100	TEM, APT	n.s.	Y: O increase (Y + O): Ti stable	Decrease	Decrease
Yamashita ¹⁷⁰										
Parish ¹⁸⁵	18Cr	H	500	1, ~ 3, 7	1.2×10^{-5}	TEM, APT	n.s.	Y: O increase (Y + O): Ti stable	Increase < 50 dpa, else decrease	Increase < 50 dpa, else decrease
Parish ¹⁸⁵										
Pasebani ¹⁸⁶										
Rogozhkin ¹⁸⁷										
Zhang ¹⁹²	SS316	Kr/He	500	0.05 ~ 8		TEM	n.s.	n.s.	Shrinkage < 10 nm	n.s.
Skuratov ¹⁸⁸	Cr16	Bi	RT	1.2×10^{-4} 1.2×10^{-3}		TEM, HRTEM	Amorphous ion tracks	n.s.	n.s.	n.s.

Irradiation Effects



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