Corrosion and Cracking of Supercritical Water Cooled Reactor Materials

Prof. Le-Fu ZHANG

Shanghai Jiao Tong University, China

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Meet the Presenters

Dr. LeFu Zhang, Professor at the School of Nuclear Science and Engineering of Shanghai Jiao Tong University, received his Bachelor, Master and Ph.D degrees in material science from Huazhong University of Science and Technology.

His research focuses on materials and water chemistry for light water reactors. He established a joint research laboratory for corrosion of nuclear power materials with Shanghai Nuclear Engineering Research and Design Institute in 2008.

Under his 15 years of leadership, 80 high temperature and pressure water circulating loops have been built for general corrosion, stress corrosion cracking, fretting wear, fuel cladding tube performance and water chemistry tests, among them 15 systems are for supercritical fluid reactors.

He is the Chinese representative in Materials and Chemistry Project Management Board, and the Chinese substitute representative in System Steering Committee of Supercritical Water-Cooled Reactor Systems in Generation IV International Forum (GIF).

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Background

Supercritical Water Cooled Reactor (SCWR)

One of the six Gen IV concept reactors:

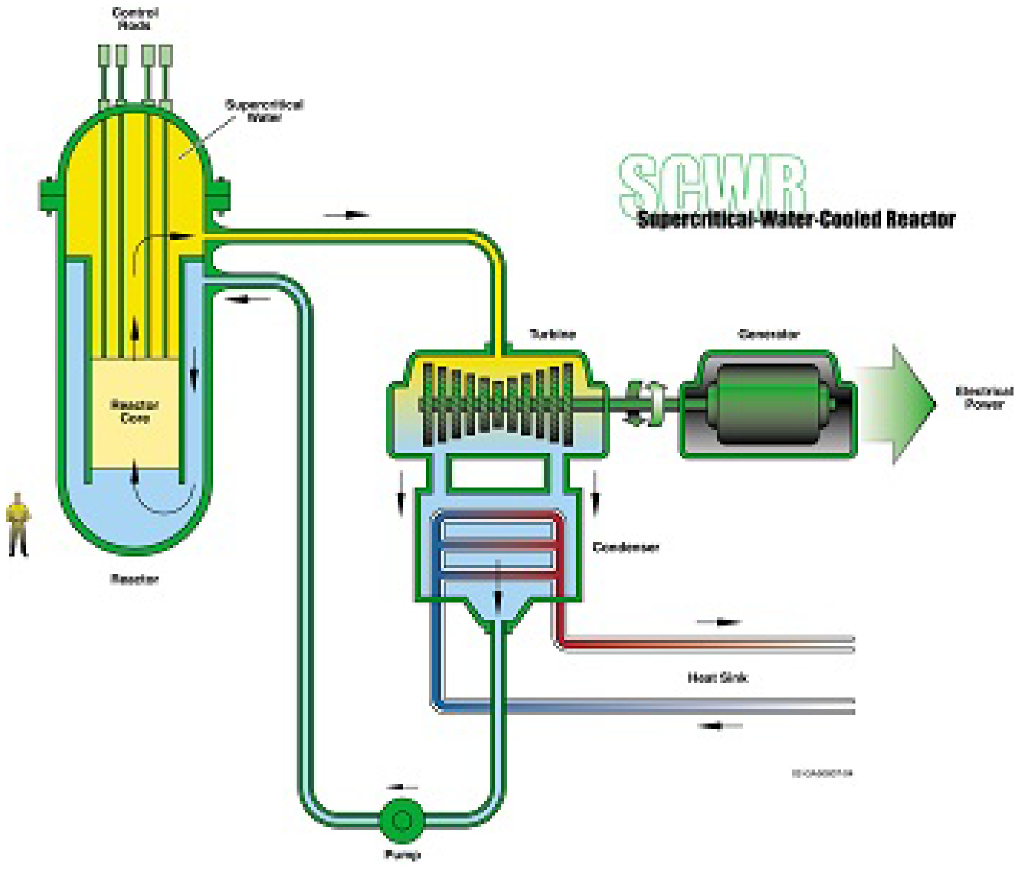
- GFR, LFR, MSR, **SCWR**, SFR and VHTR

A high capacity power reactor in Gen IV for a power plant

- High outlet temperature up to 560°C, thermal efficiency up to 45% (comparing with 35% of PWR), and 10 times higher fuel efficiency

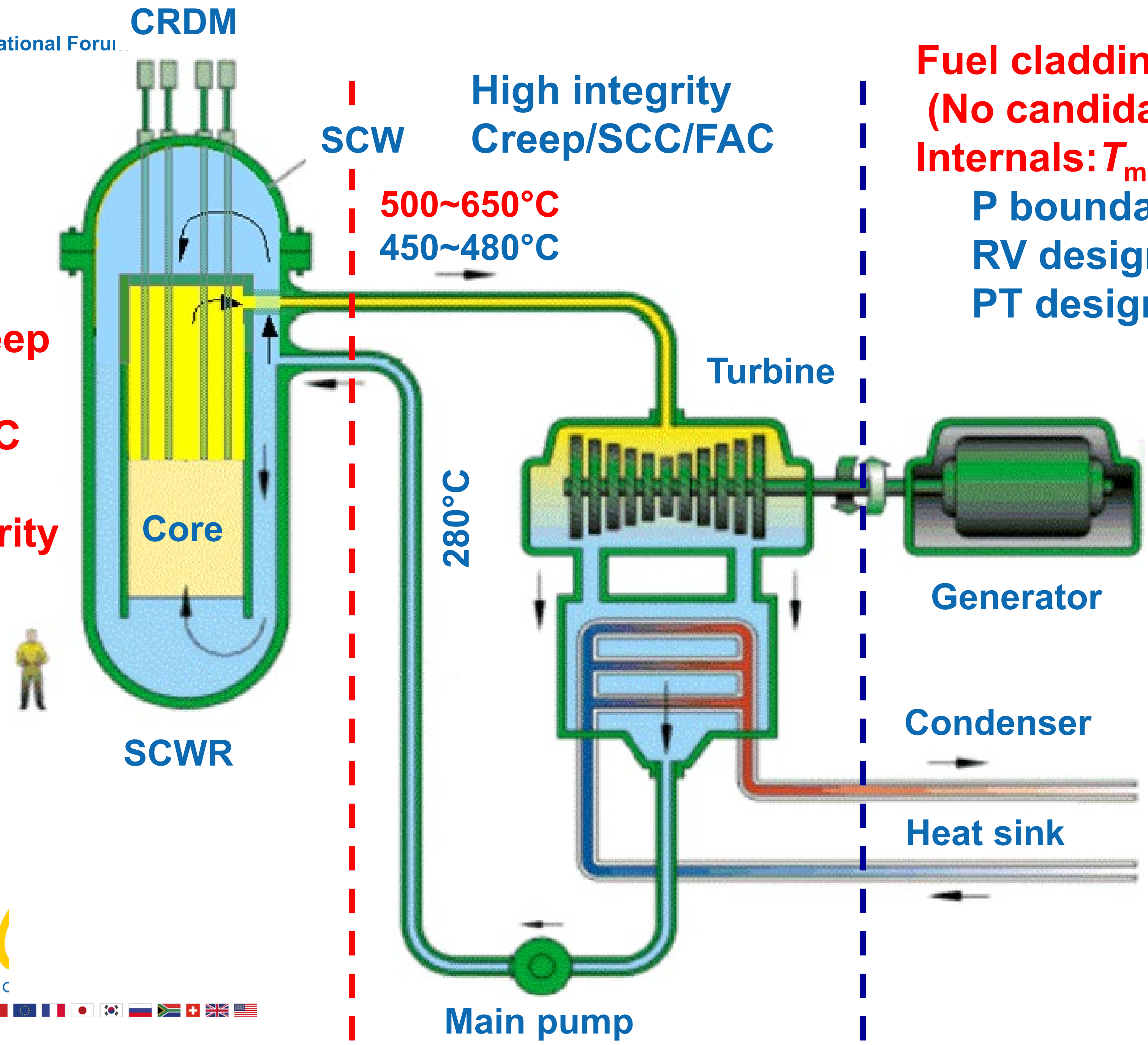
Simplified design + industrial mature turbine

- Direct thermal cycle, no steam generator
- Relatively smaller dimensions of reactor vessel, main steam line, containment, turbine, …
- Turbine is readily available and up to 650°C
- Passive core cooling systems from Gen III PWRs
- Low cost



SCWR – the best GEN IV conceptual design for electric power plant

High T Creep
Corrosion
SCC/IASCC
Irradiation
High integrity



Fuel cladding: T_{max} = 550,650,800°C
(No candidate yet)
Internals: T_{max} = 500,600°C
P boundary : ~30MPa
RV design : 2.25Cr1Mo ?
PT design : F/M steel

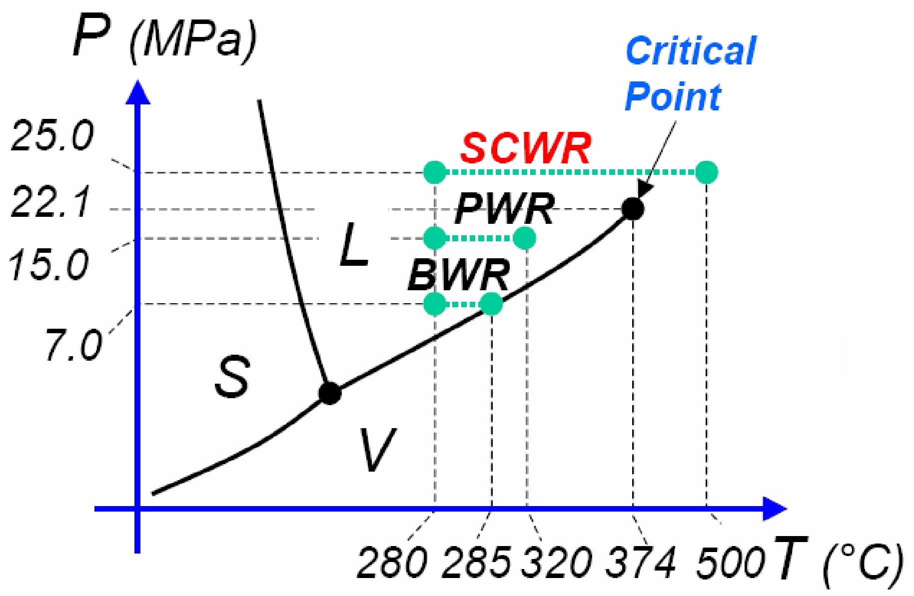
Fuel cladding material controls the coolant outlet temperature

Manufacturing of reactor pressure vessel is a great challenge

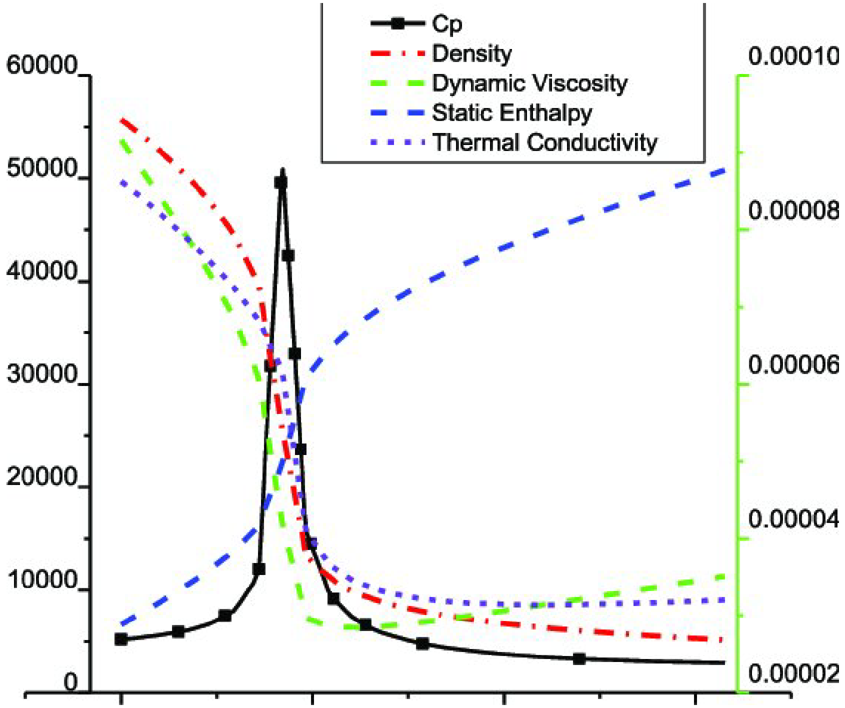
Reducing outlet temperature is necessary for a demo SCWR

Characteristics of SCW

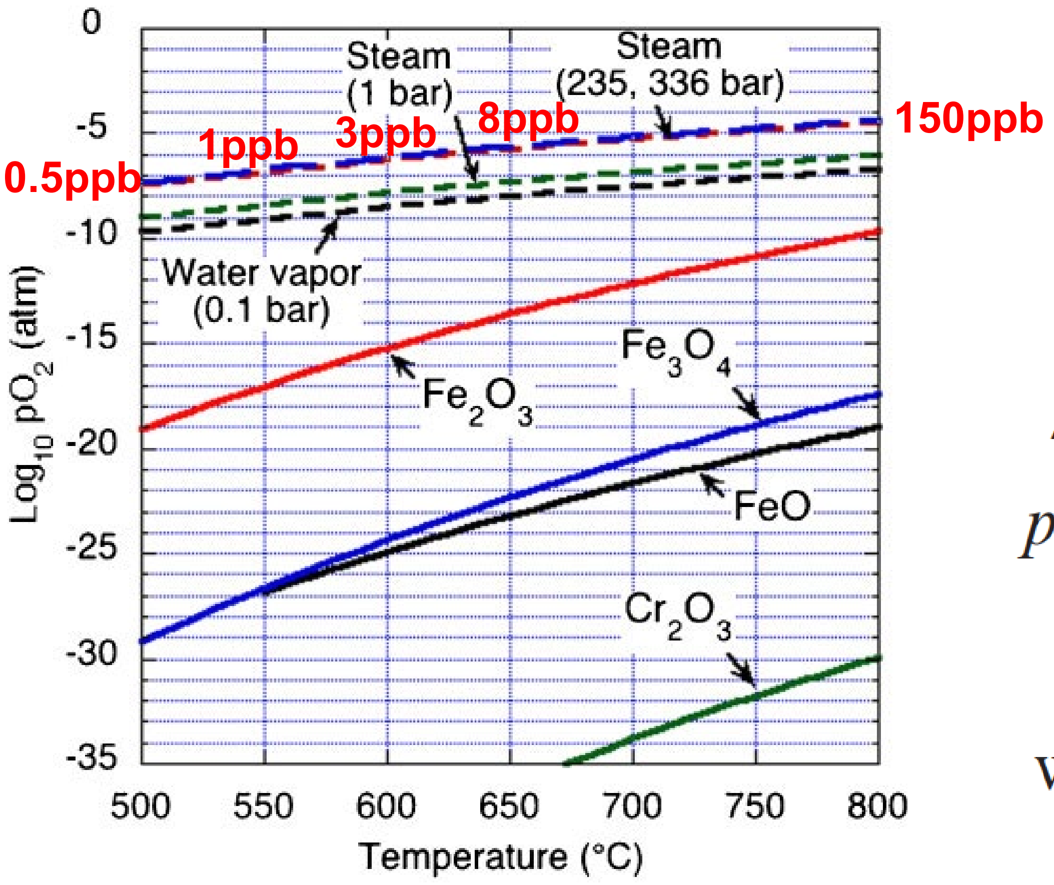
- SC point: 374°C/22.1MPa
- Density: ~ 0.1g/cm³
- High density nonpolar gas
- Mix with oxygen with any percentage
- Very high solubility of organic materials
- Very low solubility of ionic compounds



Very oxidizing gas!



Oxygen concentration in SCW



Effective oxygen partial pressures in steam under three pressure conditions, and the stability of the oxides of interest as a function of oxygen partial pressures

$$H_2O(g) = H_2(g) + 1/2O_2(g)$$

$$k_7 = pO_2^{0\cdot 5}\, pH_2 / pH_2O$$

$$\log k_7 = -\Delta G_7^0 / 2\cdot 303RT$$

$$\Delta G_7^0 = -230\,000 - 8.14T\ln(T) + 9.25T$$

$$pO_2 = [x/(2+x)]P \qquad pH_2 = [2x/(2+x)]P$$

$$pH_2O = [2(1-x)/(2+x)]P$$

$$\text{where } x << 1, \qquad k_7^2 = P x^3 / 2$$

$$pO_2 = (k_7/2)^{2/3} P^{2/3}$$

I. G. Wright and R. B. Dooley. A review of the oxidation behavior of structural alloys in steam. *International Materials Reviews* 55 (3):129-167, 2010.

Corrosion Phenomena in SCWR Core

Coolant experience subcritical, critical and supercritical state, which correspond to different corrosion mechanism.

Supercritical region

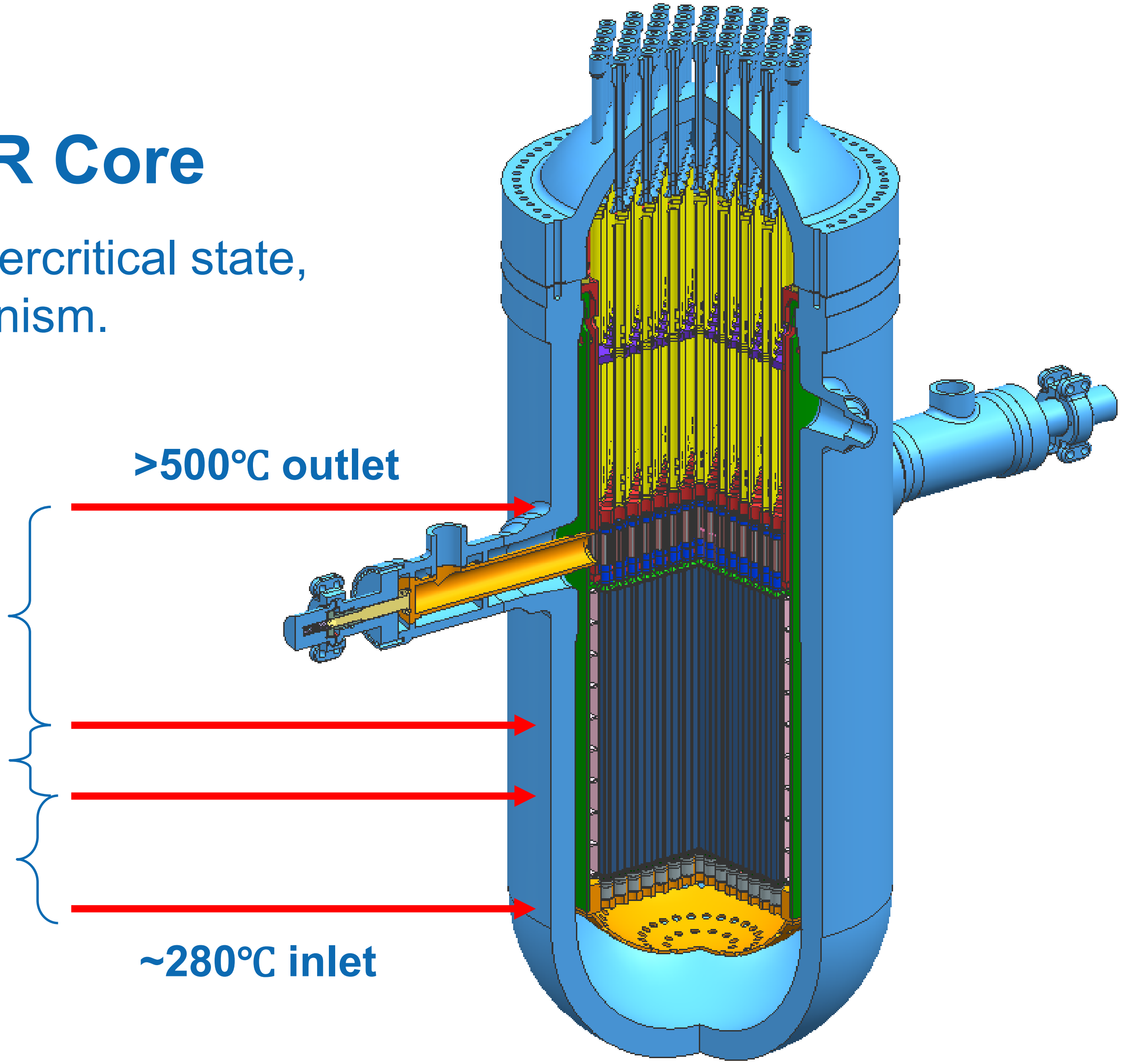
Oxidization, evaporation of corrosion products, creep, IASCC

Critical Region

Precipitation of oxides

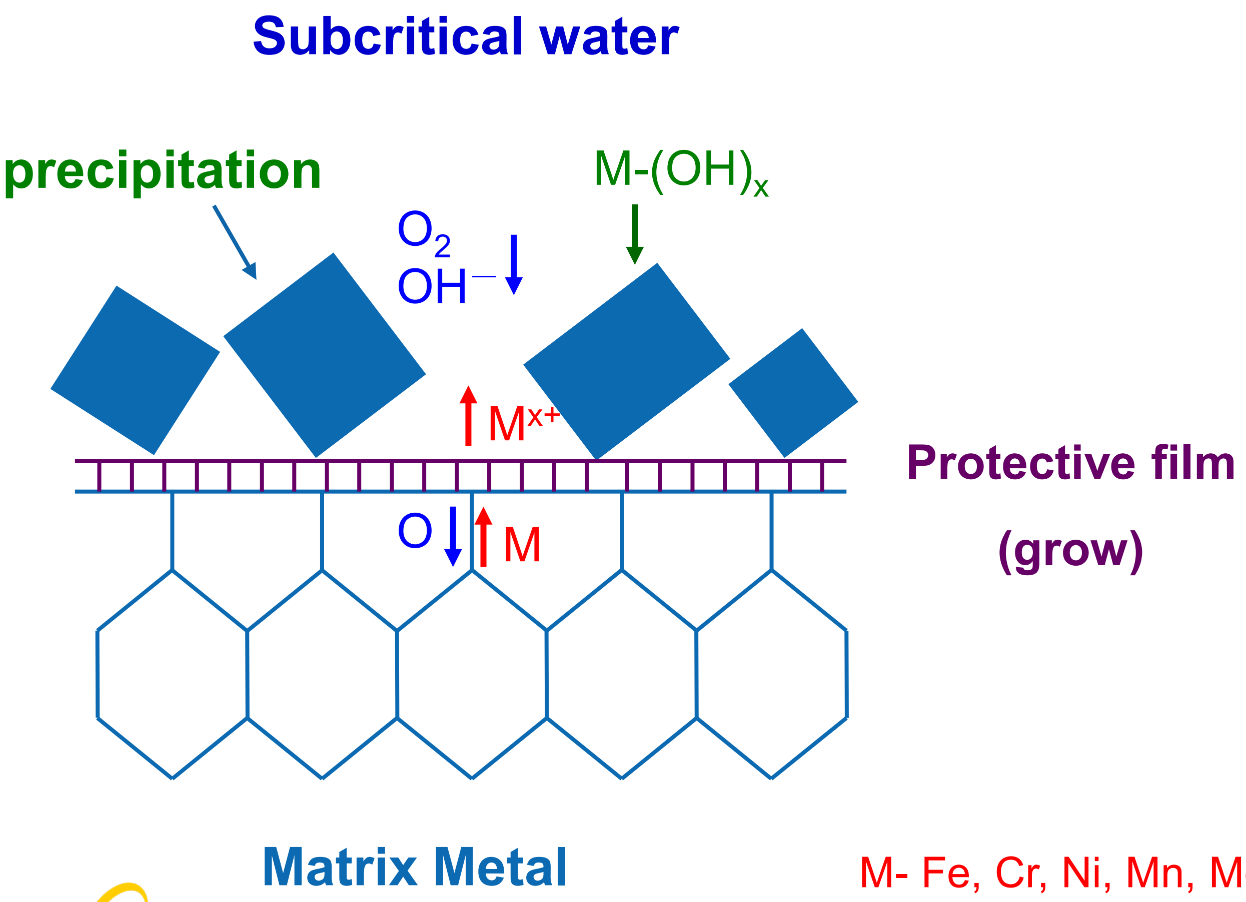
Subcritical Region

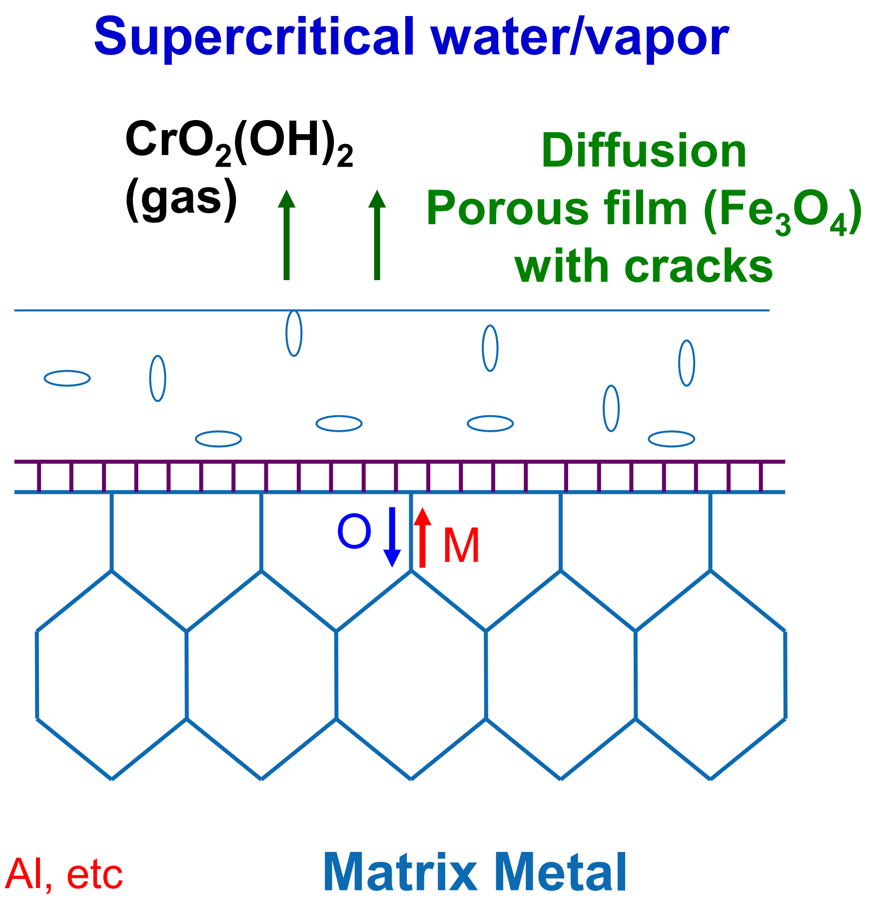
Electrochemical dissolution, metallic ions dissolved in coolant, SCC due to electrochemical factors



CSR1000 designed by NPIC, China

Formation and stability of protective oxide film





M- Fe, Cr, Ni, Mn, Mo, Al, etc

B. Stellwag. *Corrosion Science* 40 (2-3):337-370, 1998.

Protective oxides on metallic materials of interest

Protective oxide films

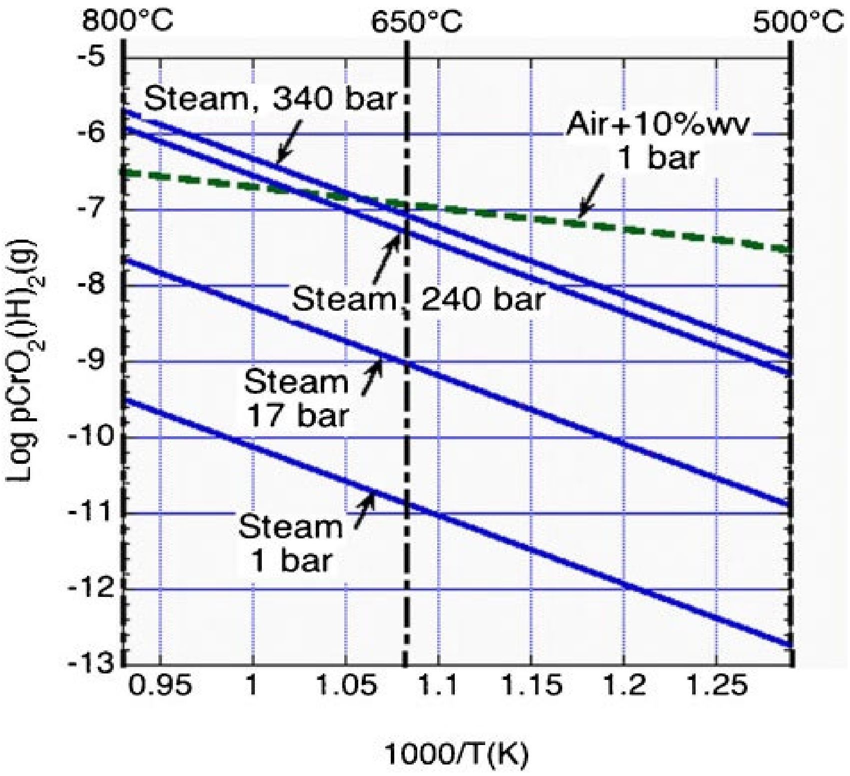
- Steels and Ni alloy: Cr_2O_3, $(Cr,M)_3O_4$, Fe_3O_4, $(Cr,M)_2O_3$
- Al、Al alloys：corundum type $\alpha-Al_2O_3$
- Zr and Zr alloys: un-stoichiometric ZrO_{2-x}

Vaporization in steam

- $1/2\ Cr_2O_3(S) + H_2O(g) + 3/4O_2(g) = CrO_2(OH)_2(g)$;
- $Cr_2O_3(S) + 5H_2O(L) = 2CrO_4^{2-} + 10H^+ + 8e$.
- $1/2\ Al_2O_3(S) + 3/2H_2O(g) = Al(OH)_3(g)$;
- $SiO_2 + 2H_2O(g) = Si(OH)_4\ (g)$;
- $SiO_2 + H_2O(g) = SiO(OH)_2\ (g)$;
- $SiO_2 + 1/2H_2O(g) = 1/4O_2\ (g) + SiO(OH)_2\ (g)$.

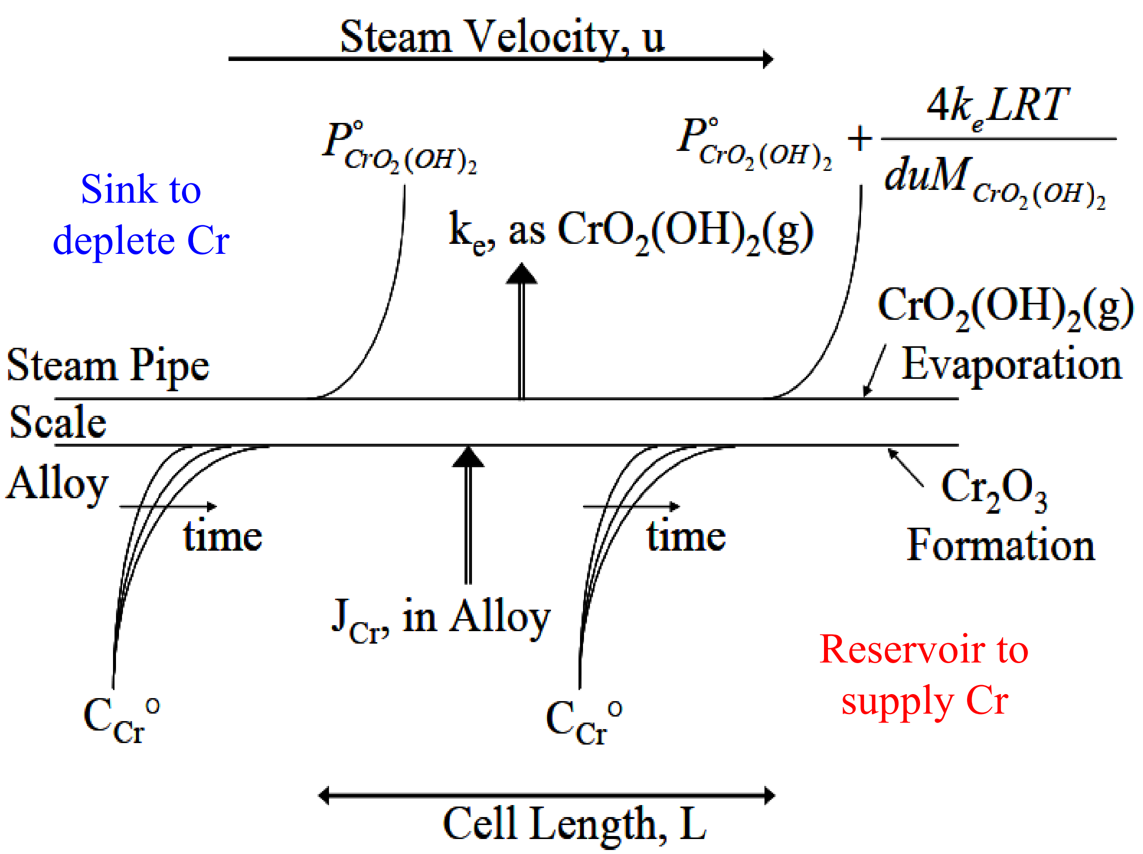
$$J_{Cr} = K_m (v/l)^{1/2} P \qquad k_{18} = pCrO_2(OH)_2/(pO_2^{3/4}\,pH_2O)$$

$$\Delta G_{18}^0 = 53\ 500 + 45{\cdot}5T \qquad pCrO_2(OH)_2 = k_{18}(k_7/2)^{1/2} P^{3/2}$$



Jacobson N, Myers D, Opila E, et al. Journal of Physics and Chemistry of Solids, 2005,66(2):471-478.
I. G. Wright and R. B. Dooley. *International Materials Reviews* 55 (3):129-167, 2010.

Cr evaporation/depletion kinetics



$$\frac{dx}{dt} = \frac{k_p}{x} - k_e$$

The Limiting scale thickness

$$x_L = \frac{k_p}{k_e}$$

In laminar flow

$$k_e\left(\frac{kg}{m^2 s}\right) = 0.664\, Re_L^{0.5}\, Sc^{0.343}\, \frac{D_{AB} M_{CrO_2(OH)_2}}{LRT} P_{CrO_2(OH)_2}$$

In turbulance flow

$$k_e\left(\frac{kg}{m^2 s}\right) = 0.0592\, Re_L^{0.8}\, Sc^{0.333}\, \frac{D_{AB} M_{CrO_2(OH)_2}}{LRT} P_{CrO_2(OH)_2}$$

Cr concentration at surface

$$C_{Cr}(0,t) = C^{\circ}_{Cr} - \frac{2k_e}{M_{CrO_2(OH)_2}}\sqrt{\frac{t}{\pi D_{Cr}}}$$

Time to Cr% ~0 at surface

$$t^* = \frac{\pi D_{Cr}}{4}\left(\frac{M_{CrO_2(OH)_2} C^{\circ}_{Cr}}{k_e}\right)^2$$

Coefficient of Cr diffusion

$$D_{Cr} \cong \boxed{D^{L}_{Cr}} + \frac{2\delta}{\lambda}\boxed{D^{gb}_{Cr}}$$

Surface shot pinning

Dislocation density

Grain size ~nano GB

Gordon R. Holcomb, Steam oxidation and chromia evaporation in ultra-supercritical steam boilers.

Short listed candidate materials for SCWR

Fuel cladding materials (<0.5 mm thick)

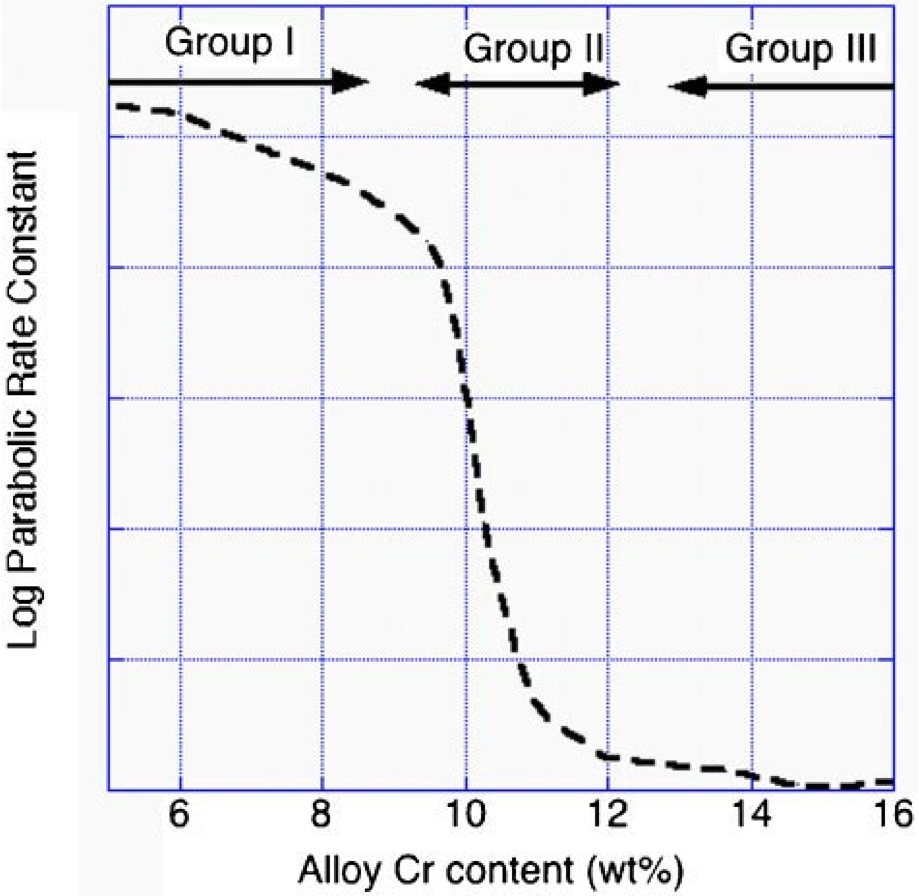
- 310s : borrowed from fossil fueled plants, corrosion resistance
- Alloy 800/800H, 825, 625: promising
- Oxide dispersion strengthened (ODS) steels
- Alumina forming austenitic (AFA) stainless steels

Reactor internals

- Austenitic stainless steels, such as 310S
- Super stainless steels

Reactor pressure vessels and primary piping

- P22/SA508cl.4 cladded with SS, super stainless steels 304, 347
- P91/92, P122, alloy 800H



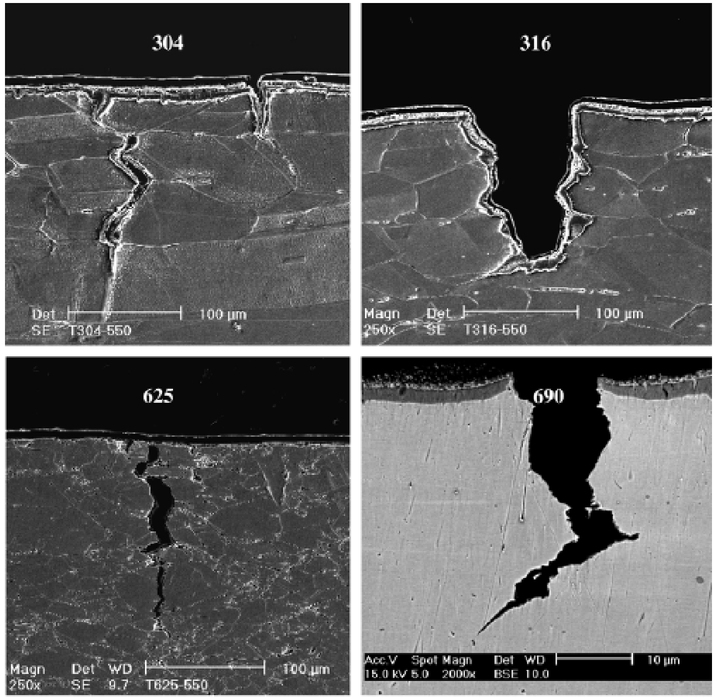
Concerns of SCWR materials

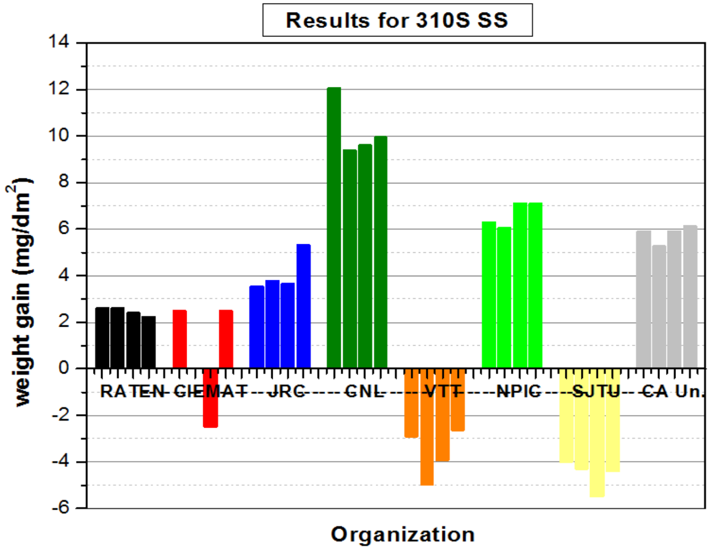
General and flow accelerated corrosion:

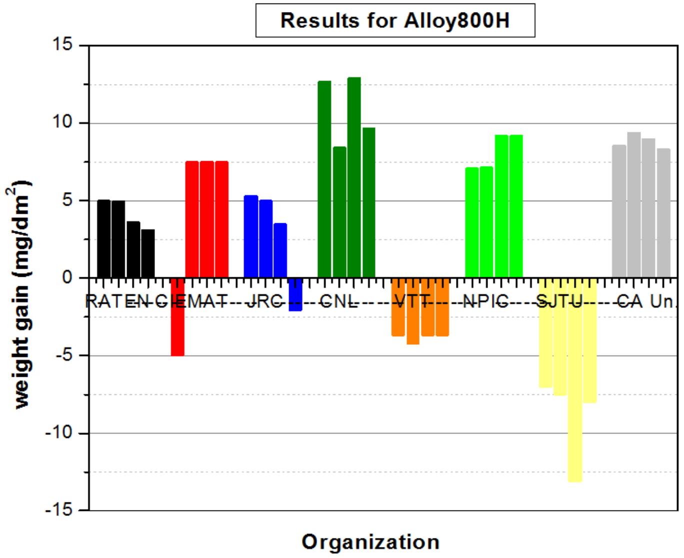
- Oxidation
- Dissolution + vaporization
- Exfoliation (oxide particles)

Creep and stress corrosion cracking

- Corrosion-Sensitization/Grain boundary oxidation
- Creep cracking
- Cyclic rupture of oxide film and repassivation at crack tip
- Blunting of fatigue crack tip







Concerns of SCWR materials

SCWR cladding materials

– Excellent corrosion performances

– Very low environmental cracking susceptibility (SCC + creep)

Commercial and novel materials

– Alloy 800H, 310S austenitic stainless steel

– AFA steels based on high Cr alloy

– ODS steel or ODS+AFA alloy

Cladding tube manufacturing

– Deformation, heat treatment, surface …

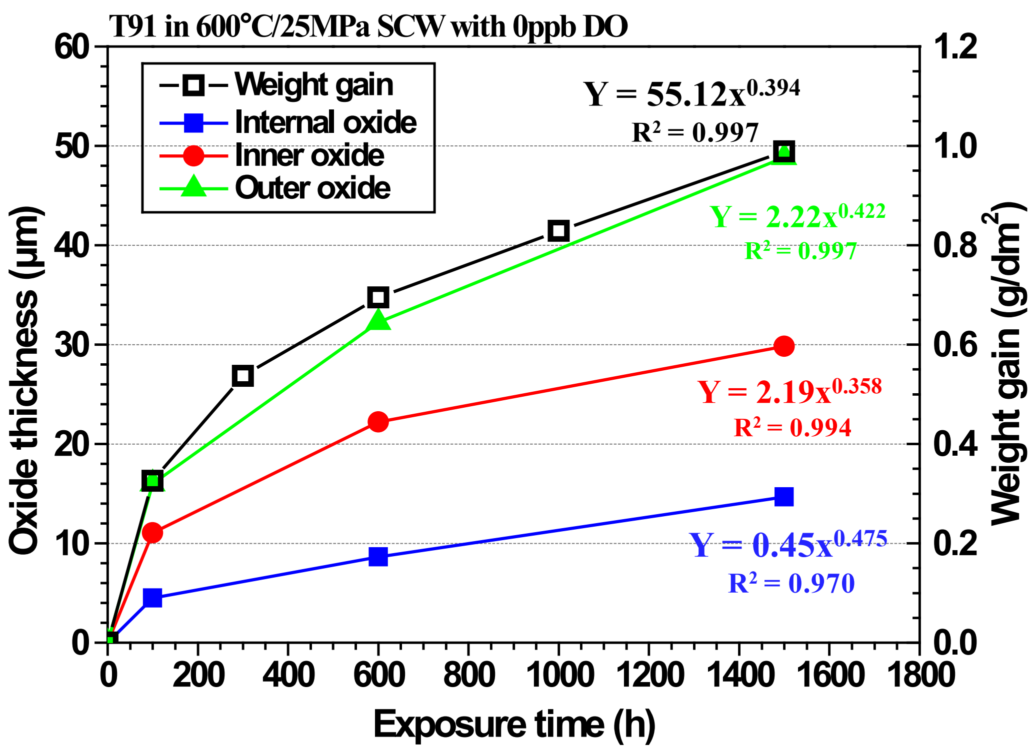
Focus on materials

- Chemical Compositions aiming at corrosion and creep
- Grain size effects
- Precipitates and precipitation hardening
- Al, Si, …
- Cold work on corrosion rate
- Effect of creep on cracking

Radiation hardening and embrittlement is not the major work at present

Commercial alloys

Ferritic/martensitic (F/M) steels

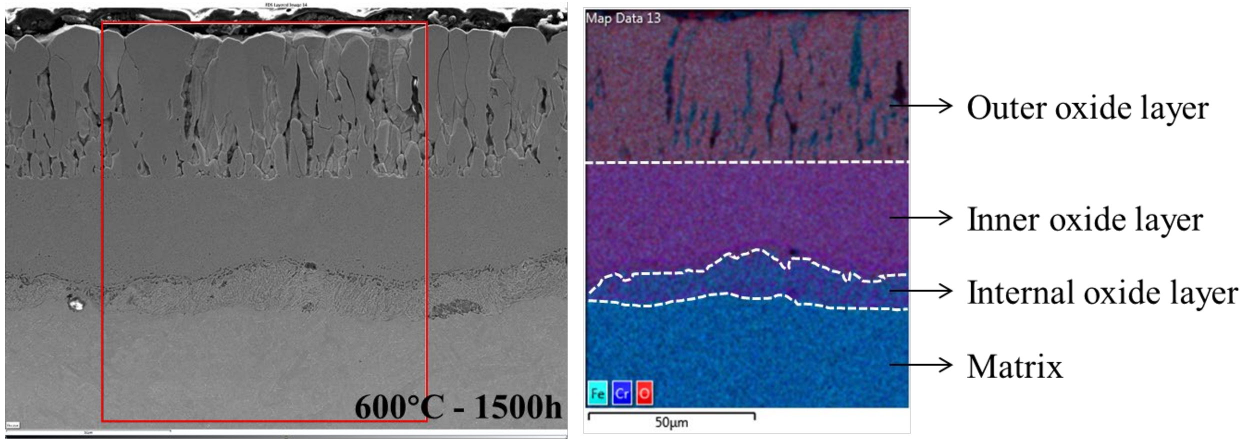


3-layered oxide film：

- outer layer：Fe_3O_4/Fe_2O_3
- middle layer：$FeCr_2O_4$，$(FeCr)_3O_4$
- internal layer：oxygen penetration

High corrosion rate：

- weak-protective oxide film
- Spallation due to mismatch of thermal expansion within temperature range 550~600℃



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Acta Materialia 194 (2020) 156-167, Acta Materialia 194 (2020) 522-539, Corrosion Science 209 (2022) 110757

Austenitic steels: 304/316/310S

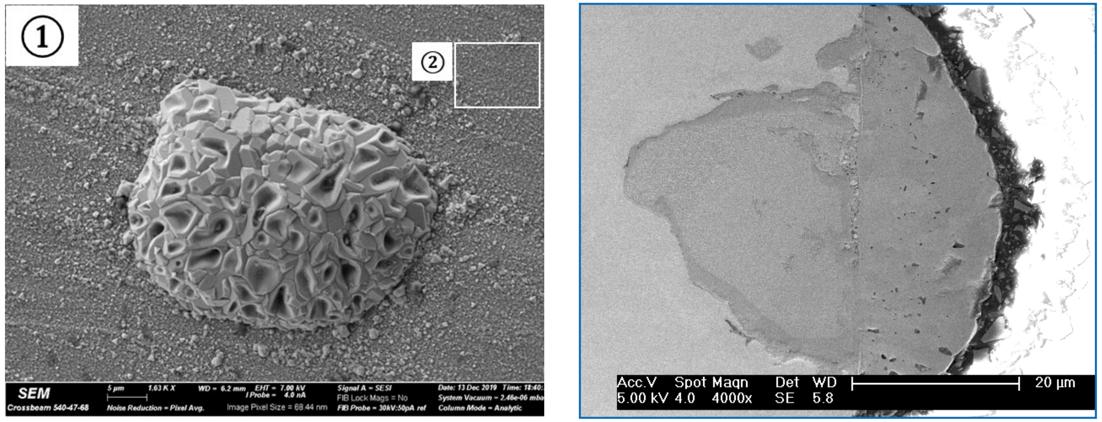
2-layered oxide film：

– outer layer： Fe_3O_4/Fe_2O_3

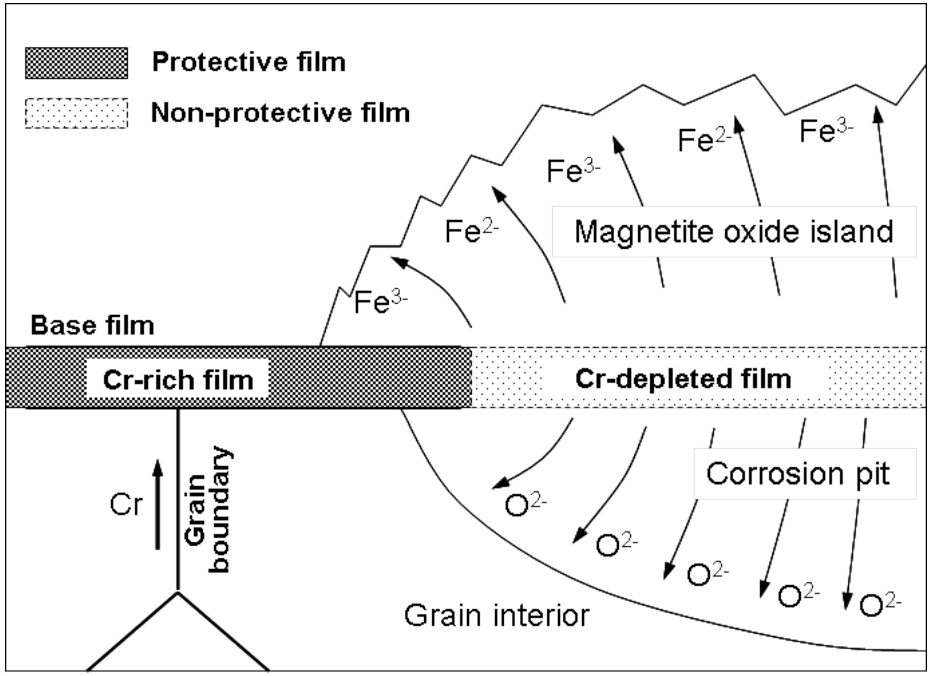
– Inner layer： $FeCr_2O_4$， $(FeCr)_3O_4$

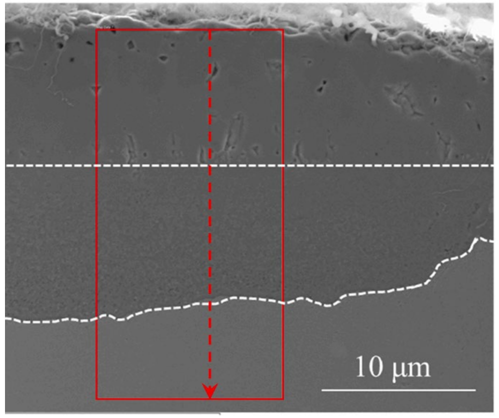
Medium corrosion rate：

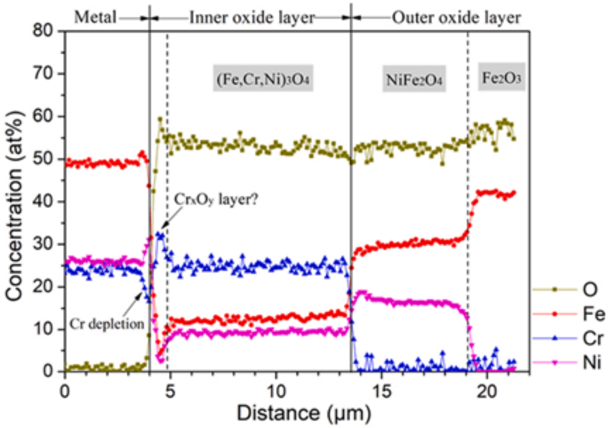
– suffer nodule corrosion



304NG SS, 300 h in 600℃ SCW

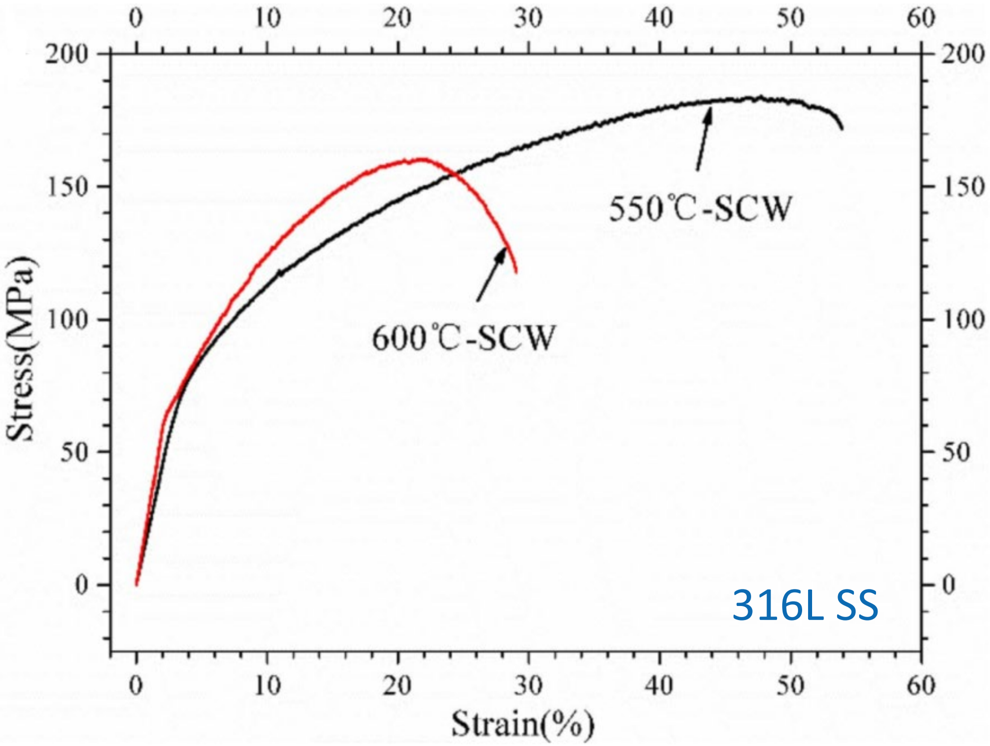






Corrosion Science 48 (8):2014-2035, 2006.
Corrosion Science 170: 108652, 2020.

Austenitic steels: 304/316/310S

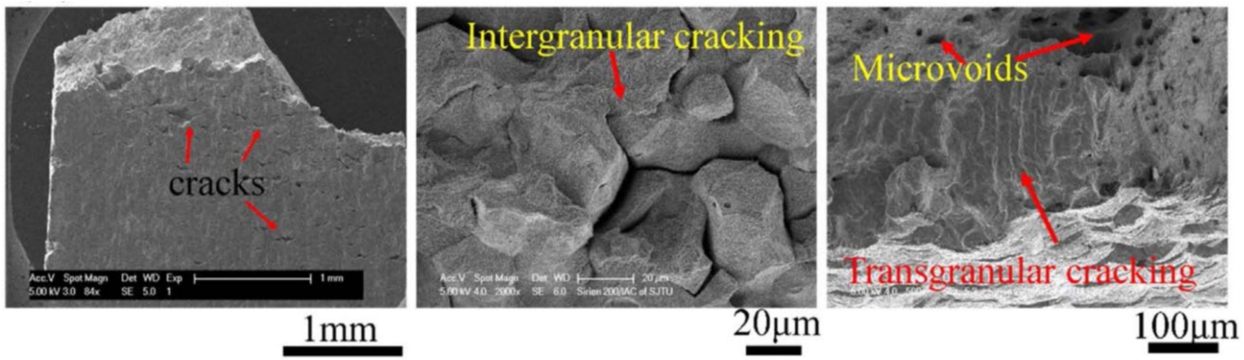


High cracking susceptibility:

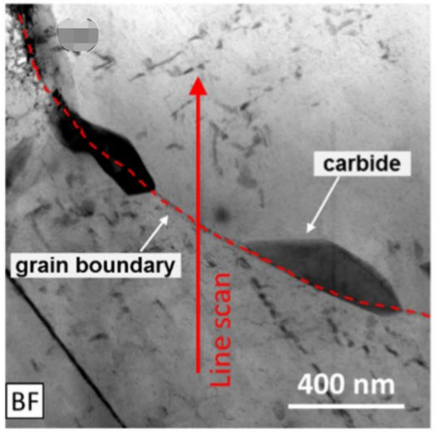
– high intergranular cracking rates in SCW environment, especially in oxygenated SCW.

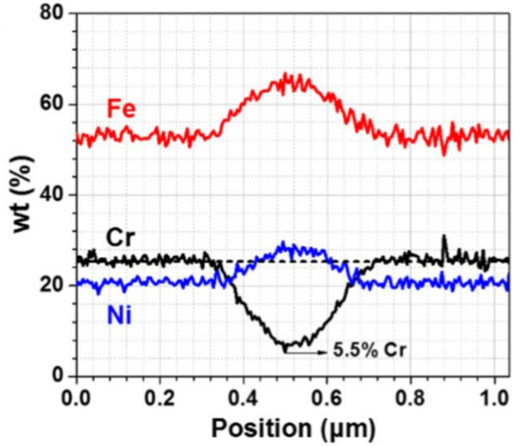
Sensitization:

– Above 400℃, austenitic steels suffer sensitization, which increases the cracking susceptibility of grain boundaries.



316L SS after SSRT in 600℃ SCW





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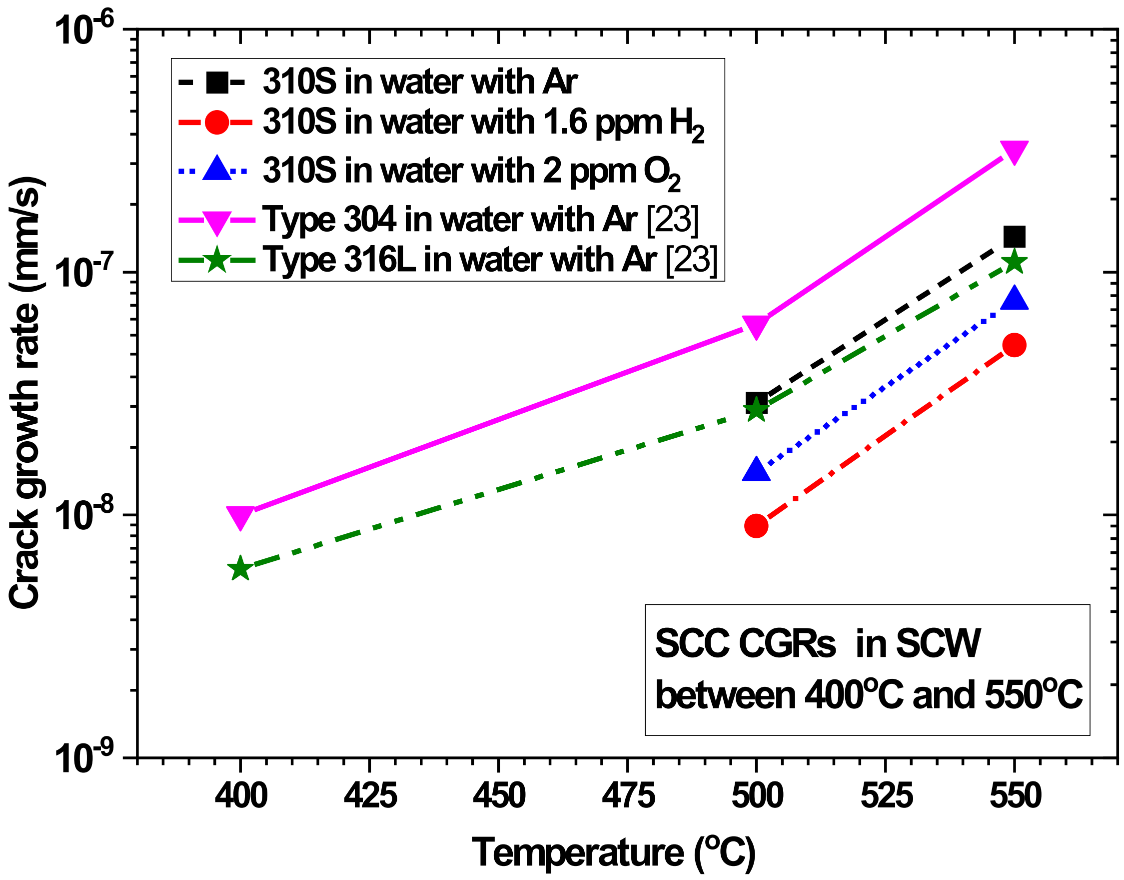
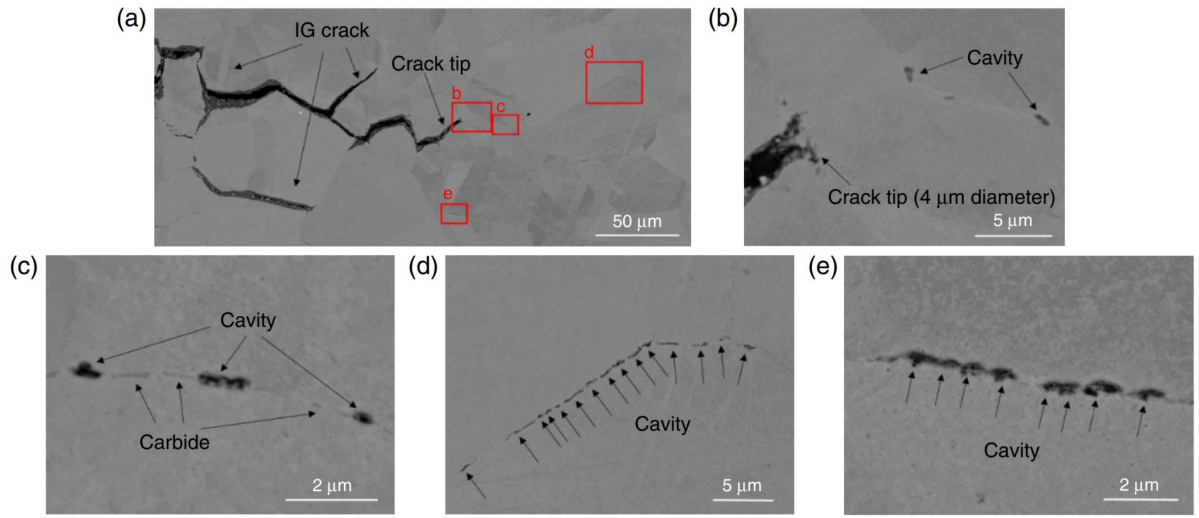
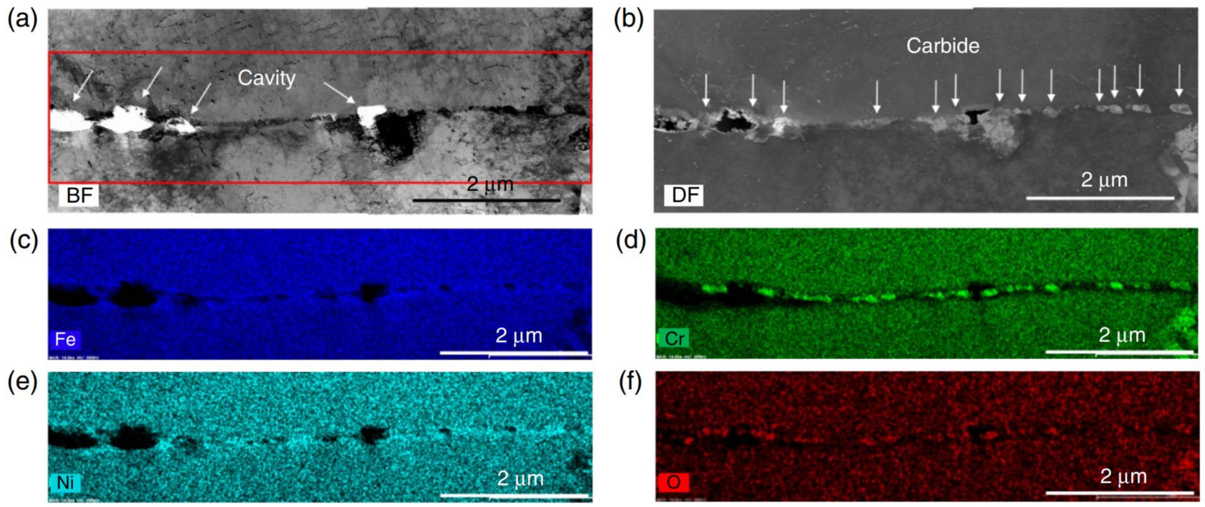
Corrosion Science 127 (2017) 157–167

Austenitic steels: 310S SS





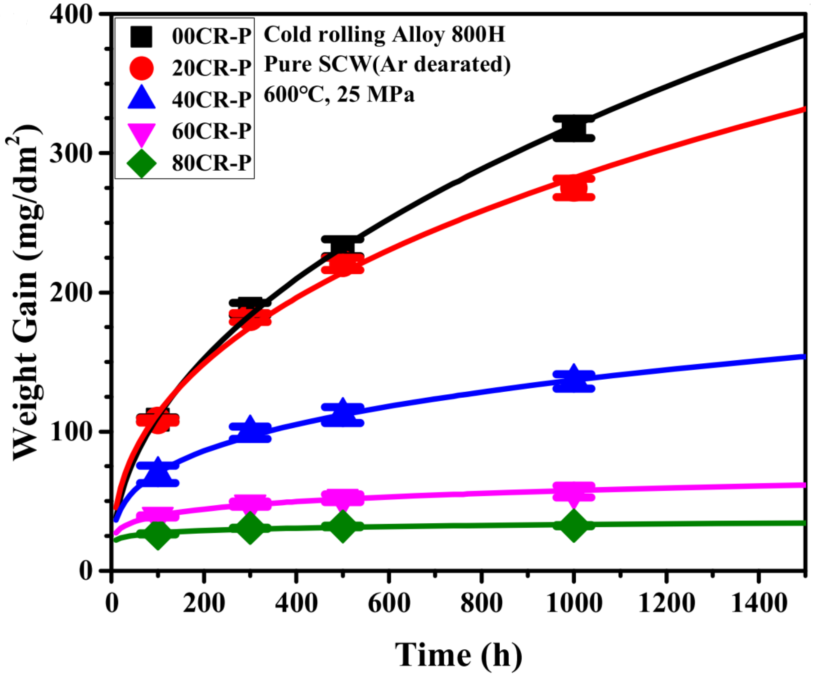


Corrosion 74 (7) 2018: 776-787

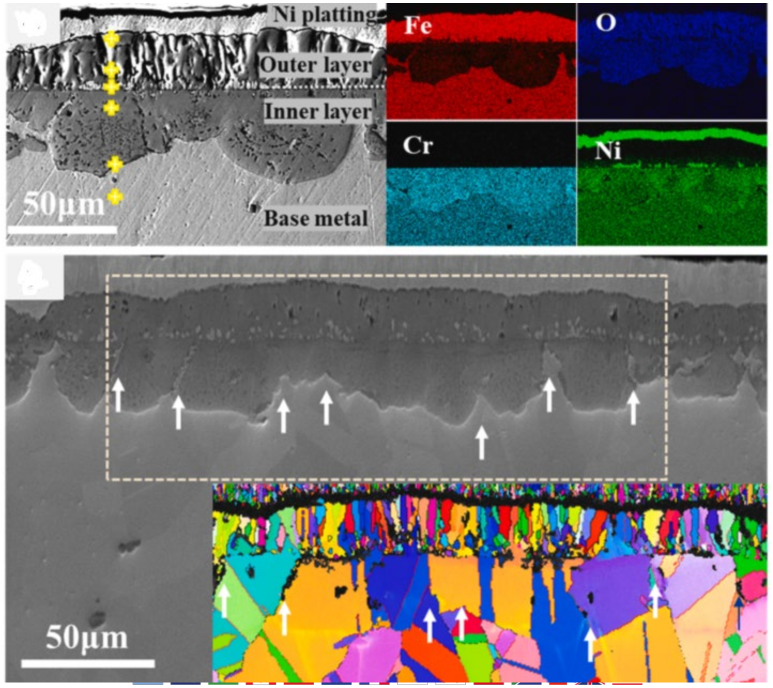
Austenitic steels: 800H

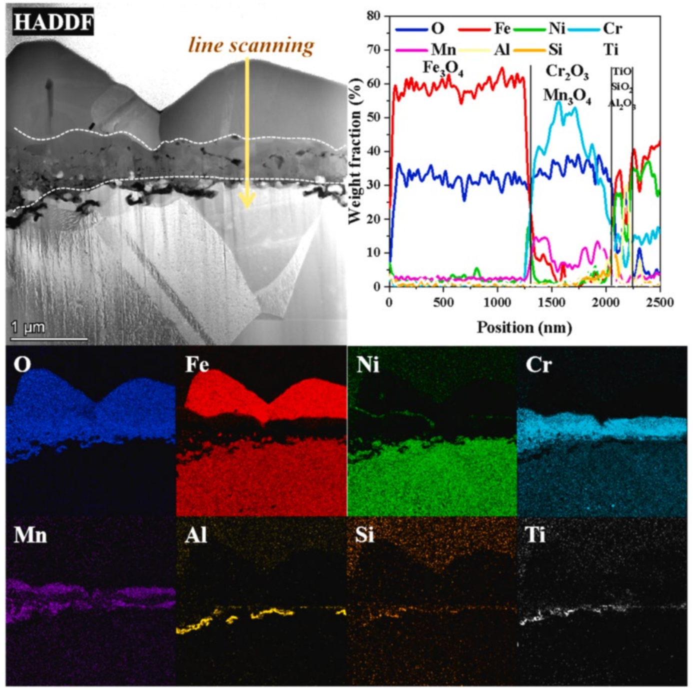
General corrosion vs cold work

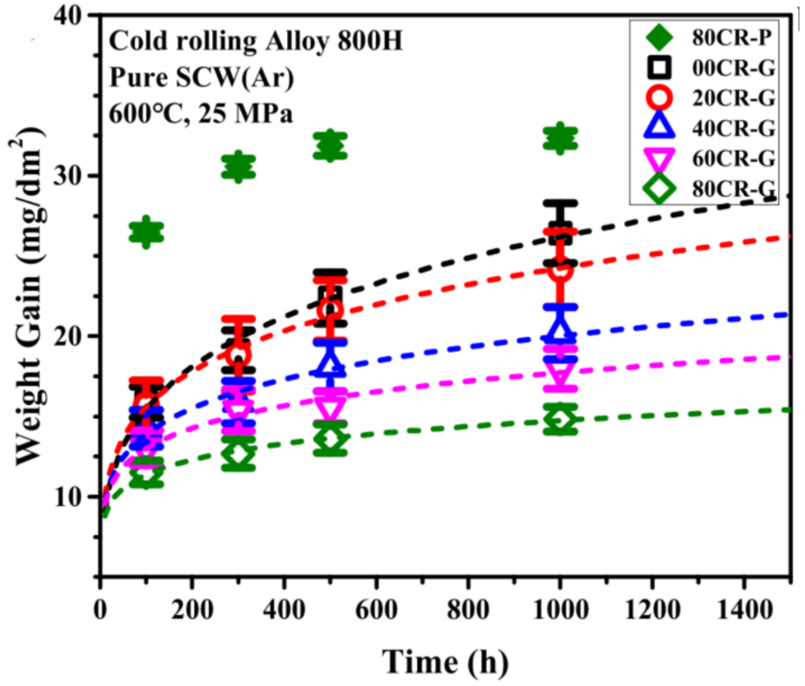
- Corrosion rate and the affecting factors
- Surface effect, fine grain surface layer
- Diffusion enhancing factors: dislocation, GB, T…



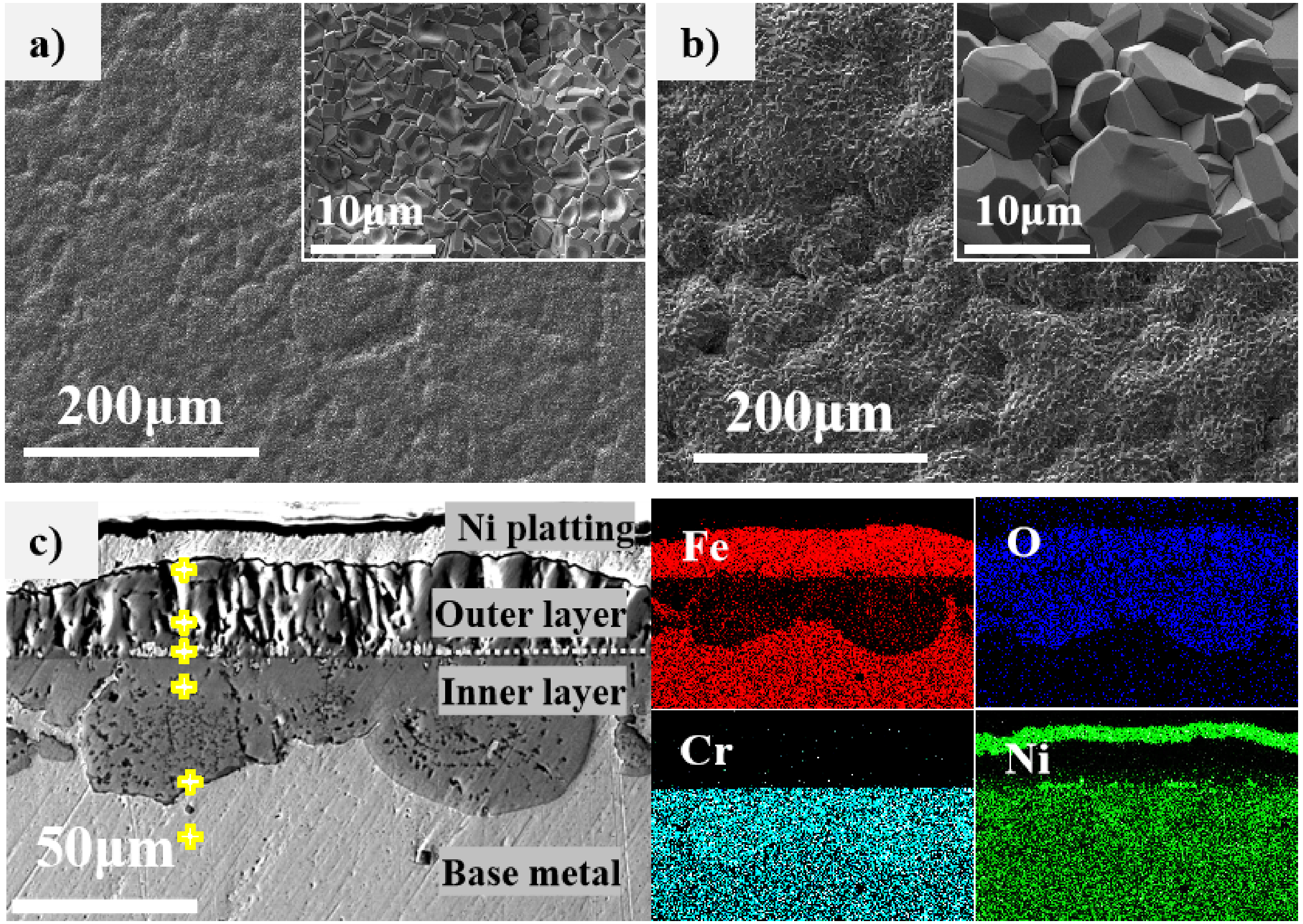
800H, 1000 h in deaerated 600℃ SCW, 0% vs. 80% cold-rolled

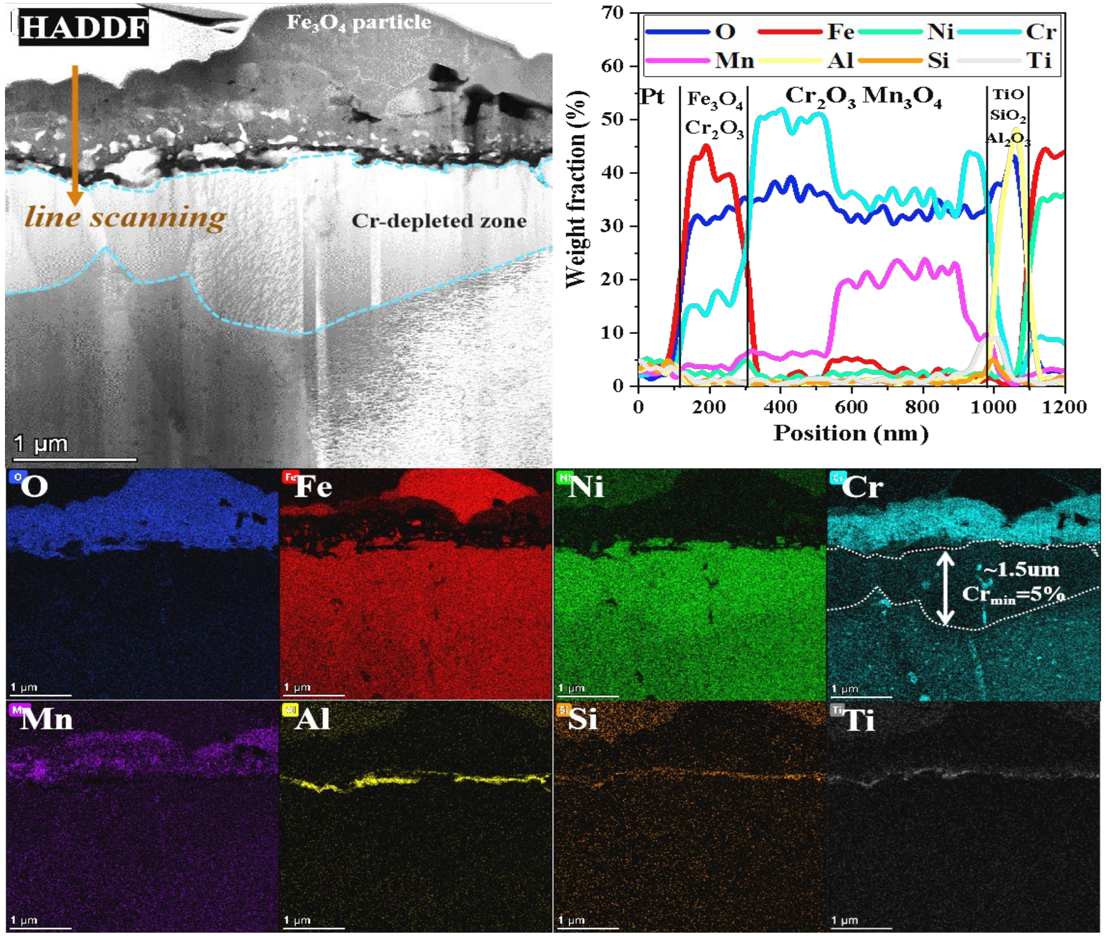






Austenitic steels: 800H, polishing vs. ground finish

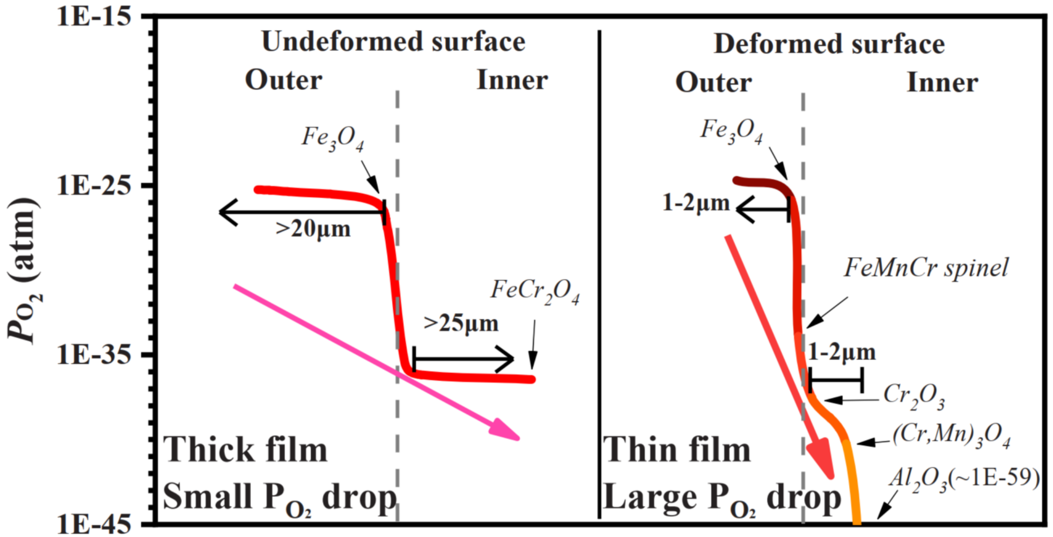


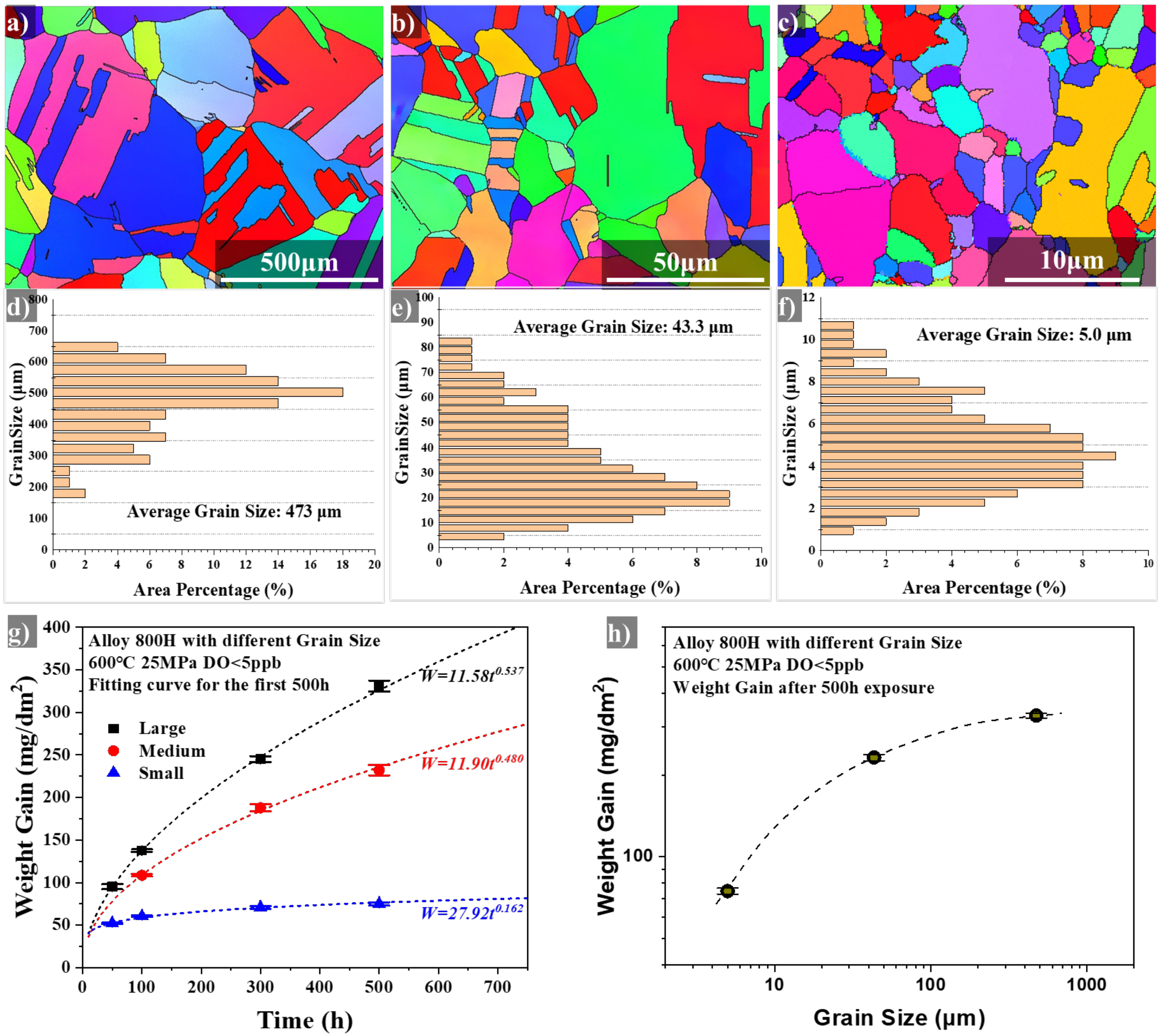


Austenitic steels: 800H

General corrosion vs grain size

- Smaller grain size → lower oxidation rate
- **Deformation** (cold rolling or surface grinding) and **grain refinement** promote the outward diffusion of Cr to facilitate the formation of Cr_2O_3

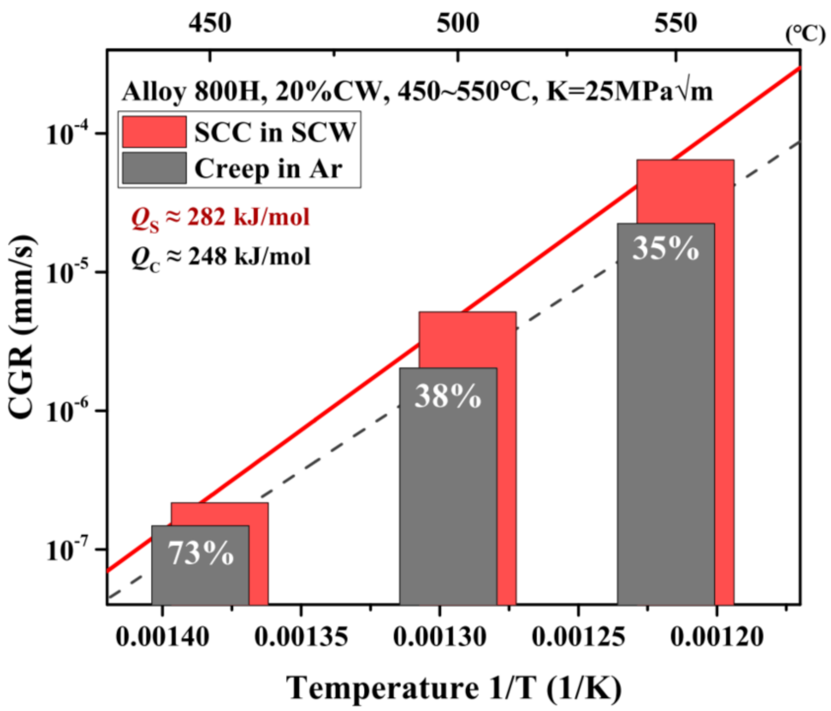


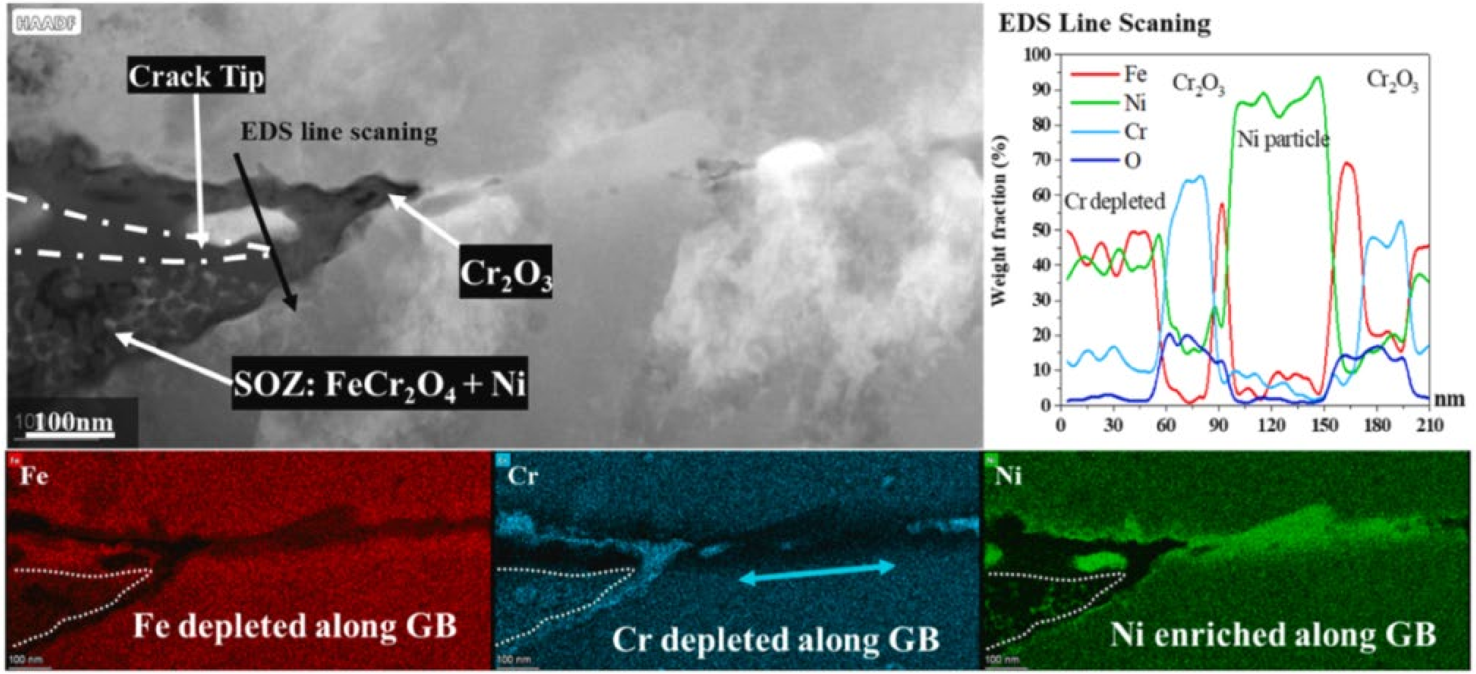


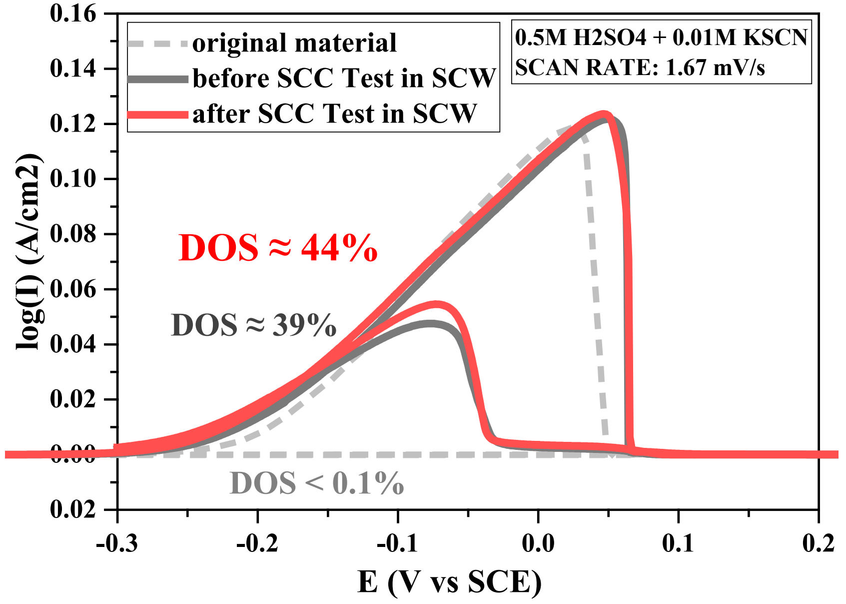
Austenitic steels: 800H

High crack growth rate after cold deformation：

- 100% intergranular crack
- High percentage contribution by creep
- In-situ sensitization, which weakens the grain boundary



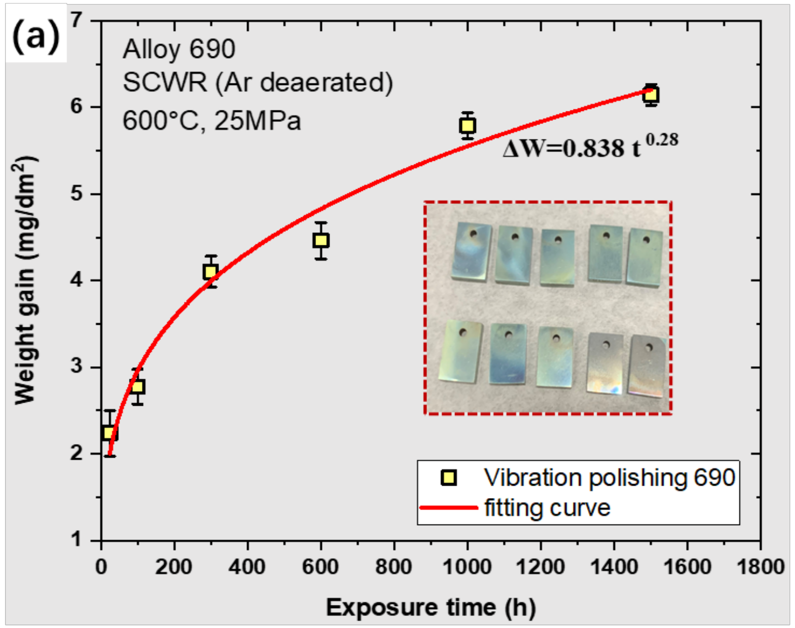


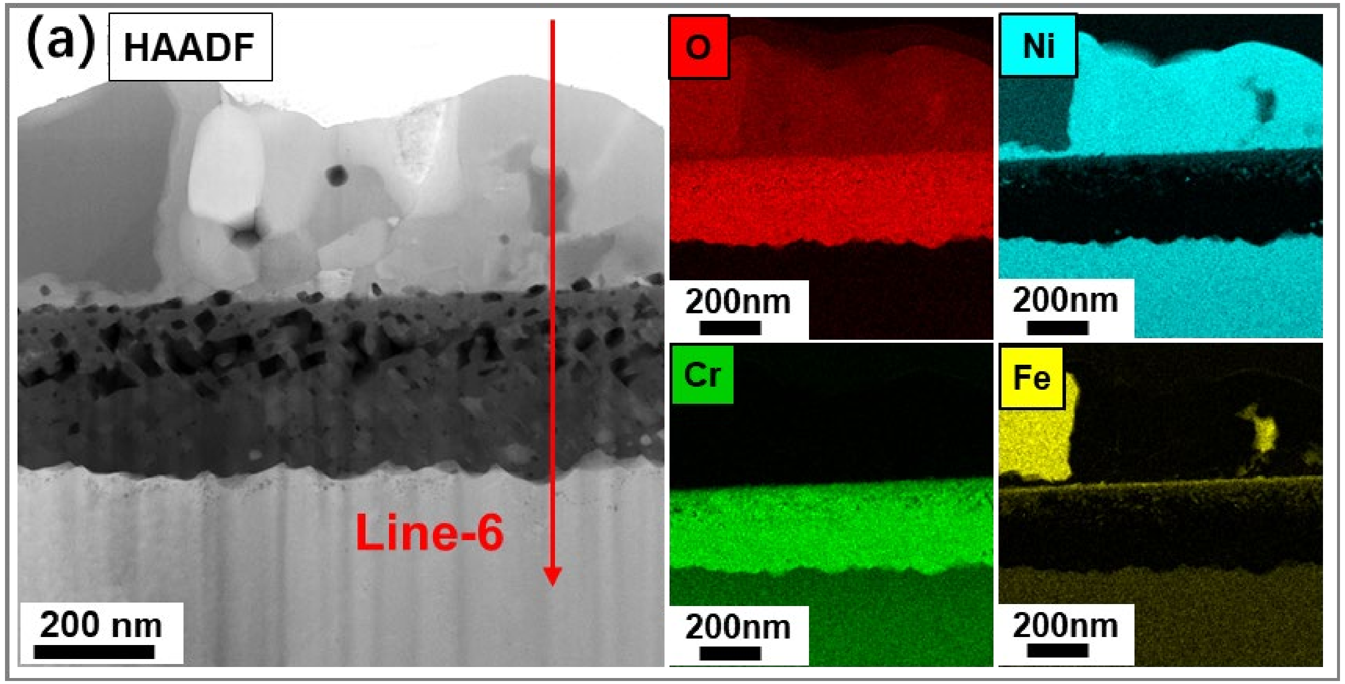


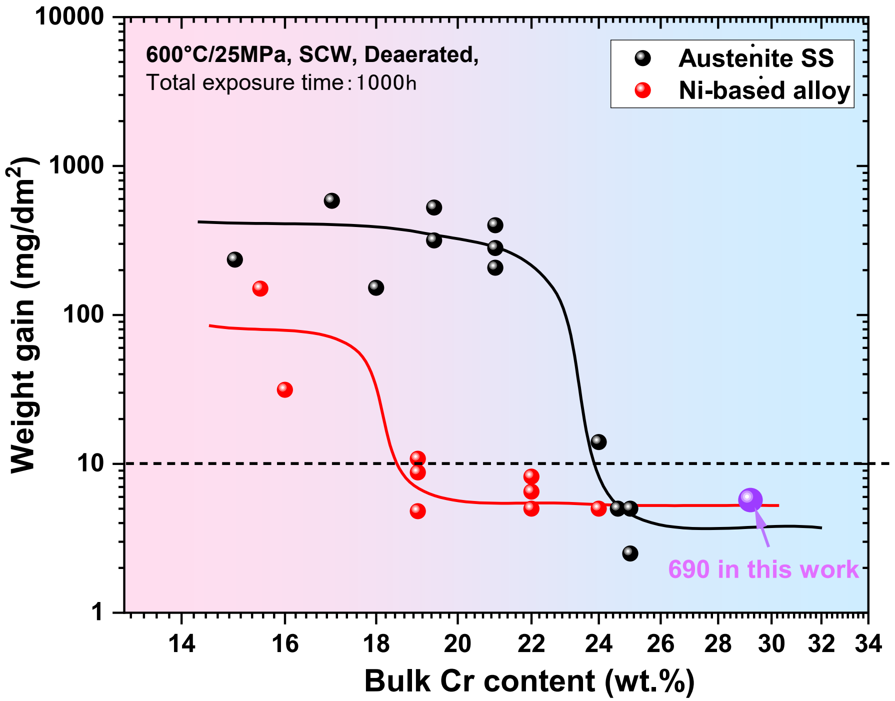
Nickel-based alloys: Alloy 690

Low oxidation rate：

- 2-layer oxide film
- High Cr content enables the formation of protective Cr_2O_3 scale.



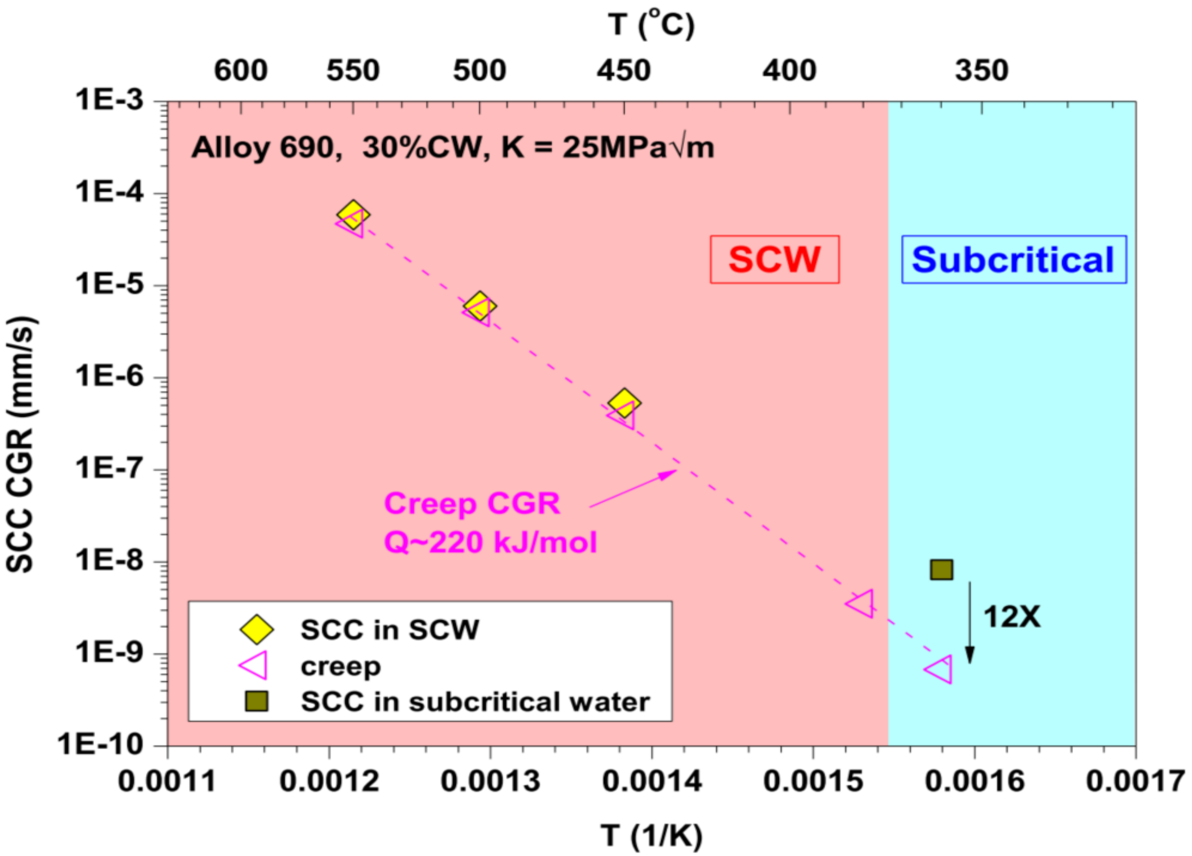


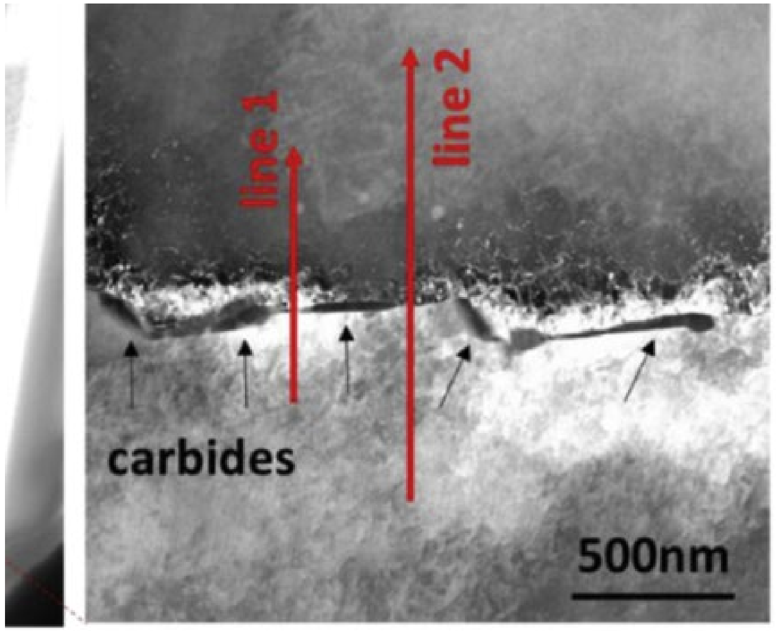


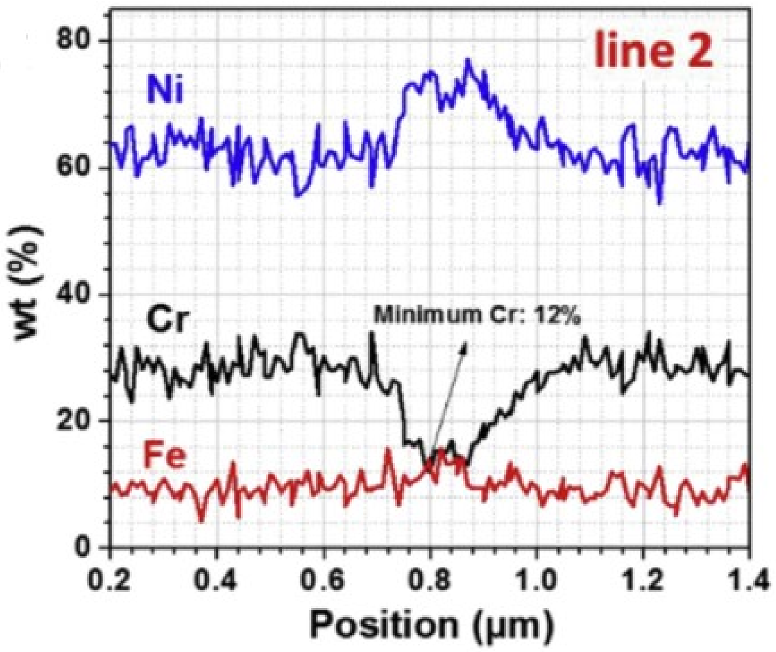
Nickel-based alloys: Alloy 690

Medium cracking rate：

- Creep and in-situ sensitization contributes.
- Cold work and T increase the cracking rates.



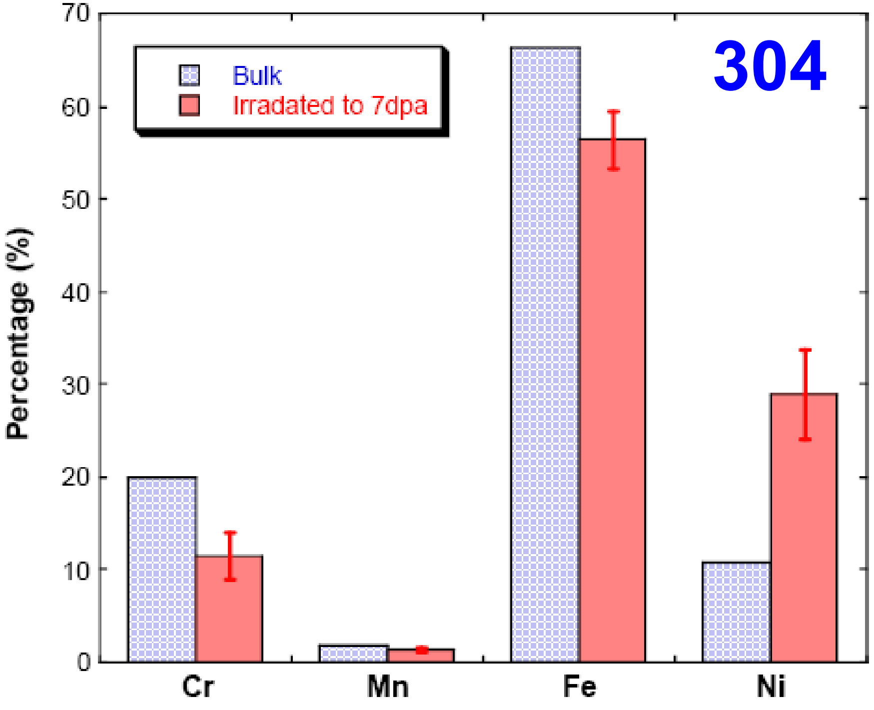


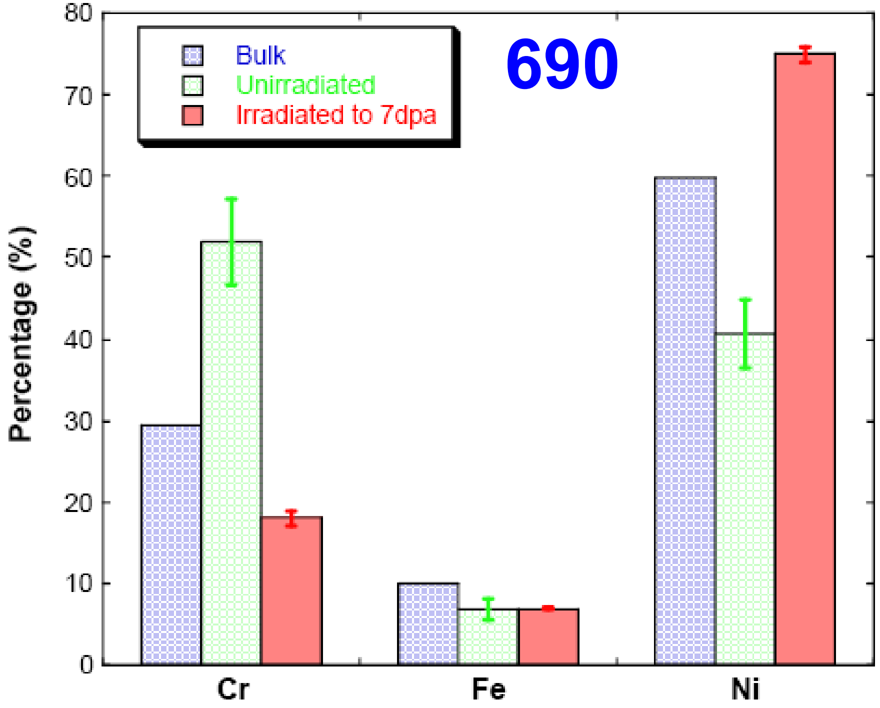


Irradiation effects

Radiation induced segregation at 500ºC up to 7dpa

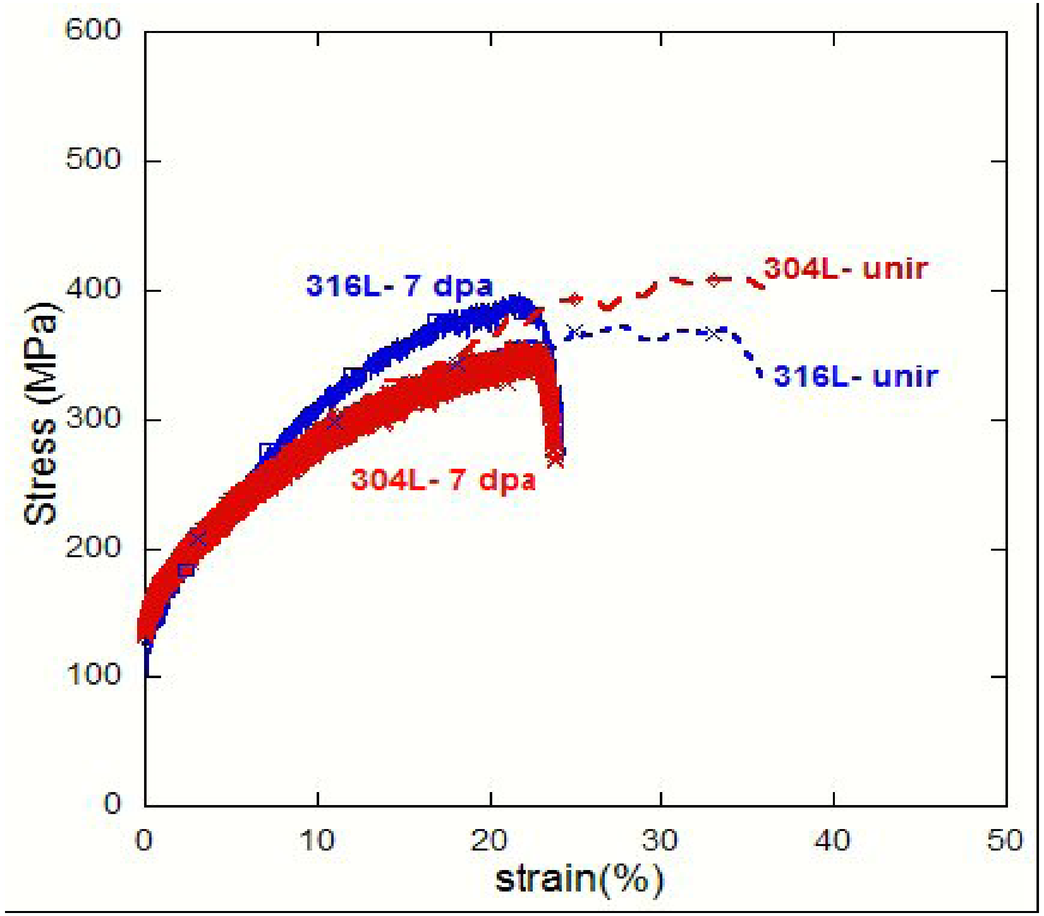
Cr-depletion and Ni-enrichment at grain boundaries

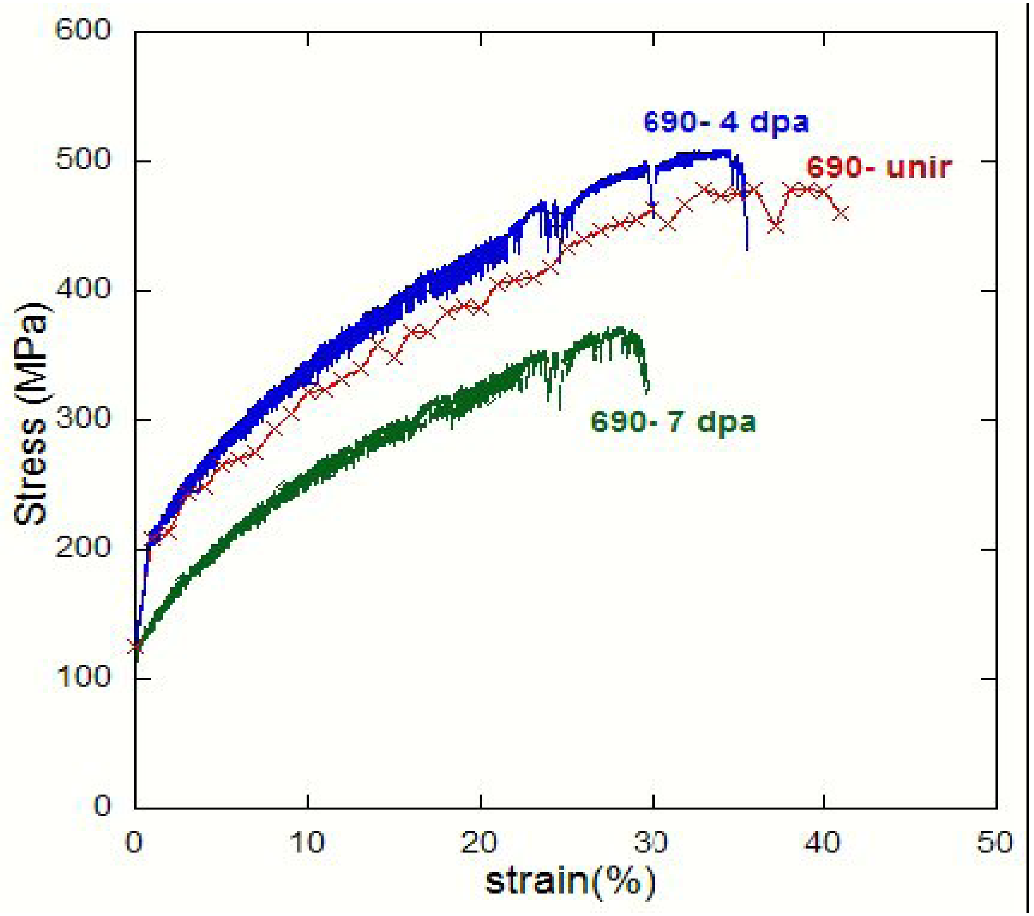




Journal of Nuclear Materials 371 (2007): 107-117

Increased SCC susceptibility after irradiation





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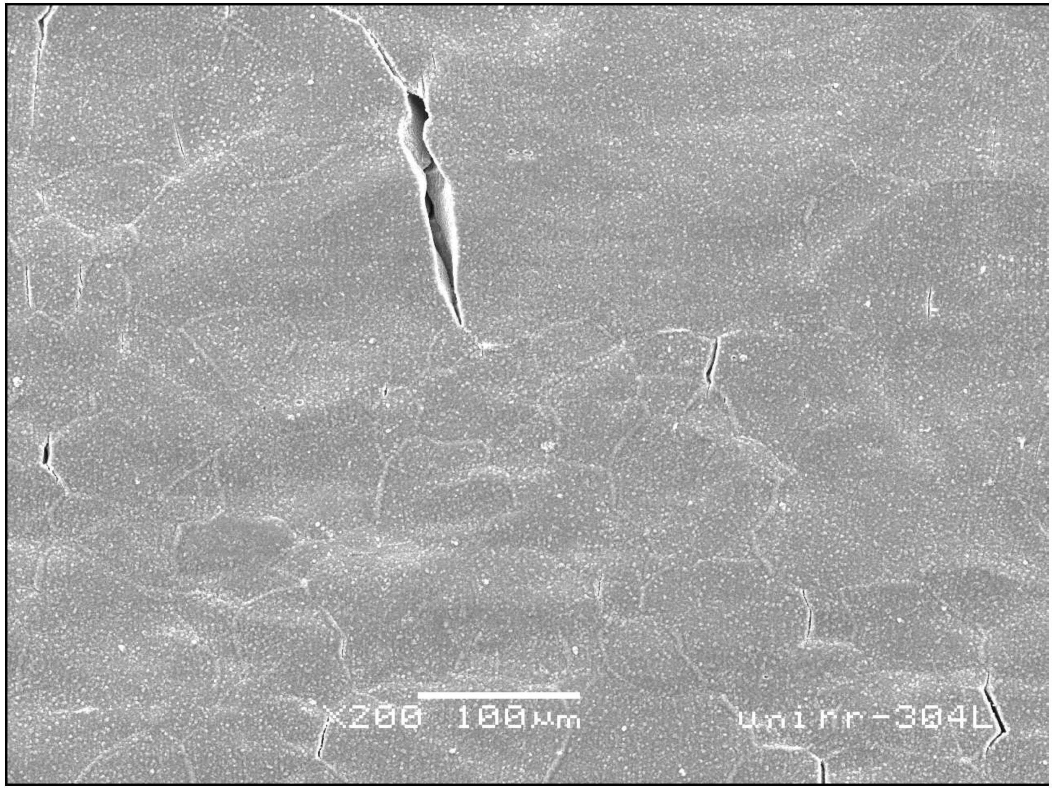
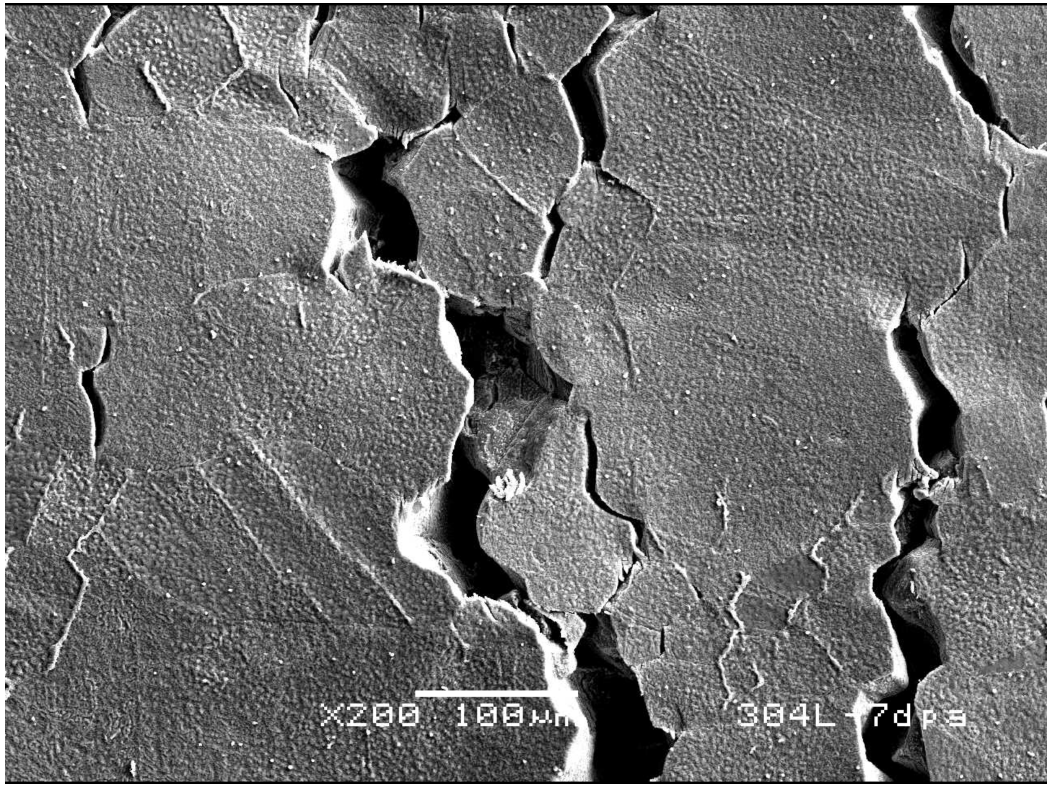
Increased SCC susceptibility after irradiation

Unirradiated sample, showing less intergranular cracks



Irradiated to 7dpa, showing much more cracks

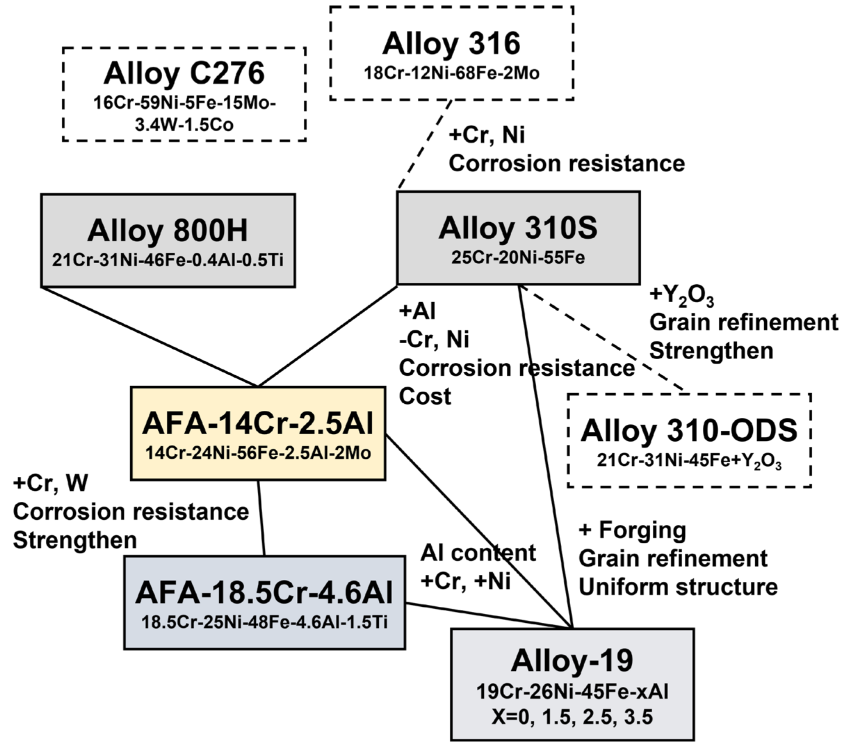


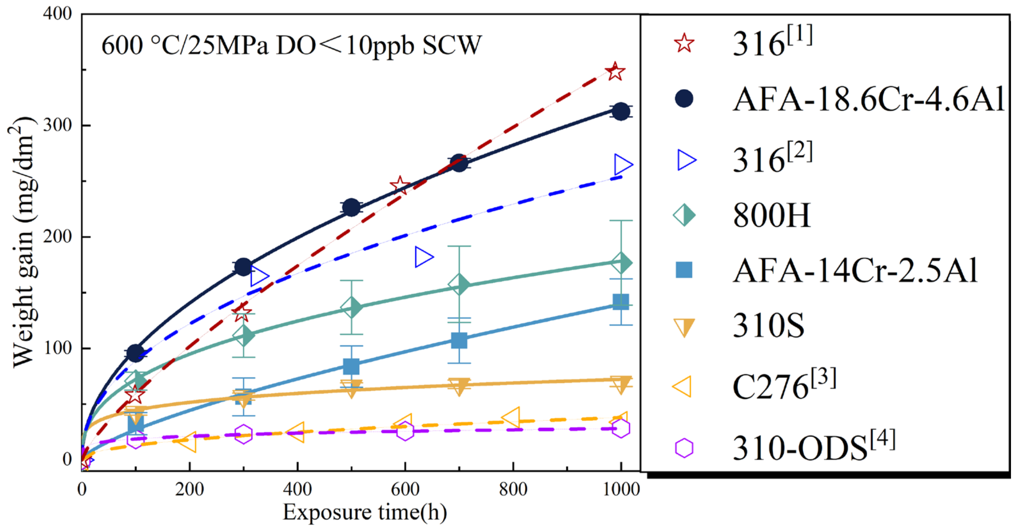
Facing the high corrosion rate of candidate materials, irradiation damage is presently not a biggest concern, but we need to consider this point in R&D of novel materials.

Novel alloys

R&D of novel alloys

- **For general corrosion performances**
  - Increasing Cr up to 25 wt%
  - Adding Al > 2.5%, Si ~1%.
- **Strengthening by ODS or precipitations**
  - ODS increases YS upto ~300 MPa at 550 °C
  - But ODS may introduce oxygen and defects
- **Cracking mitigation**
  - Cold work increases creep and SCC
  - Sensitization at operating temperature
  - GB carbides and precipitation

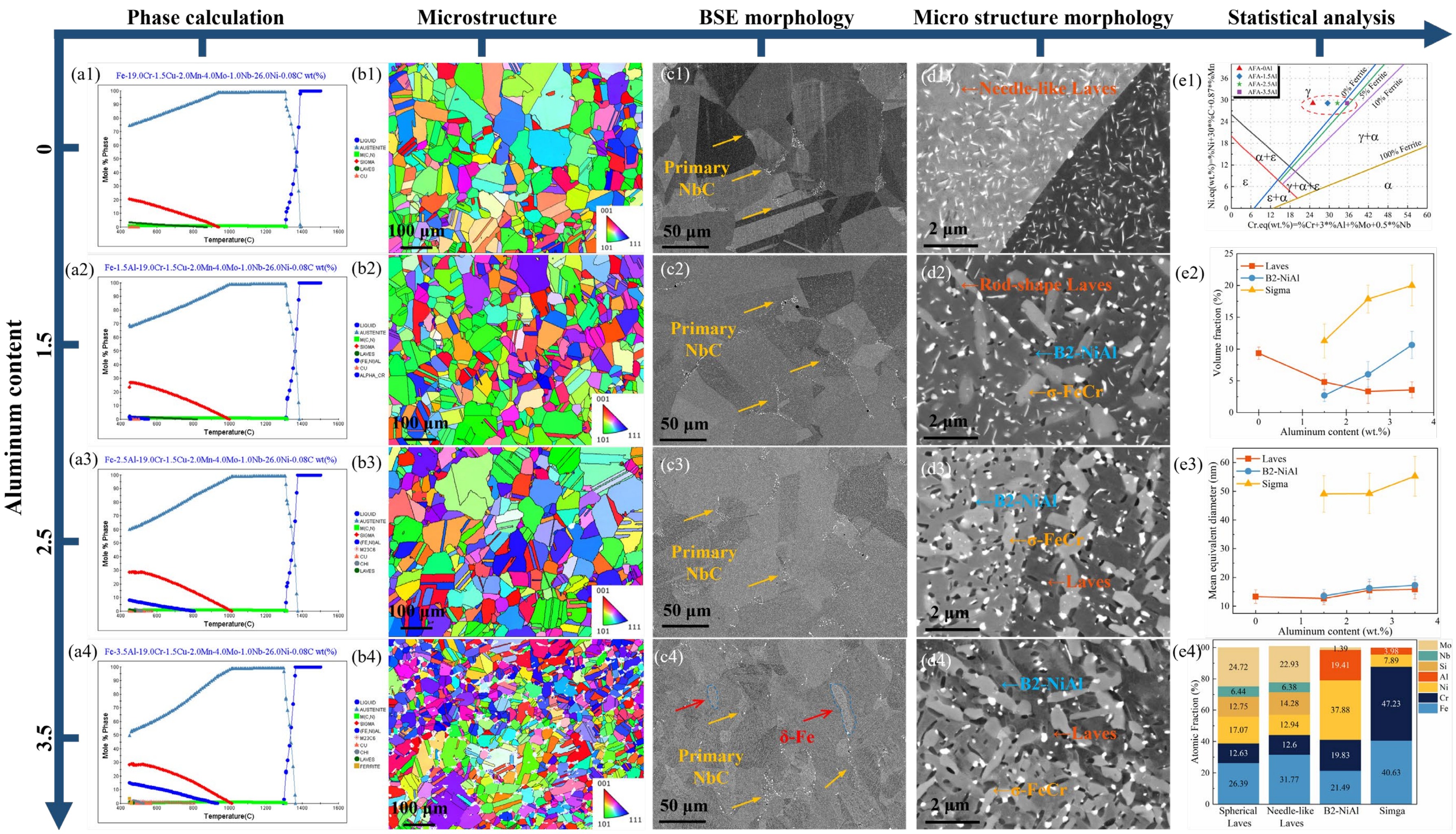




High concentration Cr AFA alloys – effect of Al

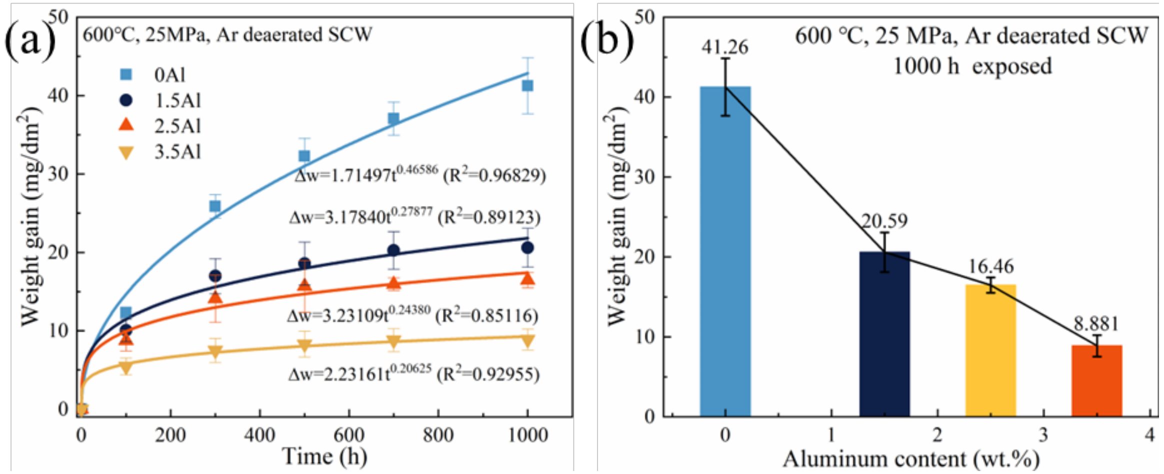
Al on microstructure:

- Precipitates volume fraction, morphology, types
- Precipitation of B2-NiAl, FeCr(sigma),
- Spheroidize Laves-$Si_2(Mo,Nb)$ phase
- Precipitation of BCC-Fe (delta) with 3.5 wt% of Al addition

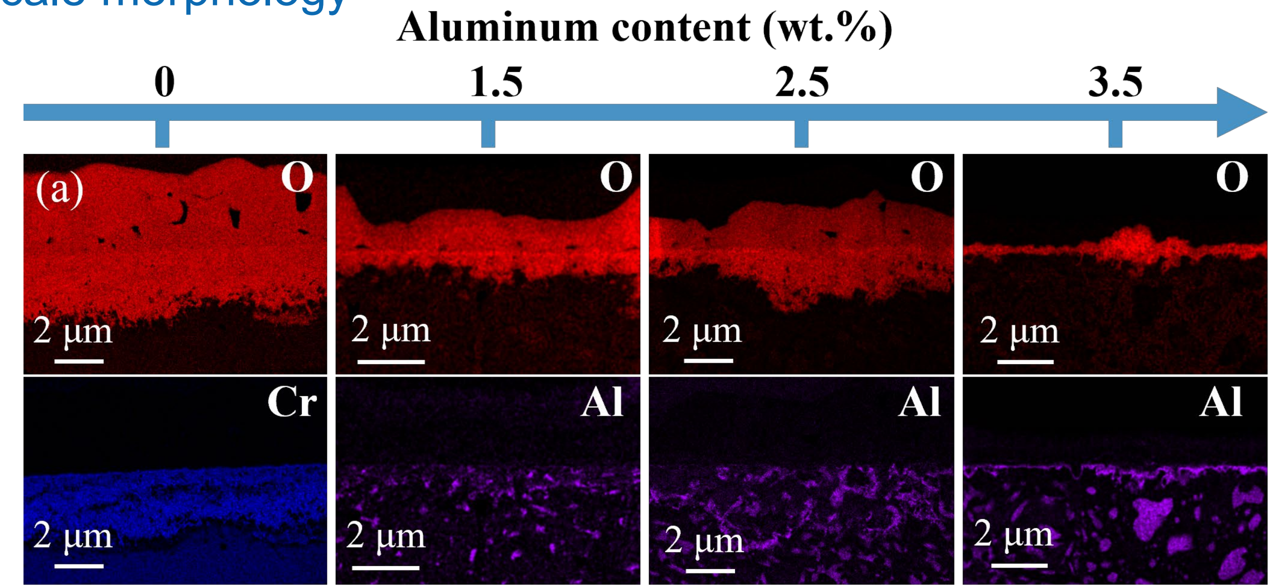


High Cr AFA alloys – effect of Al on corrosion behavior

The addition of Al effectively improves the corrosion resistance



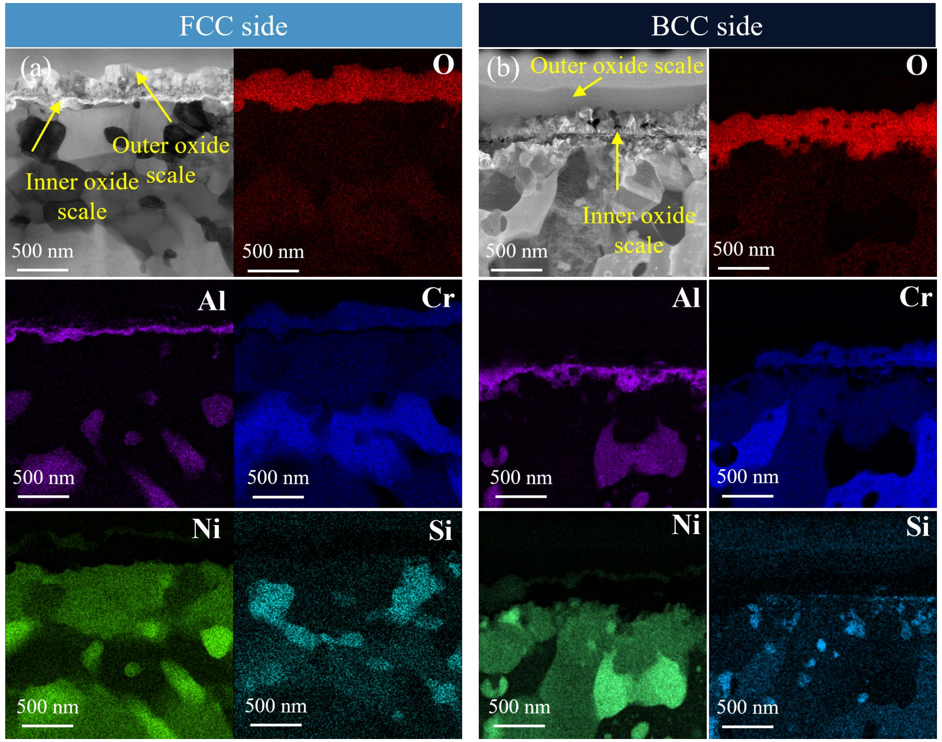
Relationship between corrosion resistance and oxide scale morphology



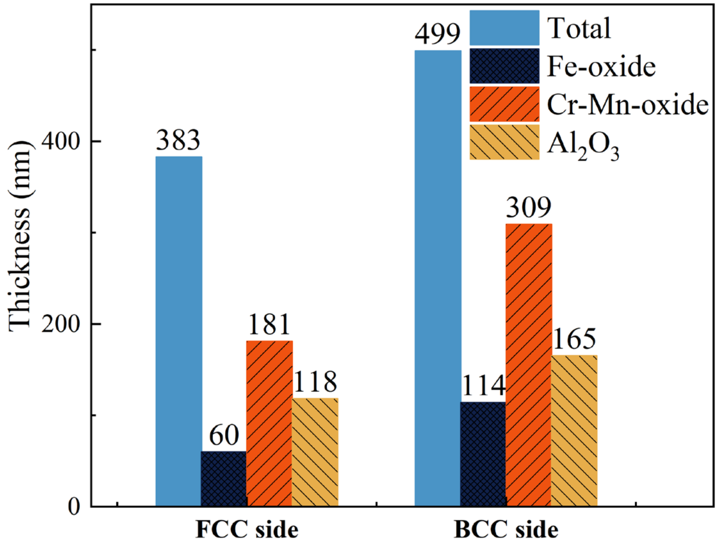
Independent and continuous Al_2O_3 scale ＞Discontinuous Al_2O_3 scale＞Cr-Al mixed oxide scale＞Cr_2O_3

High Cr AFA alloys – effect of Al

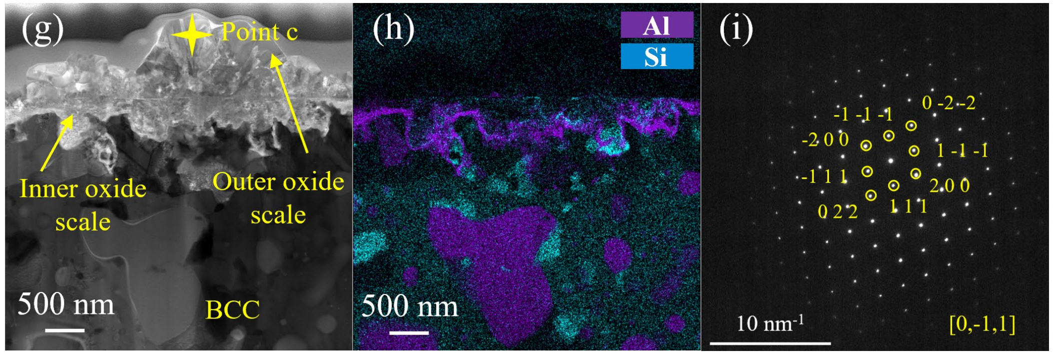
Minor effect of BCC-Fe (delta) on Al_2O_3 formation：
The precipitation of BCC-Fe (delta) needs to be avoided



- Al_2O_3 scale: uniform in FCC side and fluctuate in BCC side



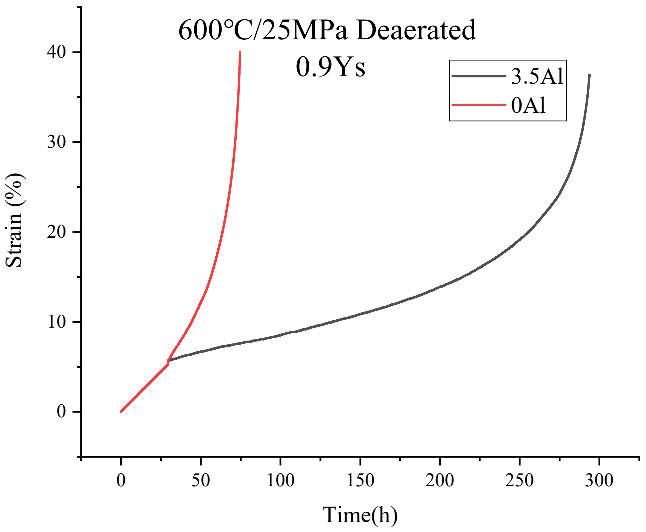
- The thickness variation is only 40 nm in two side



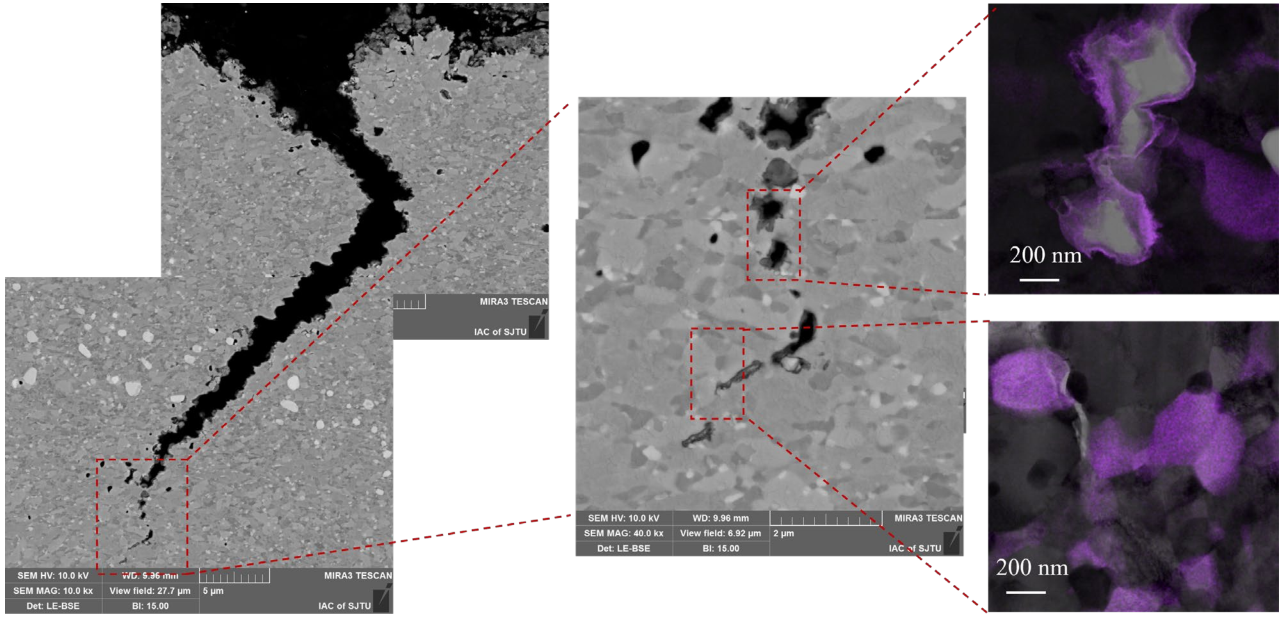
- Inhomogeneous distribution of Al in BCC side results in the fluctuation of Al_2O_3 scale

High Cr AFA alloys – effect of Al

The effect of Al element on SCC



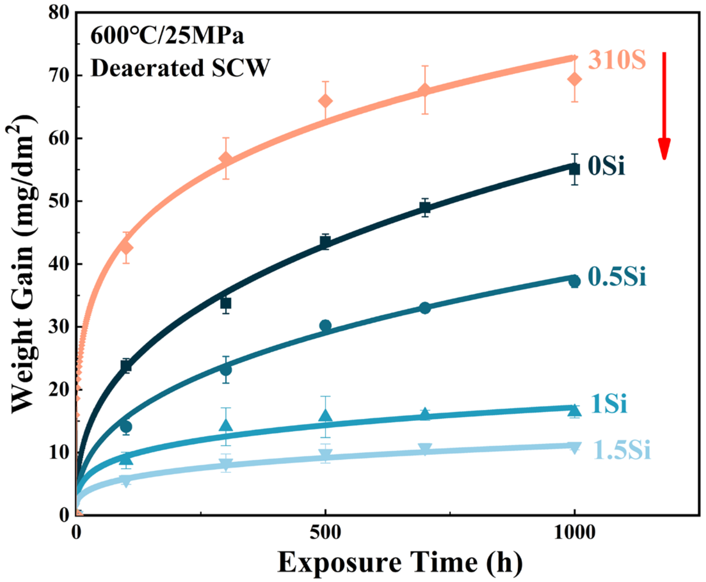
Crack initiation under constant load

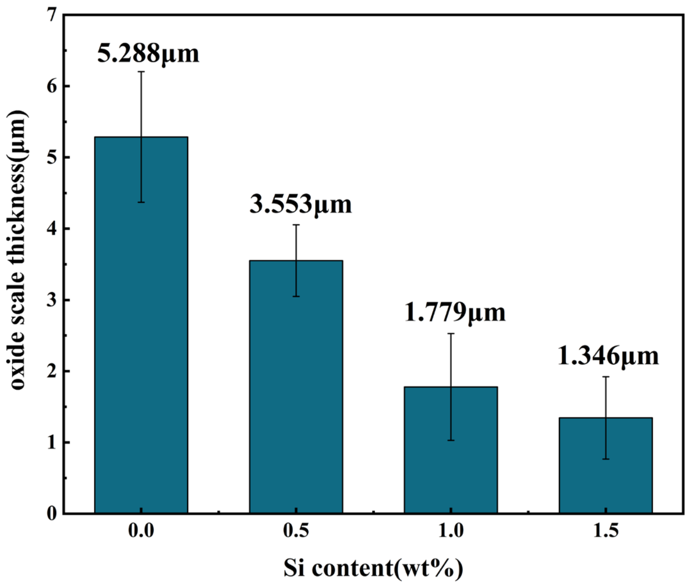


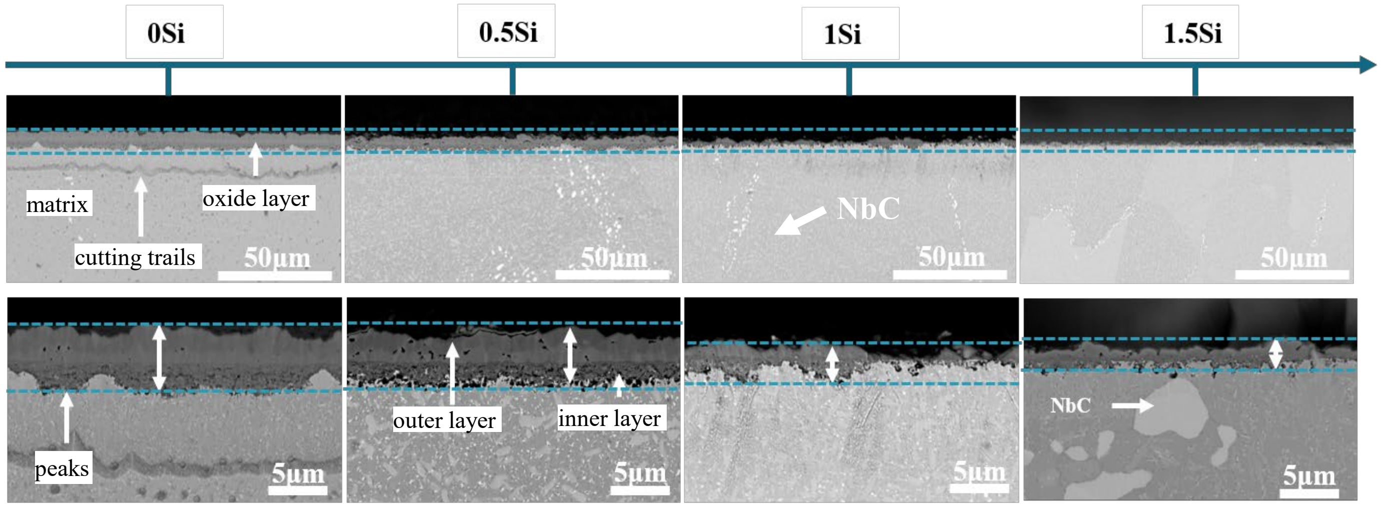
- The Al_2O_3 sale in crack tip hinders corrosion
- Precipitates impedes crack propagation

High Cr AFA alloys – effect of Si

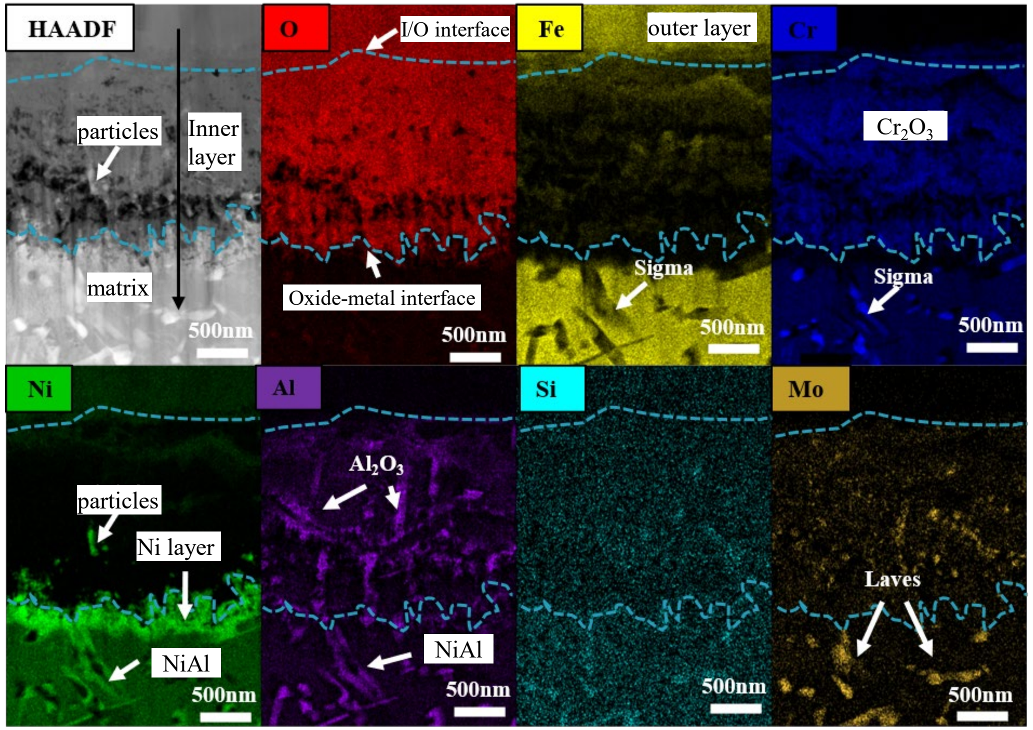
- Addition of Si improves the corrosion resistance effectively
  - ✓ The corrosion weight gain in SCW at 600 ° C@25MPa decreases with the increasing Si concentration
  - ✓ The alloy containing 1.5% Si showed 10x lower corrosion rate than 310S stainless steel

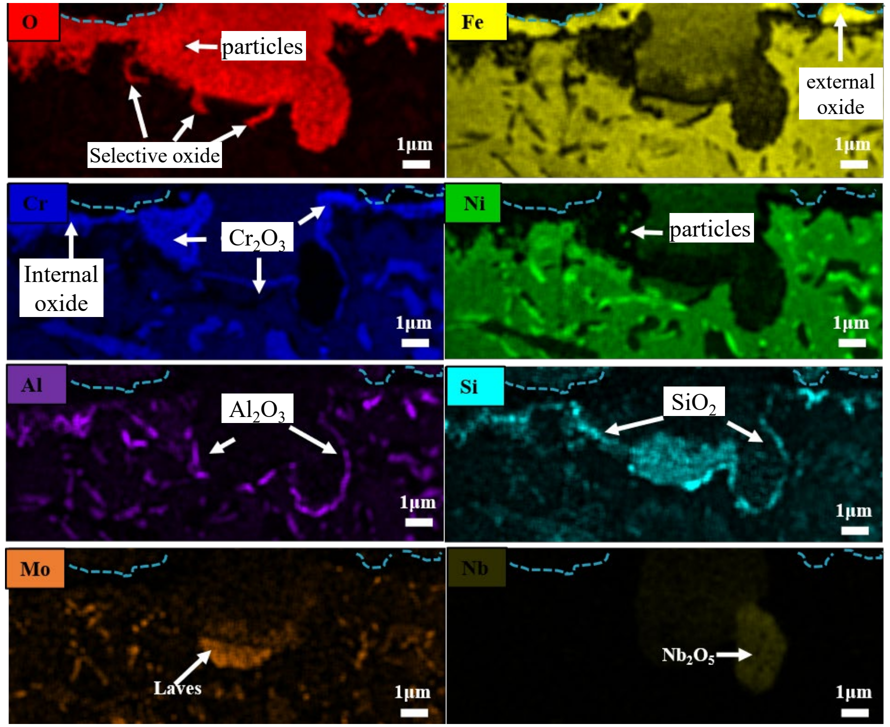






High Cr AFA alloys – effect of Si





Alloy with 0 Si: No SiO2 layer can be found in the protective oxide scale.

Alloy with 1.5%Si: A layer of SiO_2 can be found in the surface oxide scale together with Cr_2O_3 and Al_2O_3. Synergistic effects of Cr, Al and Si on corrosion resistance is of great interest in our future study.

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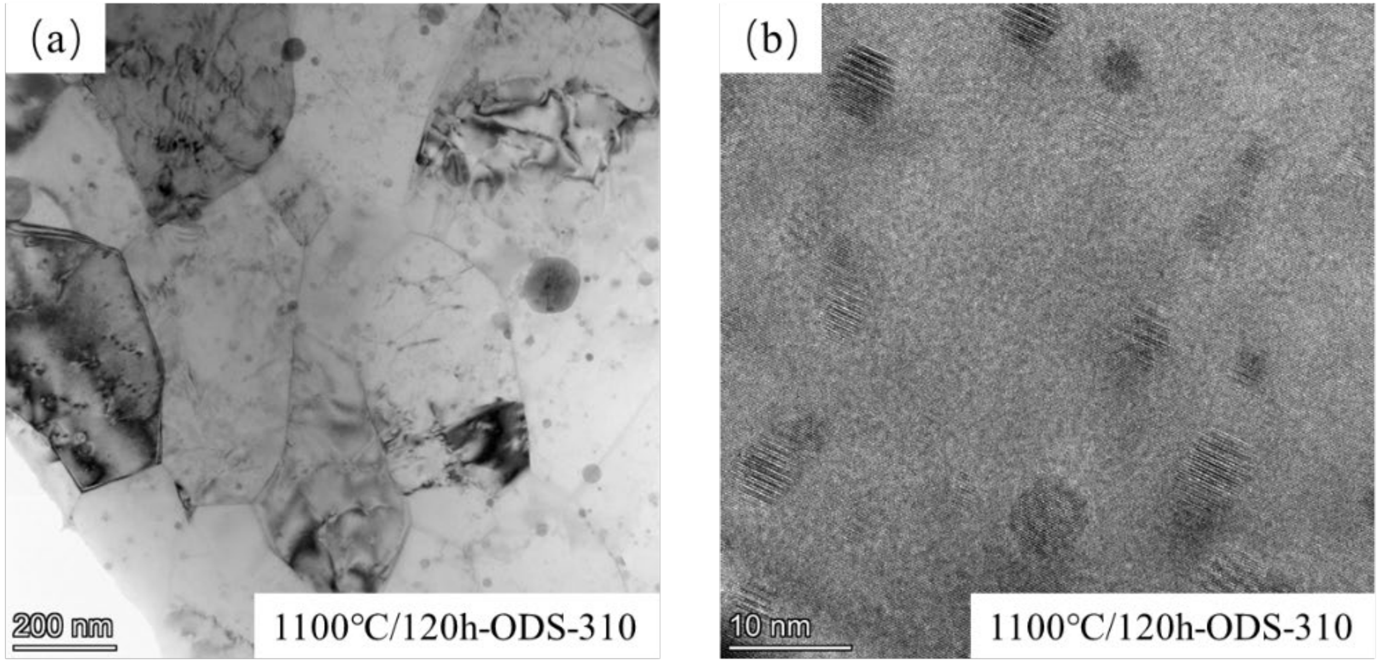
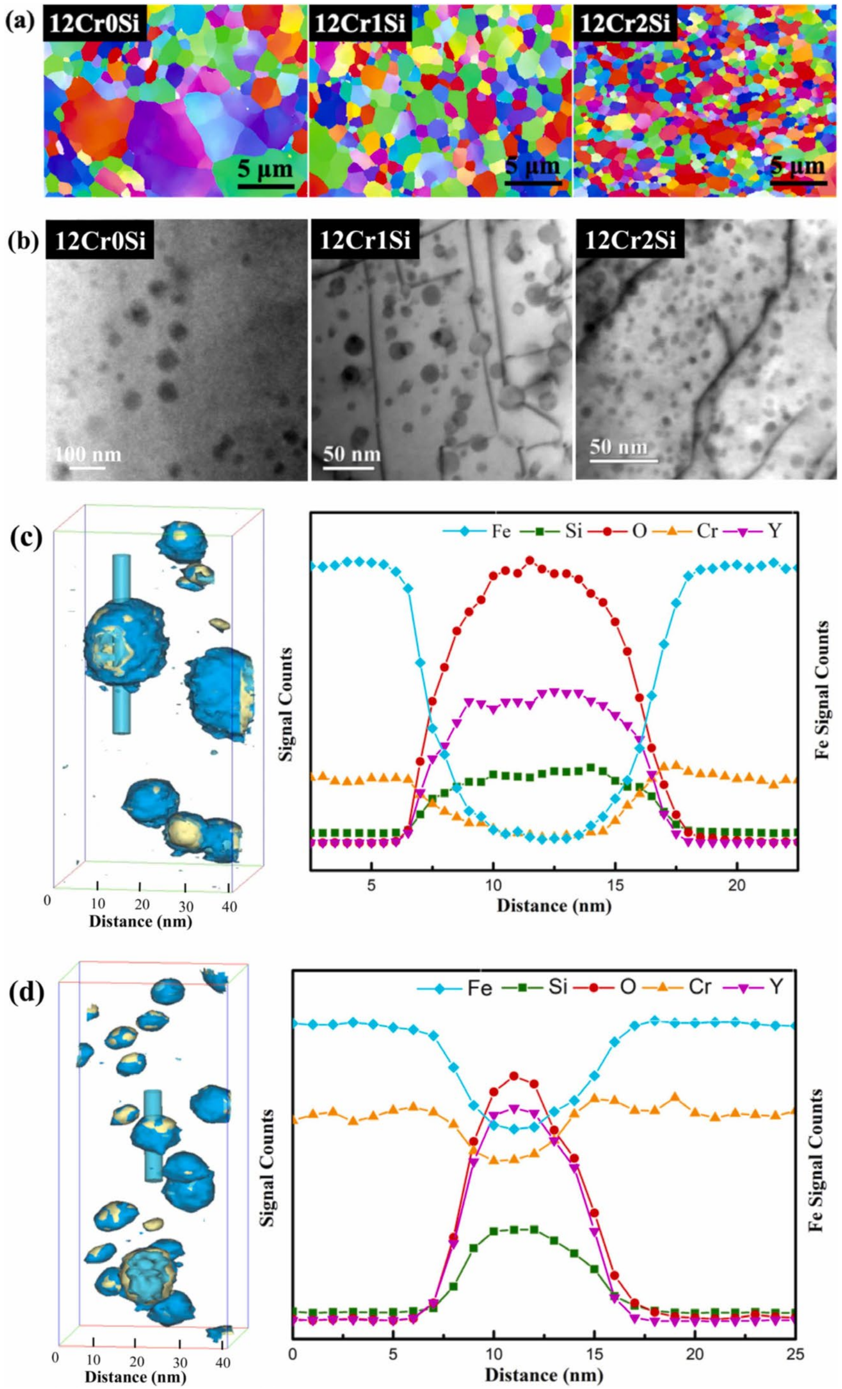
High Cr ODS alloys

The addition of nano-size Y_2O_3 refines the grain size, which may improve the high temperature strength.





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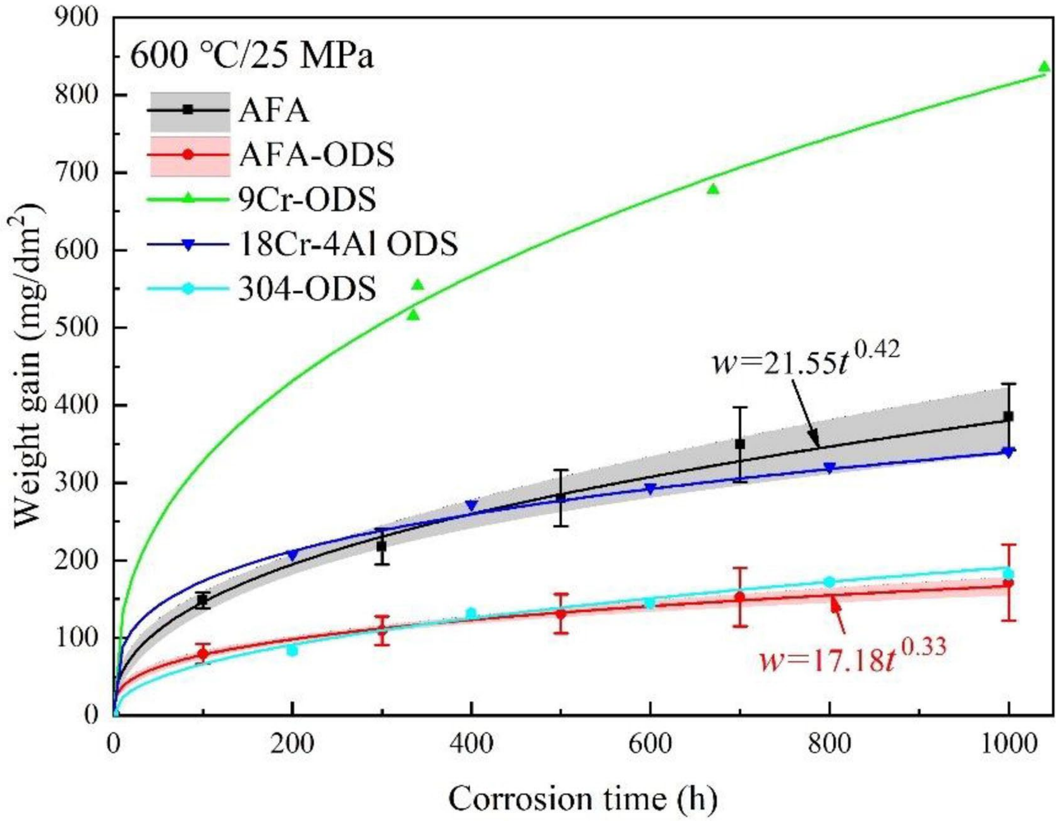
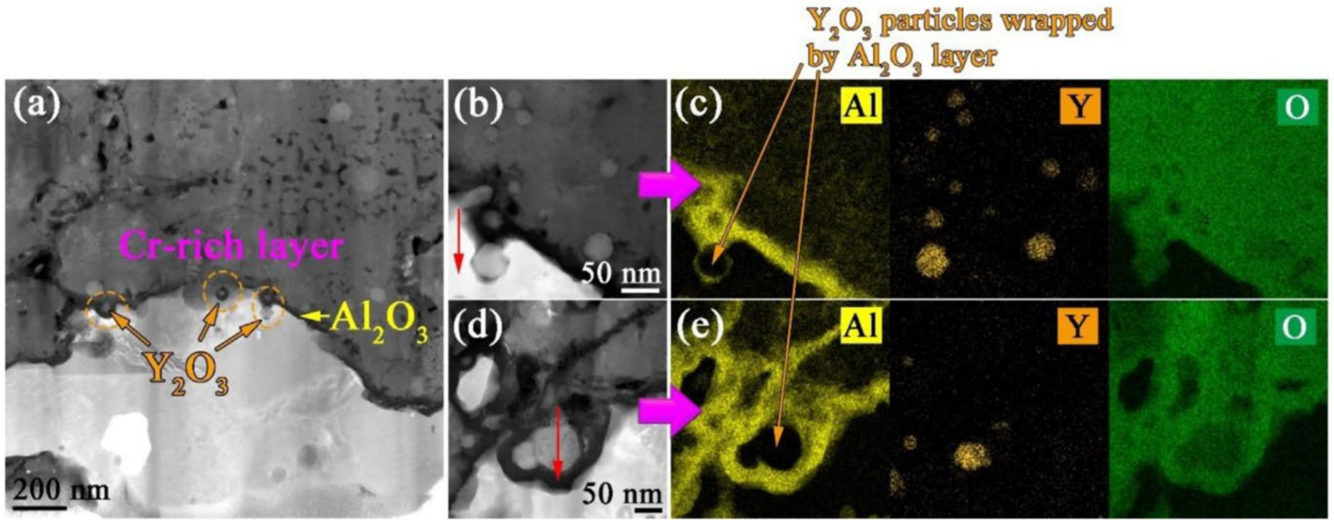
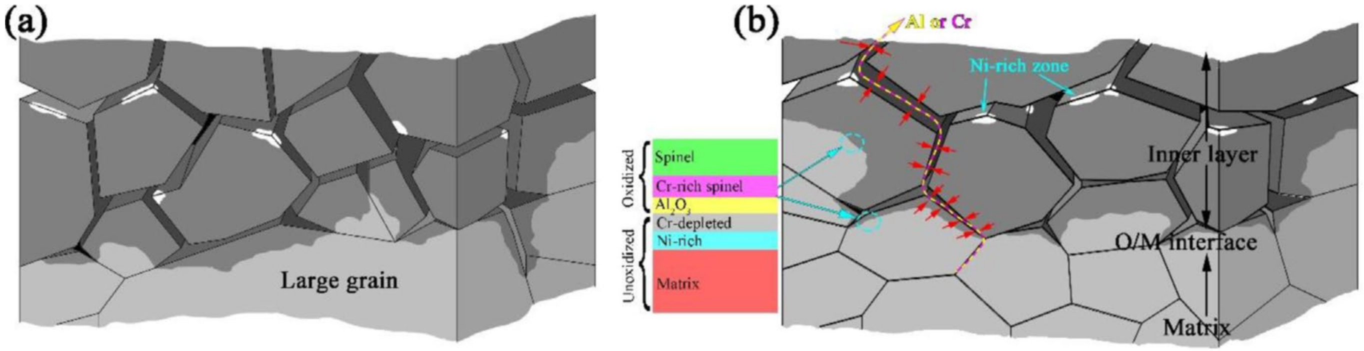
High Cr ODS alloys







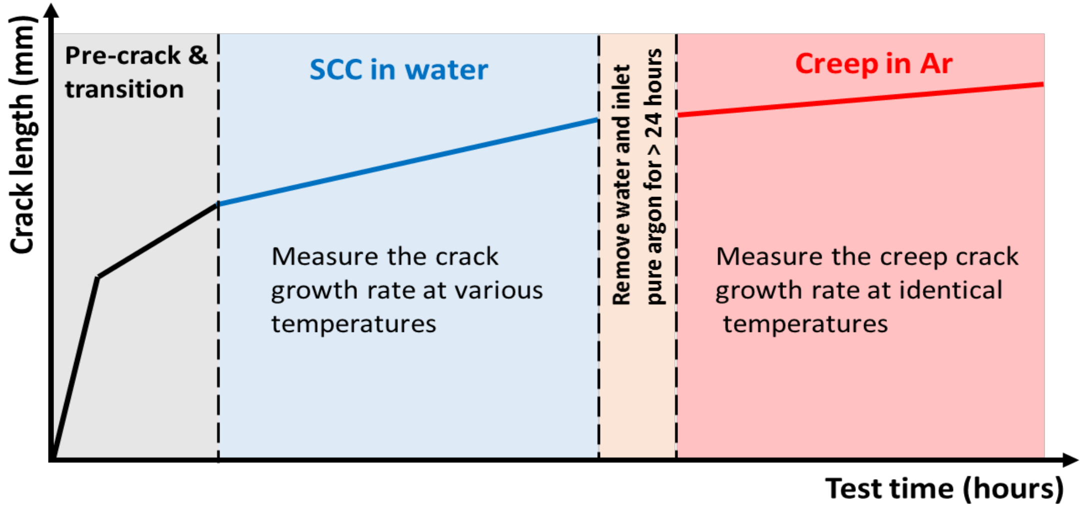
Key points to obtain good data in our tests

Formalization of testing procedures in SCW

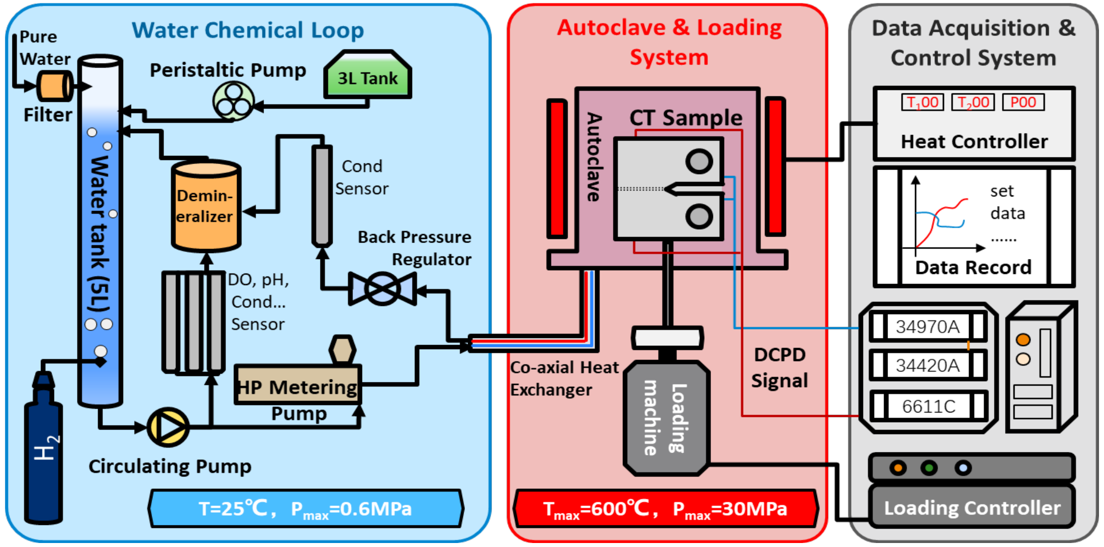
- Specimen preparation: polish to mirror surface, removing mechanical effect, better to use vibration polishing. Removal of the cold worked surface is of great importance.
- When testing surface effects, prepare the surface carefully, homogeneity and reproducibility.
- Install at least two thermocouples in the autoclave, so that the temperatures above and below of the coupons are recorded.
- Water purity: maintain high purity water (low conductivity and TOC), stable pH, and specified dissolved gases. Maintain autoclave refresh rate until the same conductivity readings from outlet and inlet. So that, the water chemistry in autoclave is stable.
- When stopping the autoclave, 1) stop the autoclave heater; 2) stop the high pressure pump after autoclave temperature drops about 20 ° C; 3) gradually depressurize the autoclave down to about 2MPa, then close the valves of autoclave inlet and outlet, and let the autoclave to cool down.

Obtaining the effect of creep on cracking

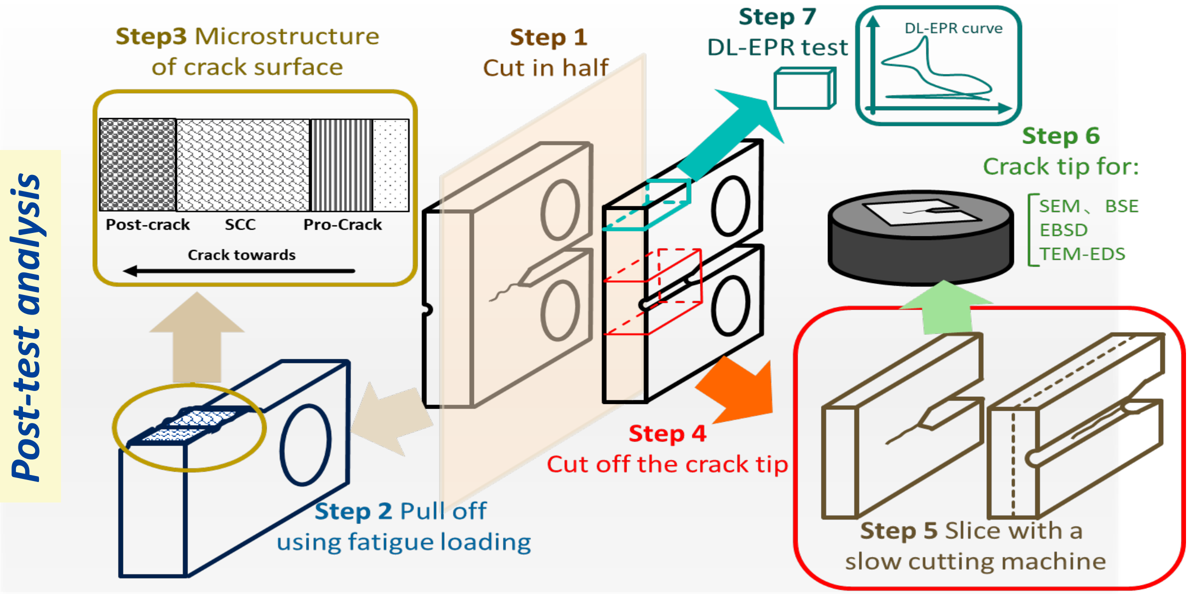
The creep CGRs can be measured after the SCC tests by removing water with argon in the autoclave to establish inert environment-no effect of corrosion.



Test System



Post-test analysis



Critical rule on obtaining good crack growth rate data:

-- getting reliable data on the same specimen

-- change the testing conditions on the fly

-- Only one parameter changed in one step

-- Repetition to confirm the data.

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Takeaways

SCWR concept is facing great challenges in cladding materials

- No commercial materials are available at present
- R&D of novel material is facing a great gap in corrosion, creep and cracking performances

The ideas for R&D of novel SCWR cladding materials

- High Cr + moderate Al% + Si%
- ODS can be considered to strengthen GB
- Bulk or surface hardening by cold working is necessary to reduce general corrosion rate

Upcoming Webinars

Date	Title	Presenter
27 September 2023	EPRI Virtual Reality Training	Robert Eller, EPRI, USA
31 October 2023	The Nuclear Workforce of The Future – Opportunities and Needs for The International Nuclear Sector	Callum Thomas, Thomas THOR, UK
02 November 2023	MOOK: The knowledge management method applied to a Gen IV project. The continuation of a successful story	Gilles Rodriguez, CEA, France