KAIST

NQe
Department of Nuclear & Quantum Engineering

NU_Html
Nuclear & High Temperature Materials Laboratory

SMR 용 고성능 구조재료 개발 현황 at KAIST

Development of advanced structural materials for SMRs at KAIST – Recent progress

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Gokul Obulan Subramanian, 안태정

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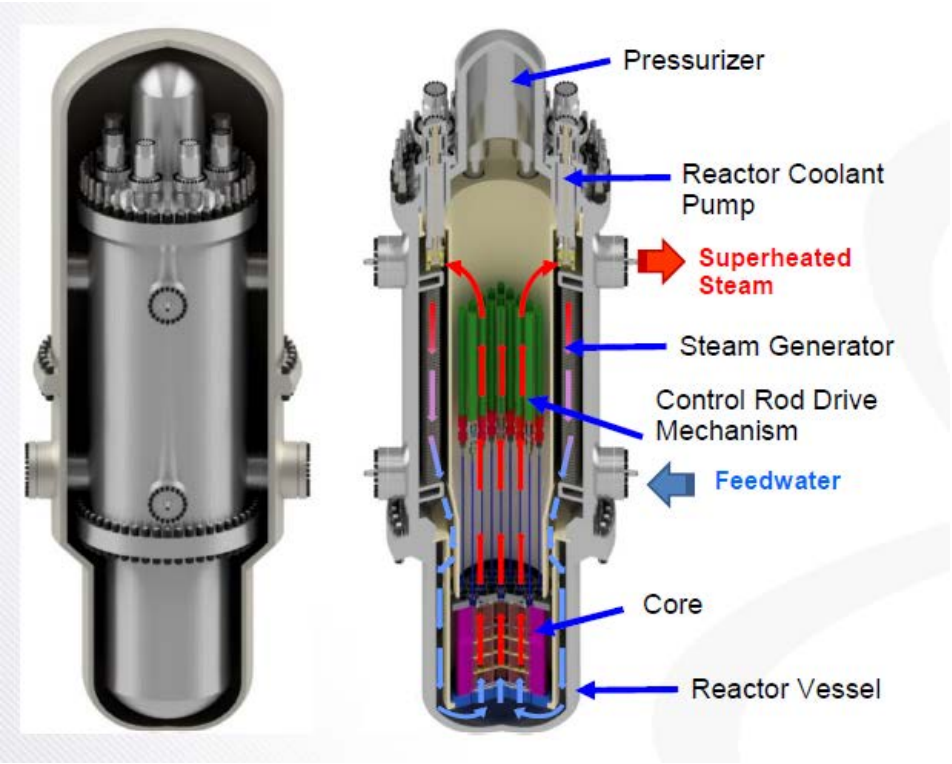
Intro: water-cooled SMRs

D. Sandusky et al., PNNL report no.22290 (2013)

- **Materials**
  - **NuScale**
    - **Almost same as PWR**
    - **May adopt 3DP RPV**
  - **i-SMR**
    - **Bigger than NuScale**
    - **Weight reduction is issue**



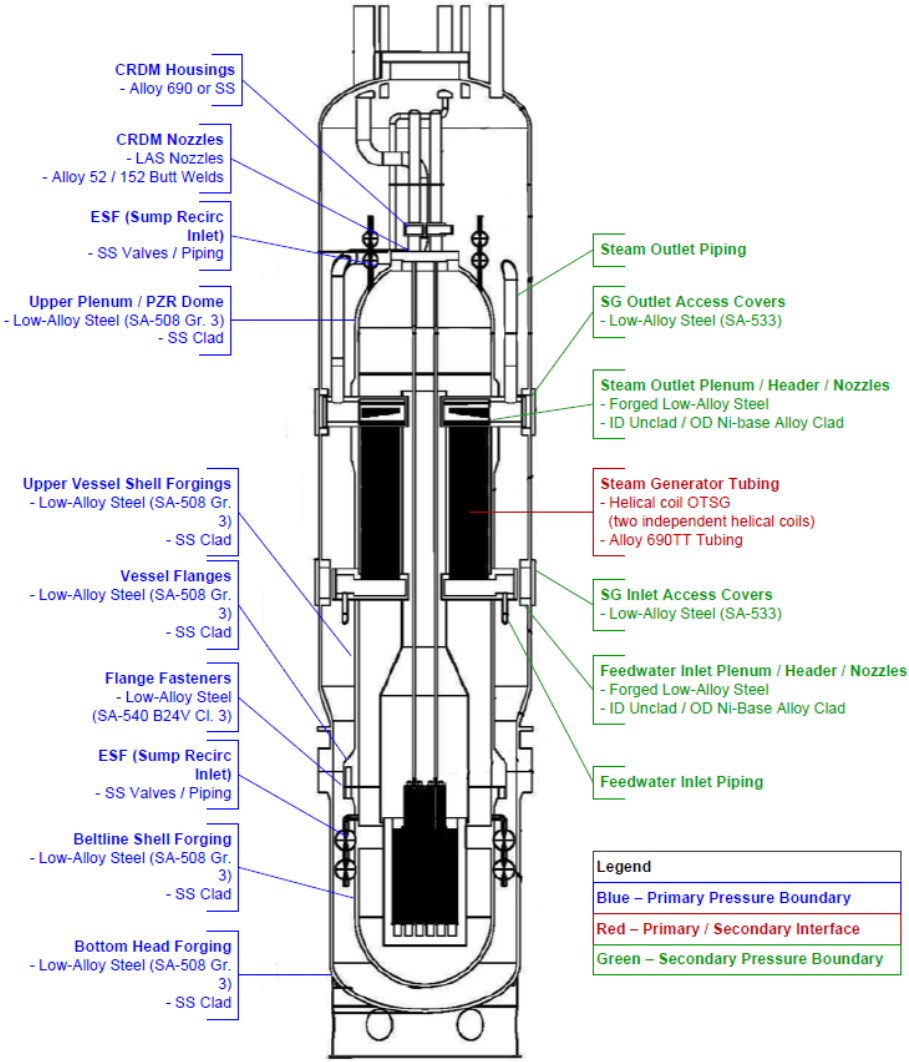


Figure 5-2 NuScale Section Drawing with Pressure Boundary Components Annotated

Intro: non-water cooled SMRs

S. Sham, Section III, Division 5 Overview, presented at ASME Div.5 WS, Nov. 8-9, 2020

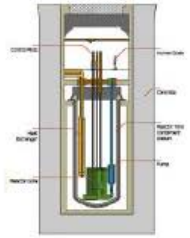
Examples of Different Advanced Reactor Designs Being Developed By Industry

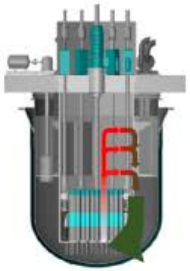
Fast Reactors

GE Hitachi PRISM

TerraPower, TWR

Advanced Reactor Concepts, ARC-100





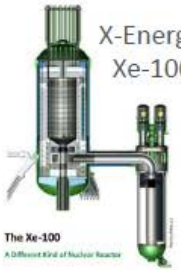
Westinghouse, LFR

TerraPower & GEH Natrium

Oklo, Aurora

Gas Reactors

X-Energy, Xe-100

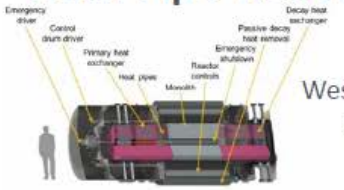


Framatome SC-HTGR

General Atomic EM2 (Gas-cooled Fast Reactor)

Ultra Safe Nuclear MMR

Heat Pipe Reactor



Westinghouse eVinci

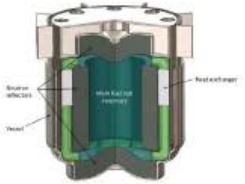
Molten Salt Reactors

Elysium, MCSFR

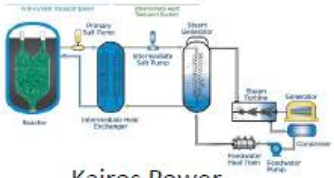
ThorCon

Terrestrial Energy IMSR

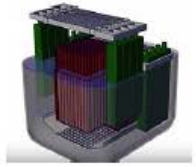
Flibe Energy LFTR (thorium)



TerraPower MCFR



Kairos Power KP-FHR

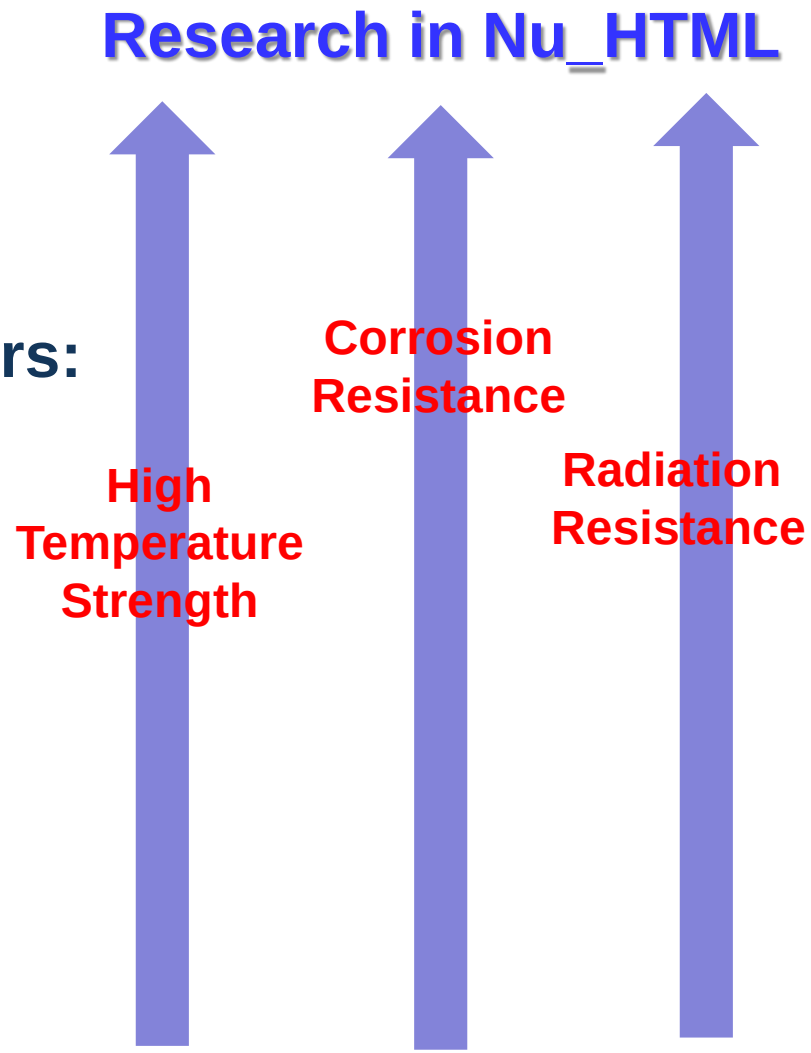


Moltex Energy, SSR

5
ASME BPV III Division 5 Workshop, November 2020

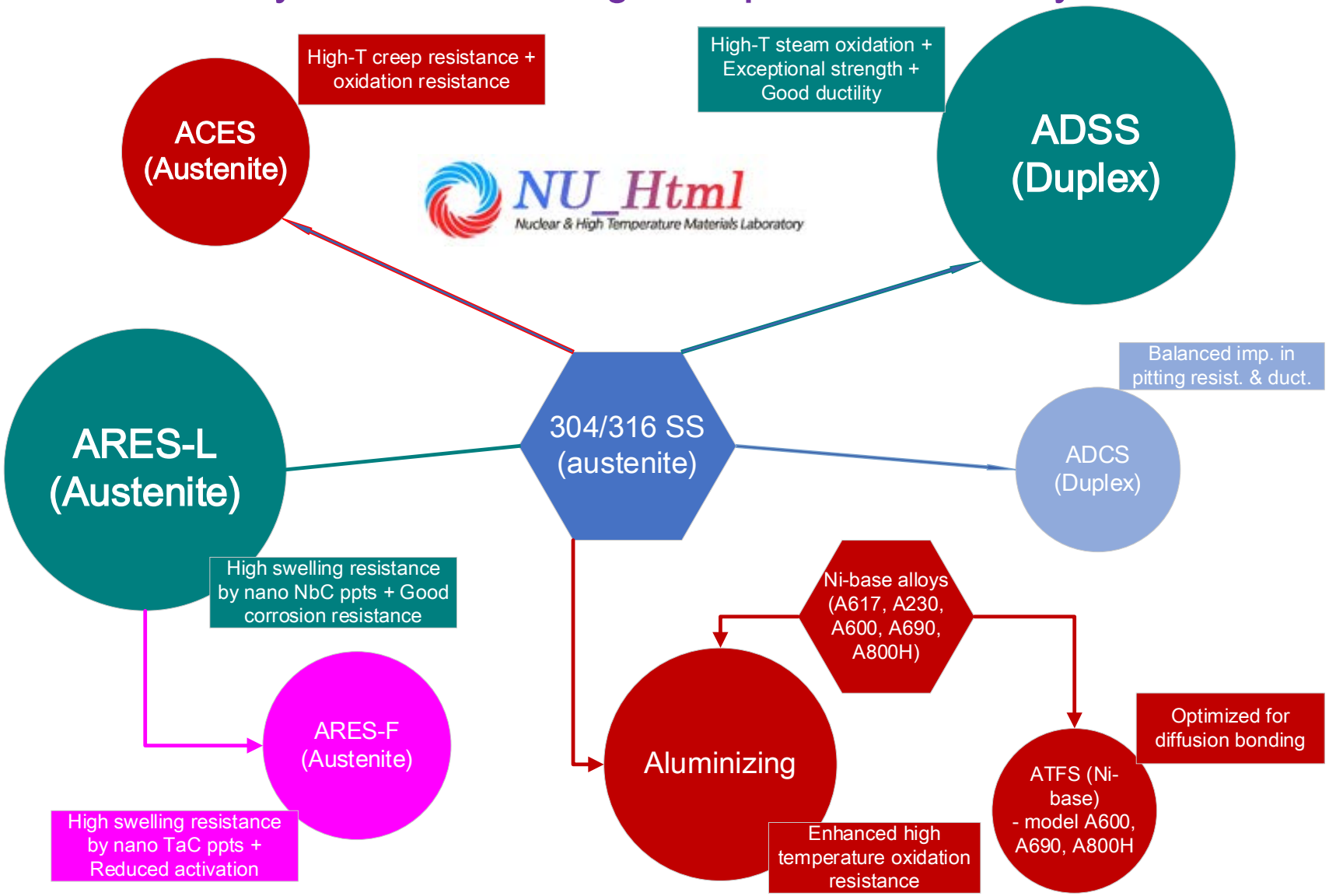
Intro: Materials Requirements

- **Very High-Temperature Reactors:**
  - ~ 900 °C with He
  - Thermal neutron spectrum
- **Fast Reactors:**
  - ~ 550 °C with liq. Na/water/S-CO_2
  - ~ 700 °C with LBE or Molten Salts
  - Fast neutron spectrum
- **Light Water Reactors:**
  - ~ 300 °C with water
  - Thermal neutron spectrum



Intro: Tree of Advanced Alloys in Nu_HTML

A2S Alloys for Nuclear & High-Temperature Power Systems



I. ADSS
for LWR & HTR

ADSS - Motivation

❑ Zr-based Fuel Cladding

- Low neutron c-x
- Poor Corrosion Resistance

Zr Cladding oxidation: **Major source** of **hydrogen** generation

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 + \Delta H$$

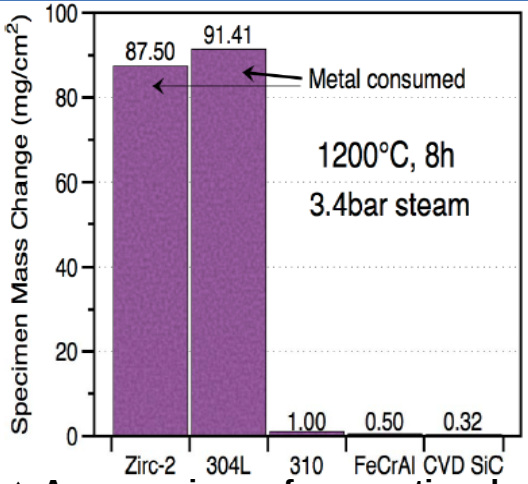
Absorption c-x (barns)

Co : 37.2
Ni : 4.43, Cr : 3.1, Fe : 2.55
Na : 0.53
Al : 0.242
Zr : 0.185, Pb, Si : 0.171
Mg : 0.063
Be : 0.0092
C : 0.0035

Better materials than Zr-alloys??

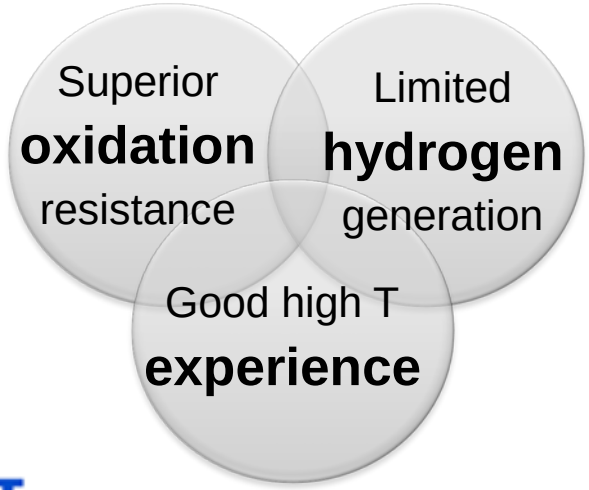
ADSS - Motivation

- Current issues of candidate ATF materials
  - **Ceramic** cladding (SiC)
    - Brittle fracture in normal operation
    - Fission products retention issue
  - **Coating** on Zr-alloy (Cr/Zr)
    - Inherent Zr behaviors (balloon/burst)
  - **Metallic** cladding (Mo, FeCrAl)
    - Poor oxidation (Mo) /Embrittlement (FeCrAl)
- Concept of ADSS alloys

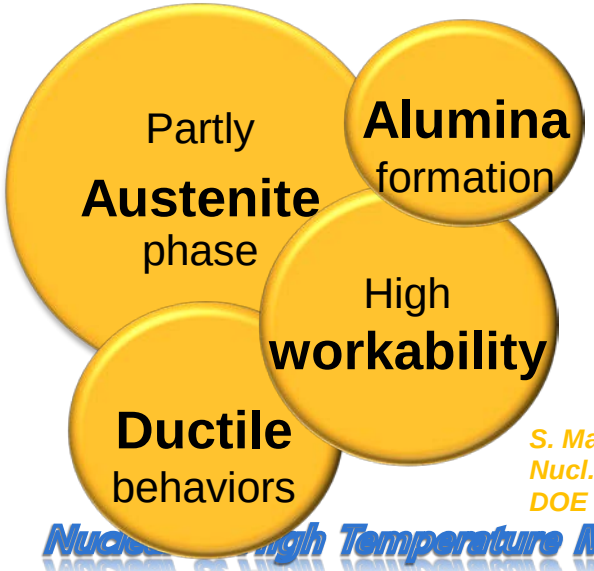


▲ A comparison of conventional alloys and ATF candidate materials in high temp. steam oxidation

Advanced Steel



ADSS alloy



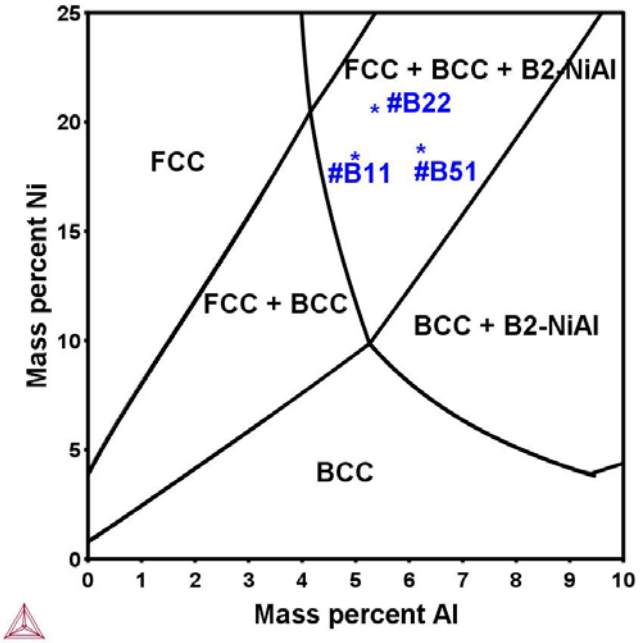
S. Maloy et. al., Advs. in Nucl. Fuel and Maters. DOE Purdue WS, 2014

ADSS – Composition and microstructure

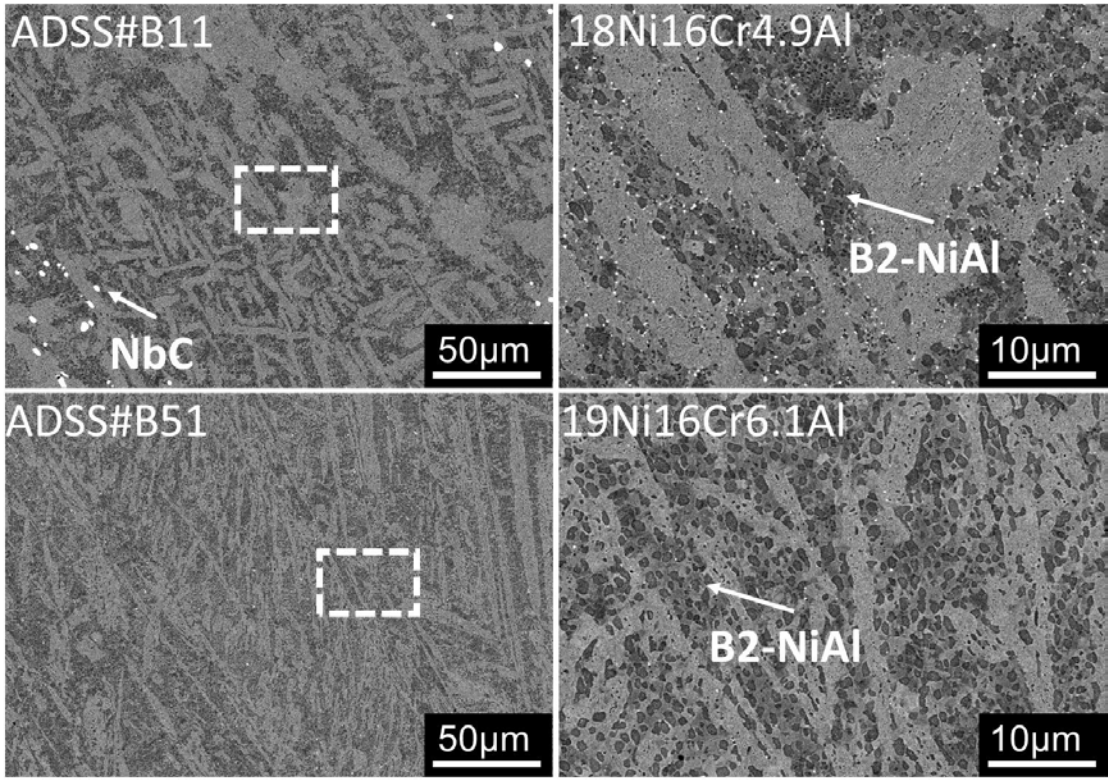
H. Kim et al. J. Nucl. Mater., 507 (2018) 1

❑ Thermodynamic modeling

- Fe-(16-20)Ni-16Cr-(5.5-7.0)Al + (Nb, Mn, C, Si)
- **Austenite(FCC), ferrite(BCC), nickel aluminide (B2-NiAl) co-exist**
- B2-NiAl phase fraction/stability depends on Ni/Al, respectively



▲ Thermo-Calc phase diagram (TCFE-9 database) for Fe-16Cr-xAl-yNi system at 900°C, and the indicated target ADSS compositions.



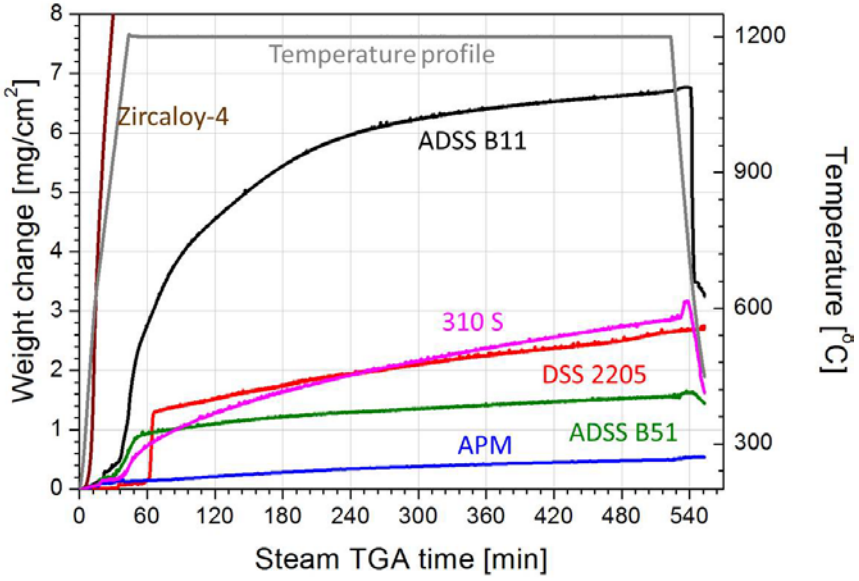
Complex Microstructure!

ADSS - Corrosion resistance

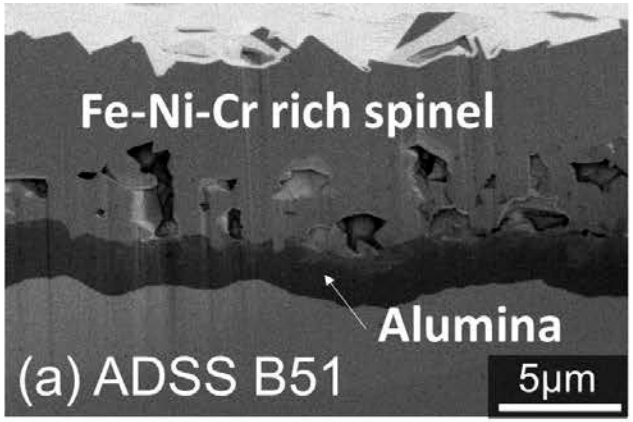
H. Kim et al. J. Nucl. Mater., 507 (2018) 1

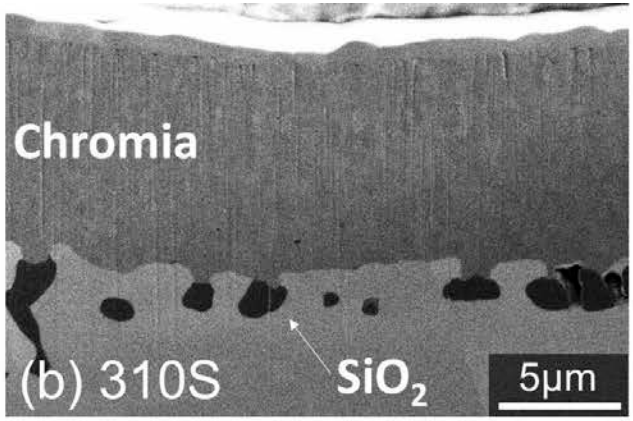
❑ High temperature steam oxidation

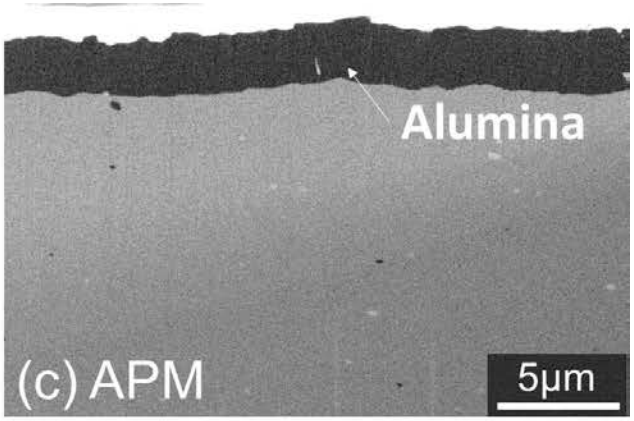
- Steam TG 1200°C 8h
- ADSS alloys showed somewhat larger weight gain, but with similar kinetics at steady-state
  - Confirmed to form protective alumina formation, comparable to FeCrAl alloys



▲ Steam TG graph of ADSS and reference alloys at 1200°C for 8h







▲ Cross-sectional oxide FIB/SEM images for ADSS alloys (a) B51, (b) 310 S, and (c) APM stainless steels after exposure in steam TG at 1200 °C for 8 h.

ADSS - Corrosion resistance

H. Kim et al. J. Nucl. Mater., 507 (2018) 1

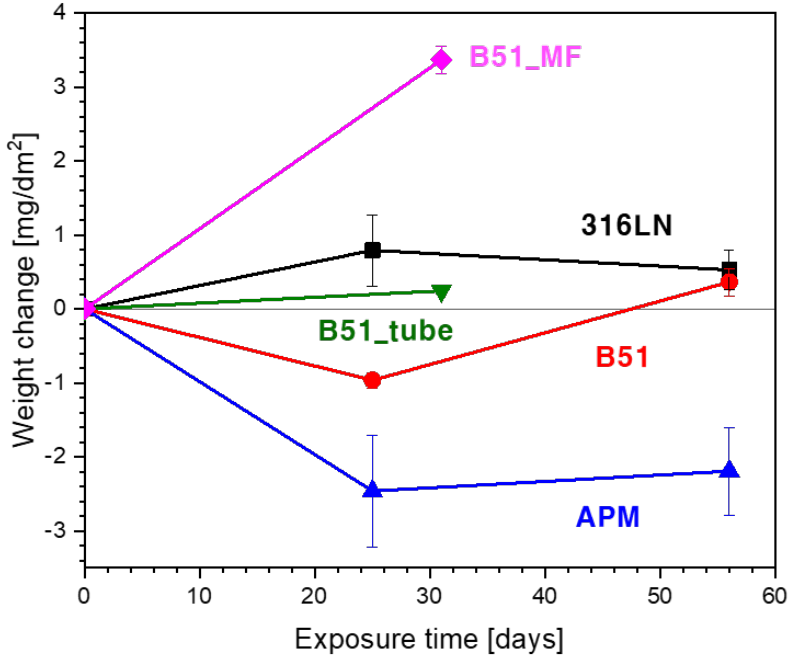
❑ PWR corrosion

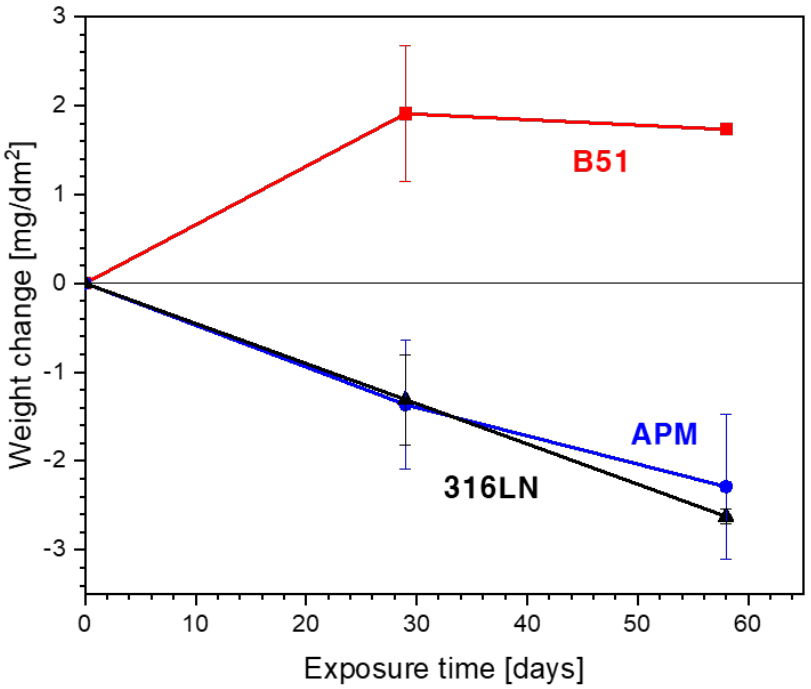
- ADSS alloys showed weight gain in PWR

Table 6
Mass gain and oxide thickness after 30 days corrosion in the simulated PWR environment.

Materials	Mass gain [mg·dm^{-2}]	Oxide thickness [μm]
ADSS alloys	0.62 ± 0.30	0.05–0.15
APM	−0.33 ± 0.06	–
310 S	Negligible[a]	<0.01
Zircaloy-4	20–30	1.3–2.0[b]

[a] Mass gain less than 0.03 mg dm^{-2}.
[b] Values estimated from the longer-term data.

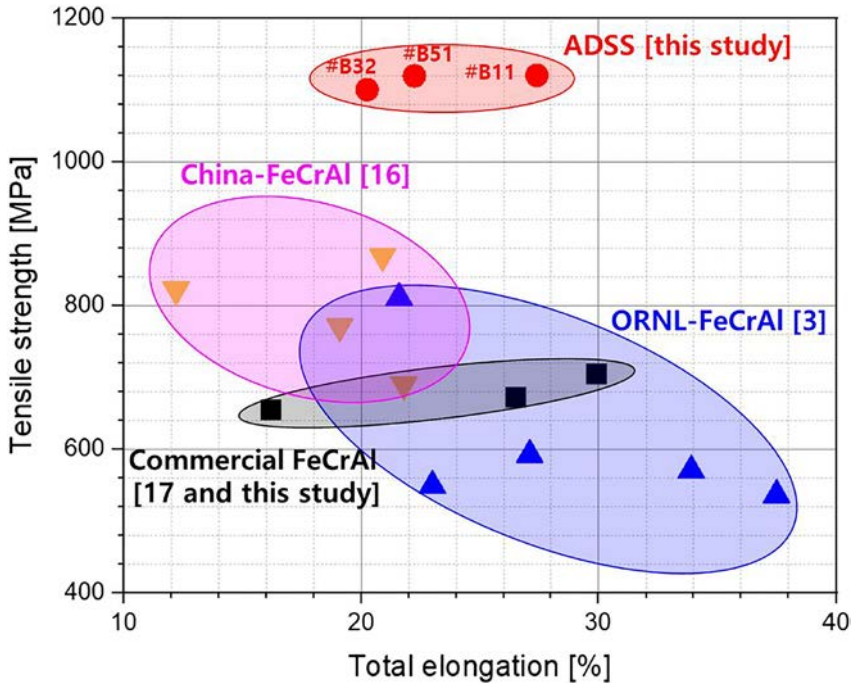


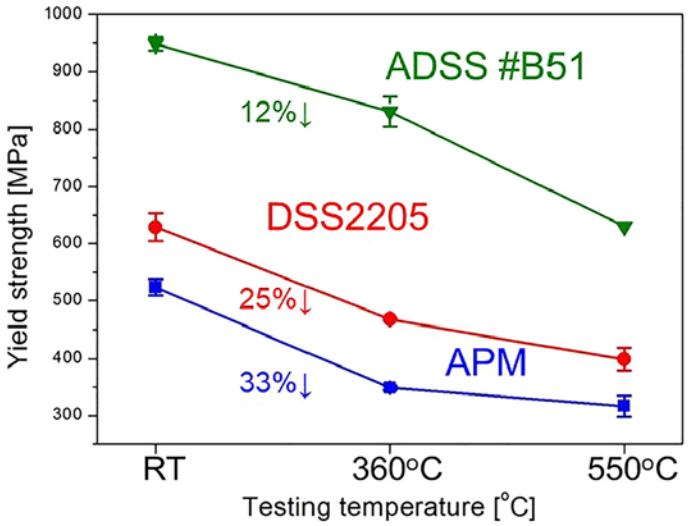


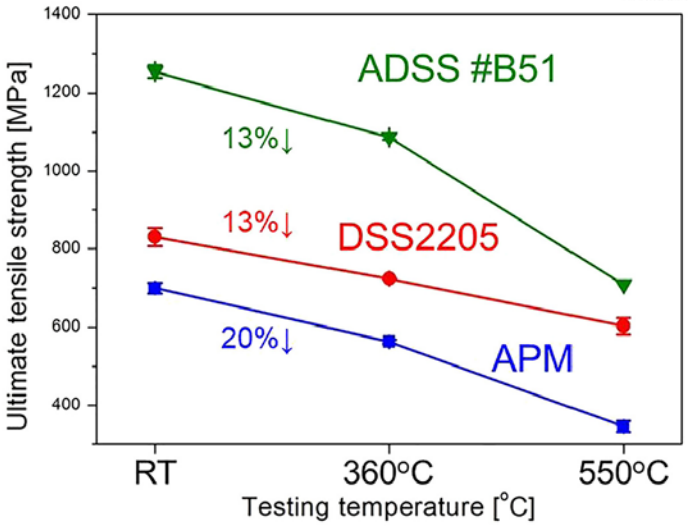
▲ Simulated PWR immersion corrosion test (left) at 320 ºC in 150 bar and (right) at 360 ºC in 190 bar

ADSS - Tensile properties

- **Mechanical properties**





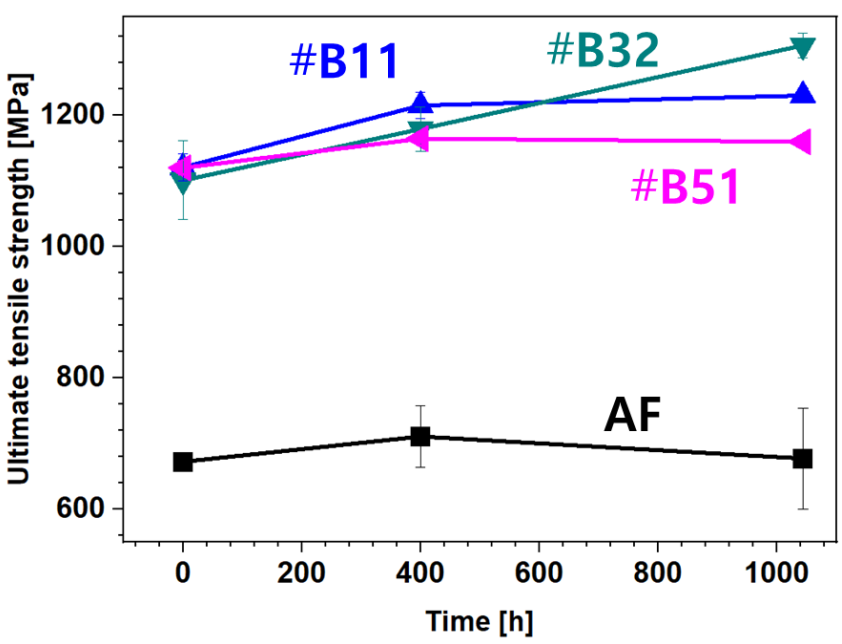


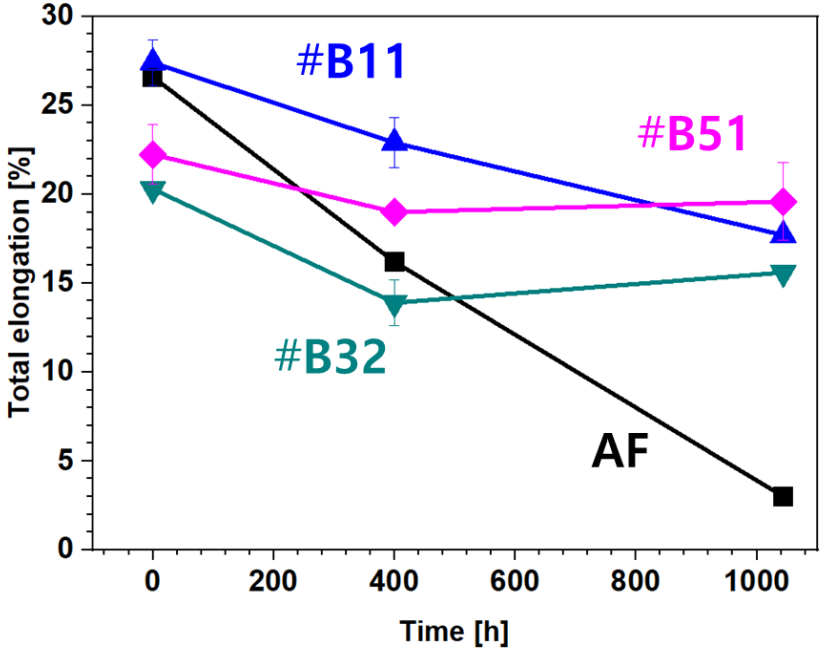
ADSS - Thermal aging

C. Kim et al. Int. J. Energ. Res. 2020

❑ 425 ºC thermal aging for up to 1 kh

- All Fe-based alloys, embrittlement (YS↑, elongation ↓)
- The degree of thermal aging, ADSS << AF
  - Due to austenite phase in ADSS
- Austenite phase : ADSS #B11 > ADSS #B32
- Degree of thermal aging : ADSS #B11 < ADSS #B32

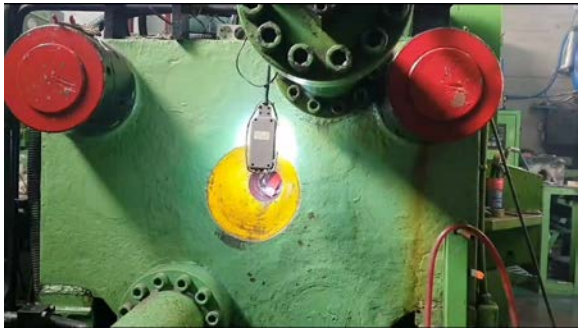


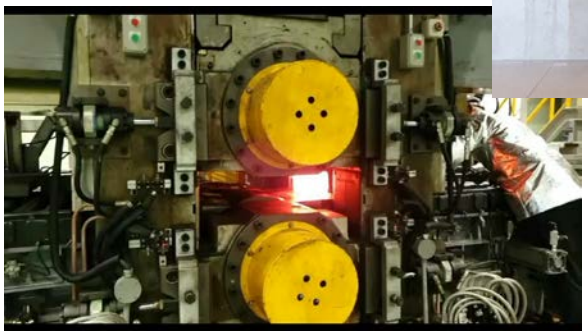


▲ YS and total elongation of ADSS alloys and AF after thermal aging at 425 ºC for up to 1 kh

ADSS - Fabrication of thin tubes

❑ Fabrication of thin ADSS tubes

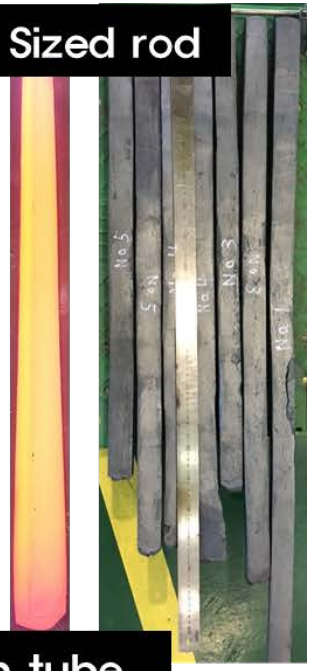




As-cast ingots

Sizing by hot forging and/or rolling

Sized rod



Fabricated bar (master bar)

Thin tube
1.6m O.3t

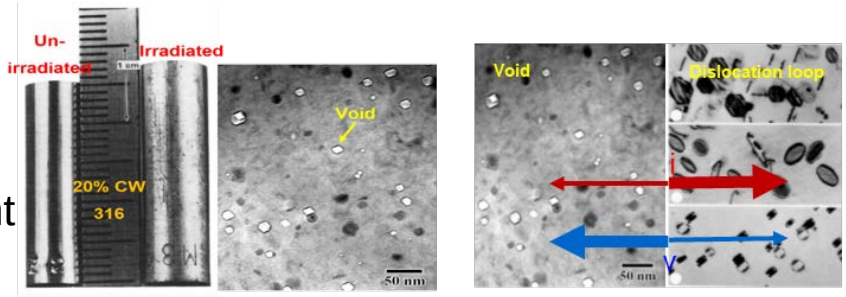
II. ARES
for LWR & HTR

ARES - Motivation

[1] S.M. Bruemmer et al., the 10th Int. Conf. on EDM in Nucl. Po. Sys. (2002) 61
[2] S.M. Bruemmer et al., J. Nucl. Mater. (1999) 274:299
[3] R. Pathania et al., Int. BWR & PWR Mat. Reliability conf. (2012)

❑ Material degradation in current LWRs

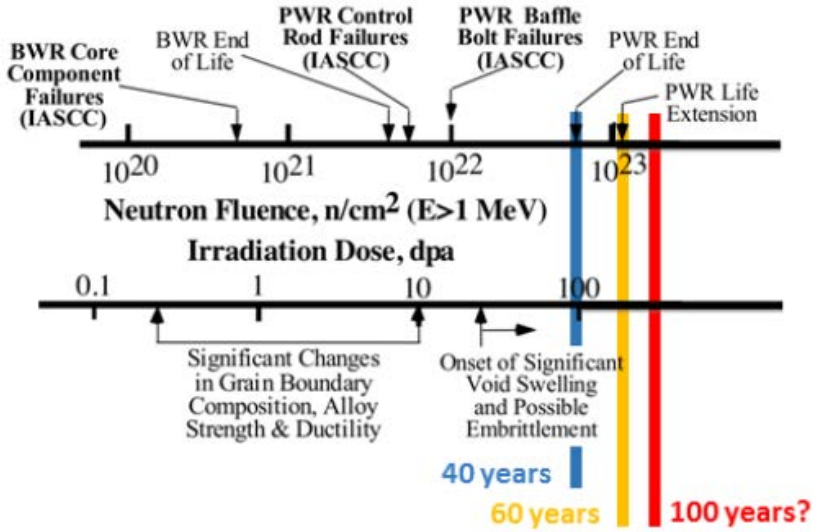
- Stress Corrosion Cracking (SCC)
- Irradiation Assisted SCC (IASCC)
- Radiation induced segregation
  - Cr, Mo depletion / Ni, Si and P enrichment
- Radiation hardening
- Irradiation creep



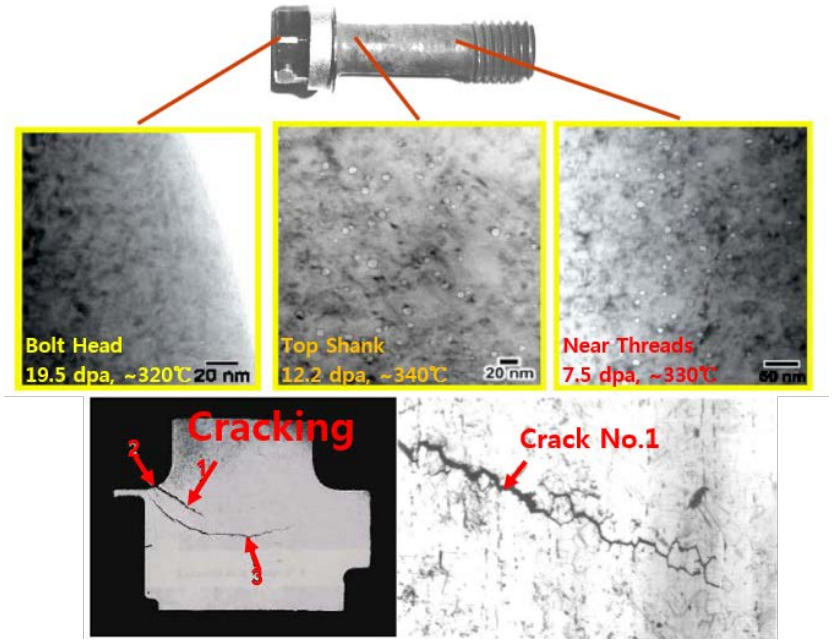
▲ Swelling of 20% CW 316 under neutron irradiation [2]

❑ Possible long-term material degradation issues

- Radiation induced swelling
- Transmutations (B, Ni to He / Mn to Fe)
- Phase stability



▲ Irradiation Induced degradation of austenitic SS [1]



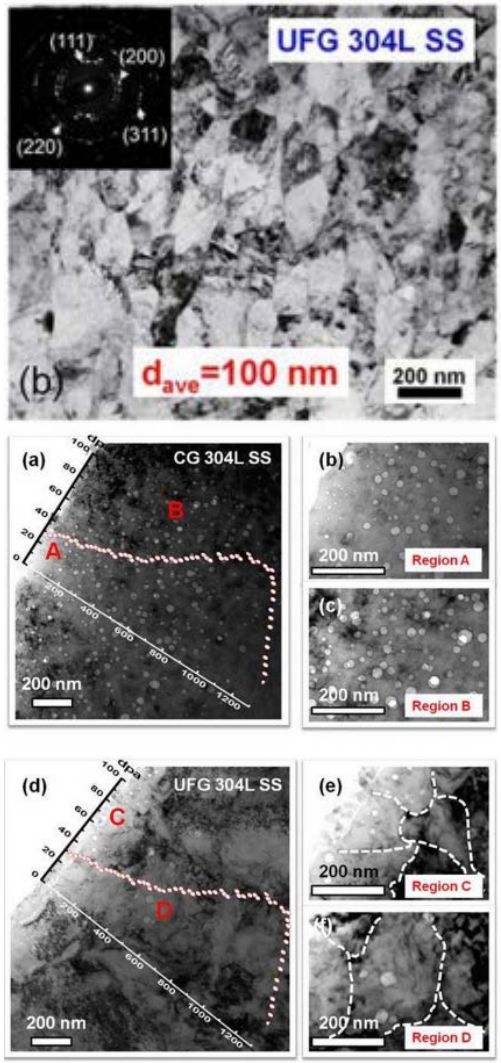
▲ Microstructure of baffle bolt irradiated in Tihange reactor [3]

ARES - Motivation

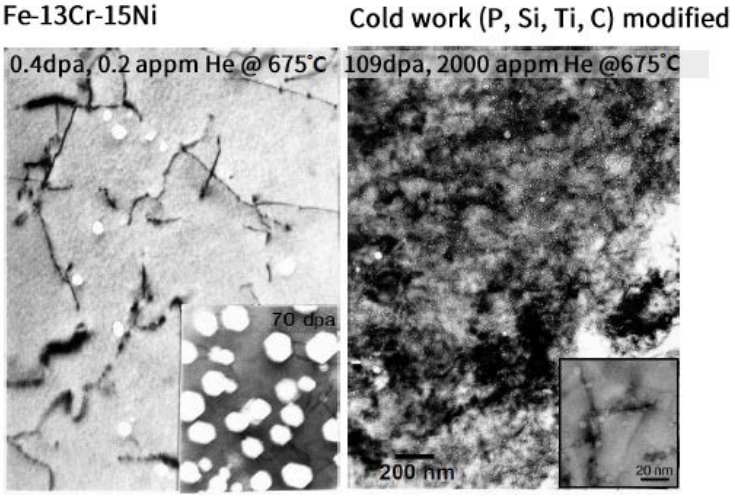
[1] C. Sun et al., Sci. Rep. 5 (2015) 7801
[2] E.H. Lee et al., Phil. Mag. A 61 (1990) 733
[3] G.R. Odette et al., Annu. Rev. Mater. Res. 38 (2008) 471
[4] E.J. Pickering et al., Int. Mater. Rev. 61:3 (2016) 183
[5] L. Tan et al., JOM 68 (2016) 517

<Potential Sink Sites>

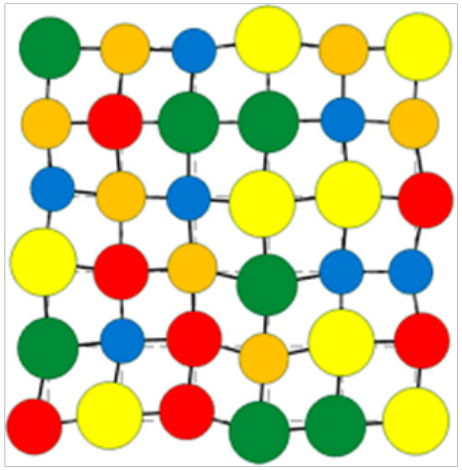
Nano-grain [1]



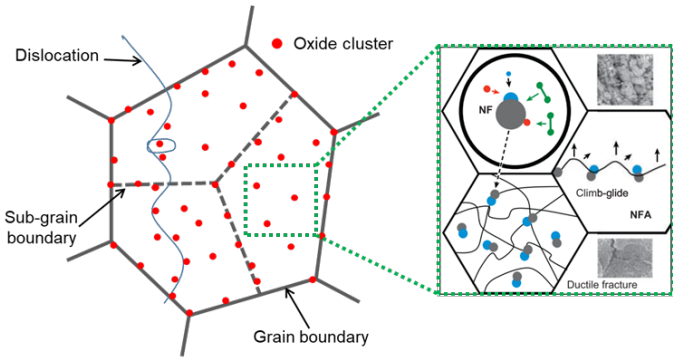
Dislocation + nano precipitates [2]



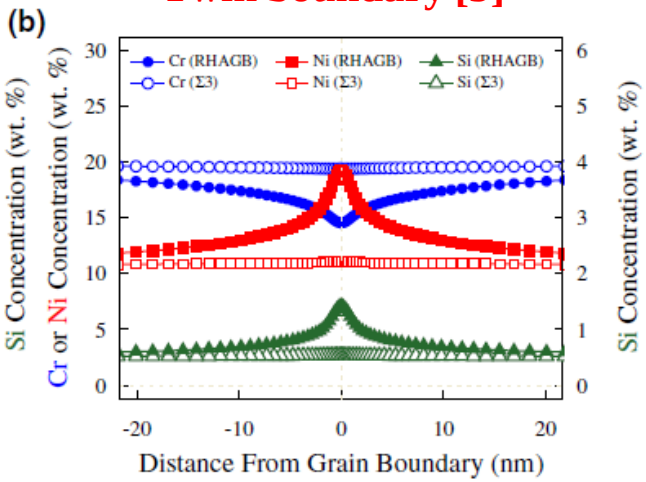
HEA [4]



FMS or ODS [3]



Twin boundary [5]



ARES – Comp./TMP/Micro.

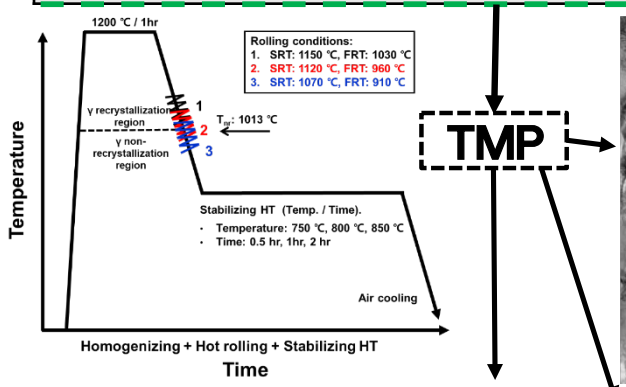
[1] J.H. Shin et al., Materials Science and Engineering: A 775 (2020) 138986, [2] KR 10-1943591, [3] US 16476597 (app.), [4] KR 10-2019-0147897 (app.), [5] US 17045267 (app.)
[6] S.J. Zinkle et al., Nuclear Fusion 57 092005 (2017) 17

*Nano Carbide dispersed Advanced radiation REsistant austenitic stainless Steels (ARES)

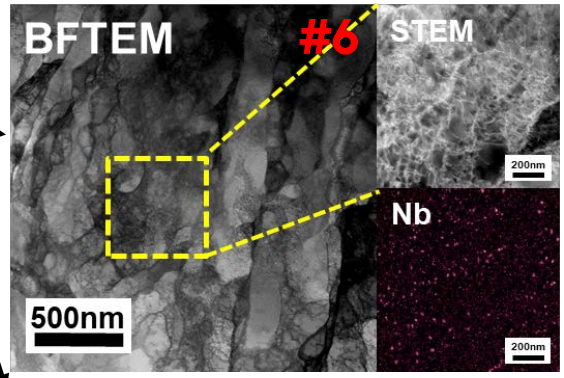
❑ Development of advanced radiation resistant austenitic SSs

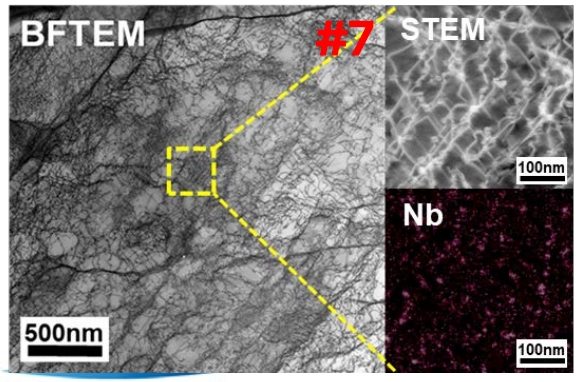
- Principal alloy design strategy [1–5]
  1. Control the chemical composition ▶ High resistance to IASCC (or SCC)
  2. Development of new conceptual thermo-mechanical processing (TMP) ▶ Formation of **sink sites**

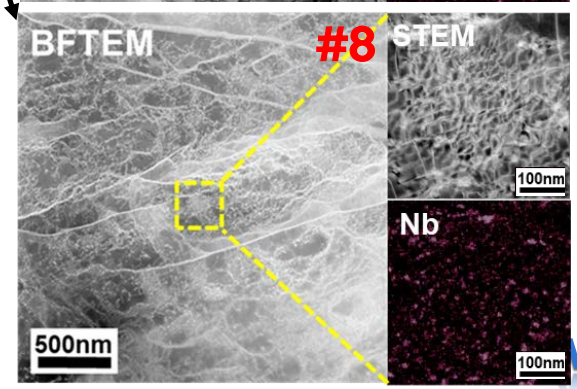
Wt.%	Fe	Cr	Ni	C	Mn	P	S	Si	Nb	Ti	N	Mo
ARES #6	Bal.	24.13	21.07	0.042	1.32	0.0100	0.0020	0.23	0.27	0.023	0.008	-
ARES #7	Bal.	24.03	20.88	0.035	3.41	0.0062	0.0021	0.21	0.45	-	0.010	-
ARES #8	Bal.	24.12	20.94	0.034	3.44	0.0053	0.0022	0.21	0.46	-	0.010	0.77



TMP

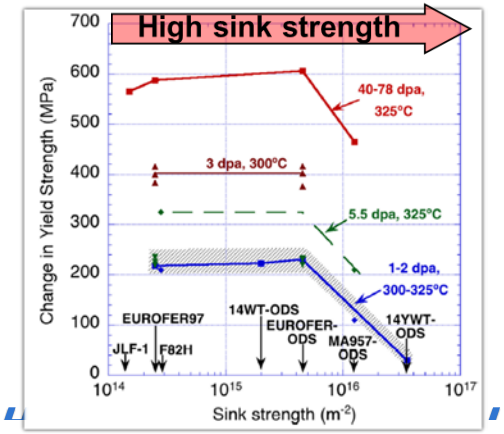






	Grain size (μm)	Precipitates	
		Mean diameter (nm)	Mean density ($X10^{22}$ m^{-3})
ARES #6	10.3	8.4	1.1
ARES #7	23.1	7.8	6.8
ARES #8	10.8	5.8	13.2

Our Goal

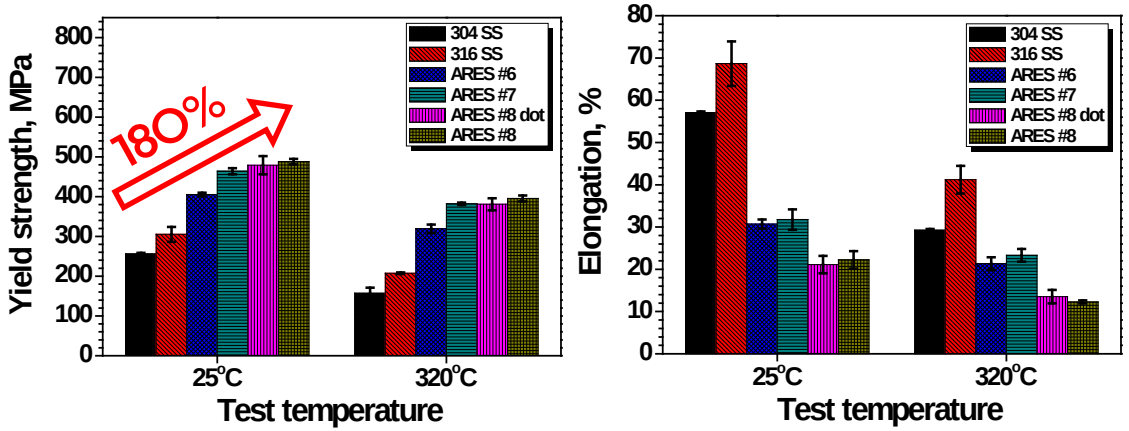


▲ Effect of initial sink strength depending on materials [6]

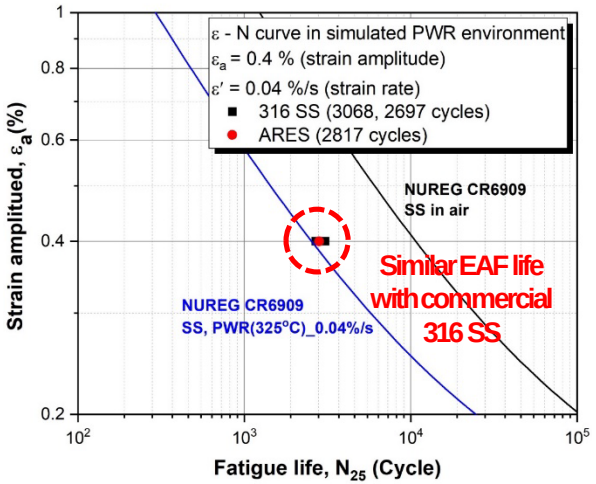
ARES – Mechanical/Corrosion

❑ Evaluation of mechanical and corrosion properties

- Mechanical property (tensile test)

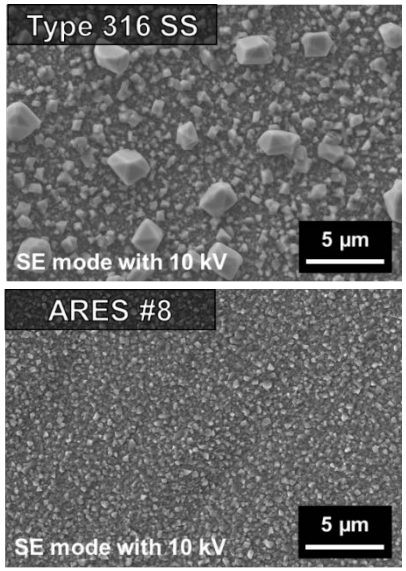


3. EAF test



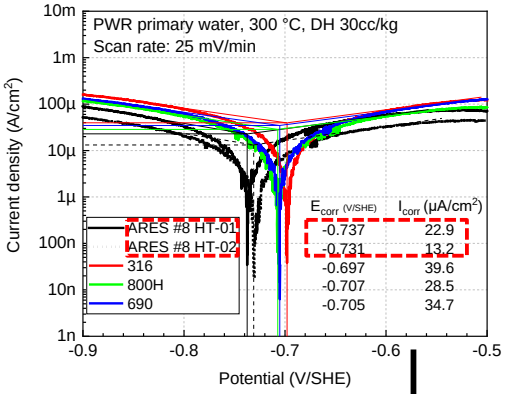
- Corrosion properties

1. SCC test

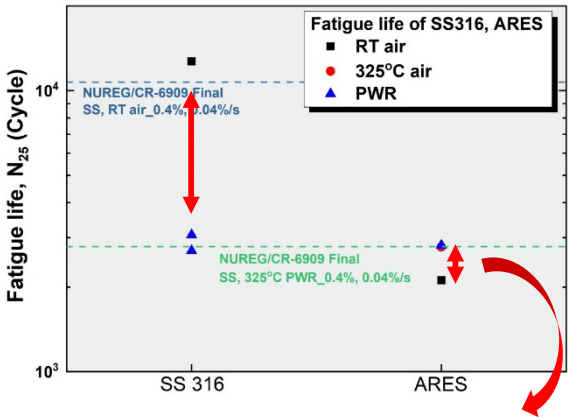


▲ Surface morphology on 316 SS and ARES #8 (400℃ and 20 MPa for 1332 h)

2. In-situ electrochemical test



Higher oxidation resistance in ARES



Surface treatment by laser peening to improve the LCF life

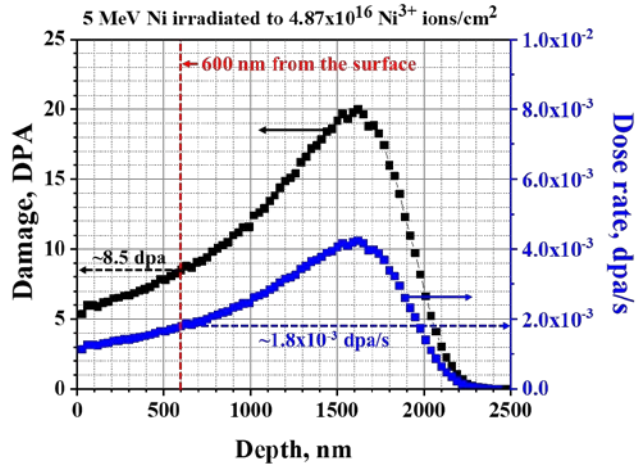
ARES – Heavy ion irradiation

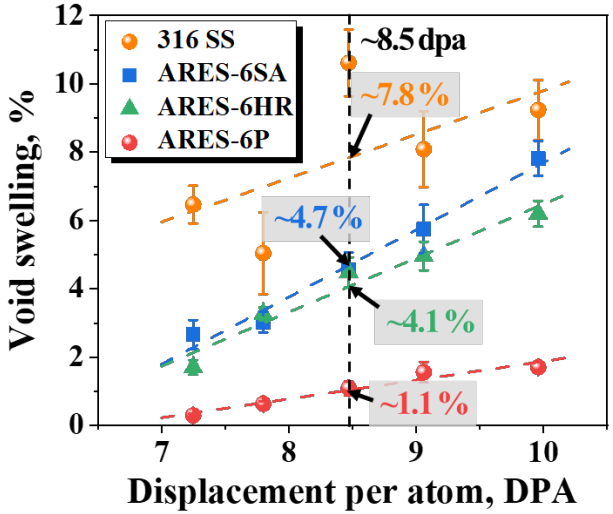
J.H. Shin, submitted to JNM, under revision (2021)

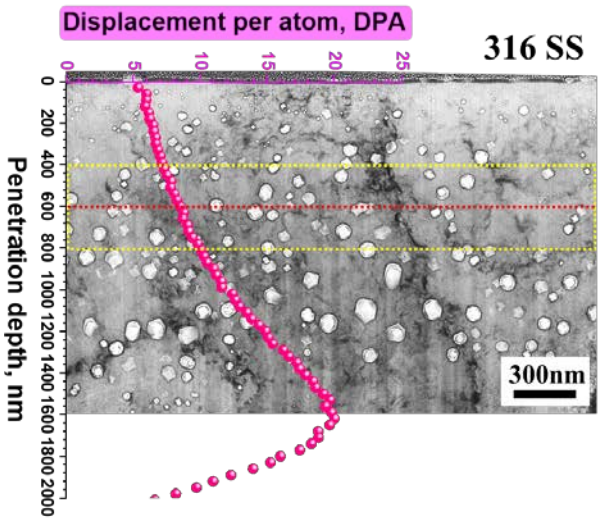
❑ Effect of nanosized NbC precipitates on void swelling

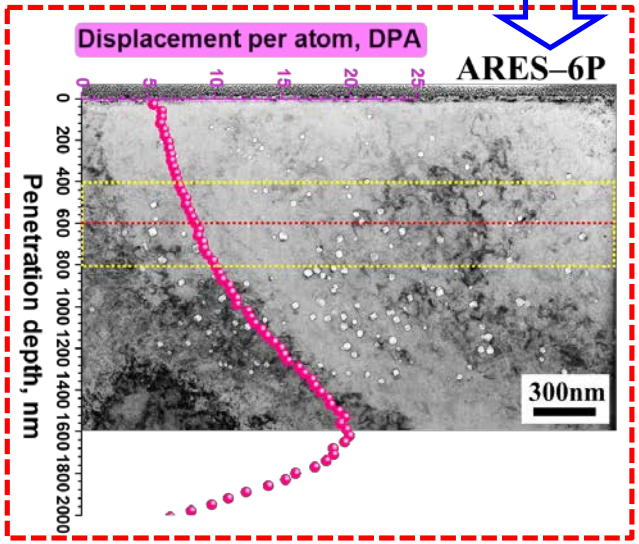
- Irradiated by MIT (prof. M.P. Short) / 8.5 dpa

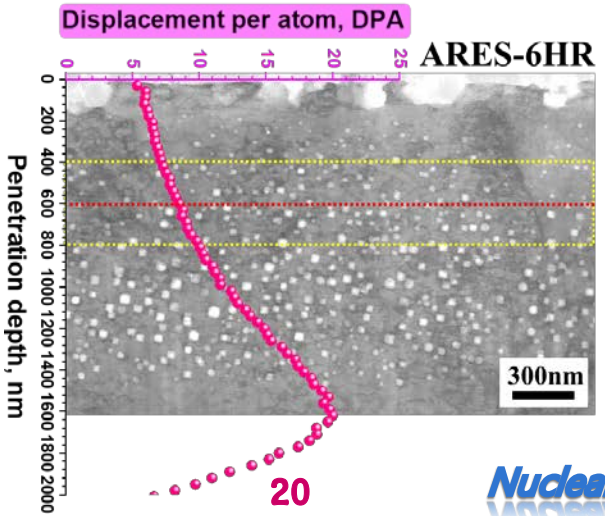
Drastically enhanced void swelling resistance of ARES-6P

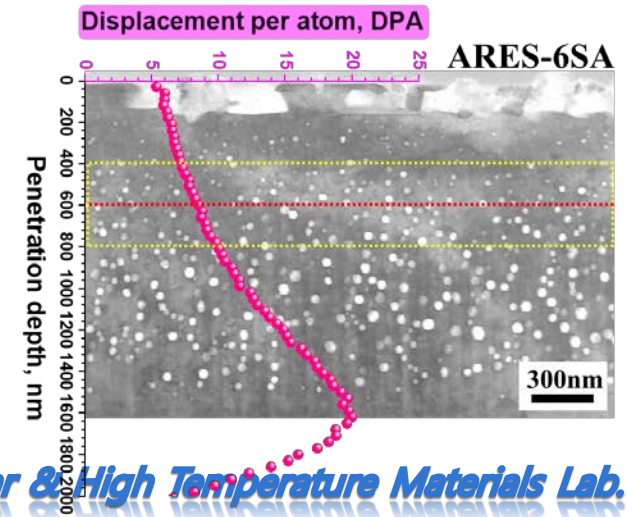




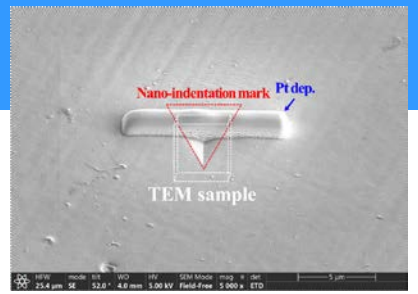






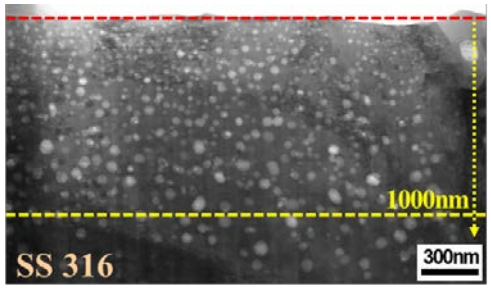


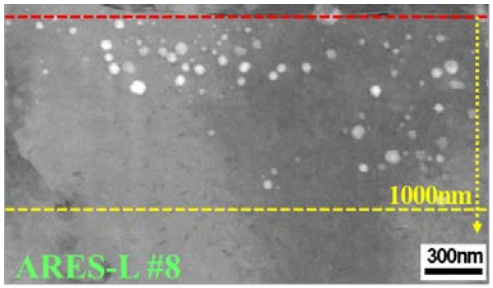
ARES – Heavy ion irradiation

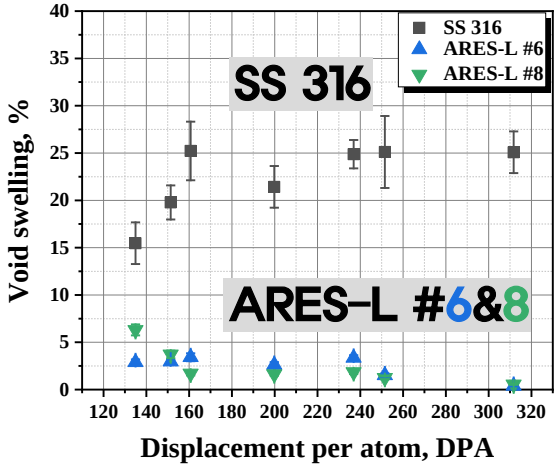


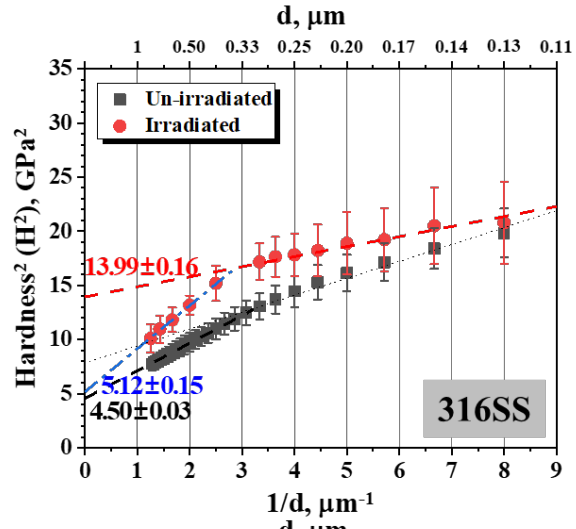
❑ Radiation hardening resistance

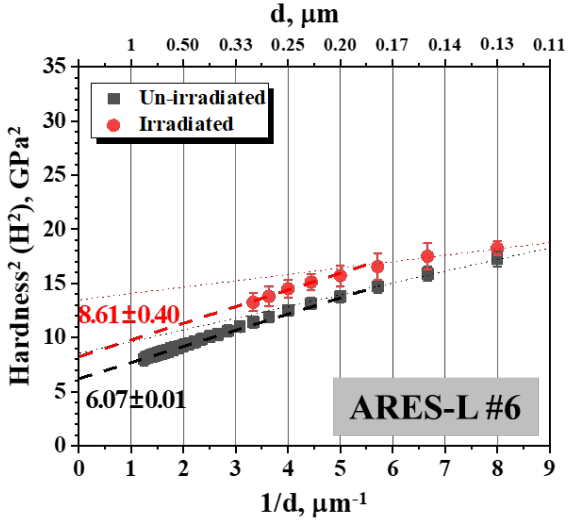
- Irradiated by Texas A&M (prof. Lin Shao) / **200 dpa**
- Nano-indentation test

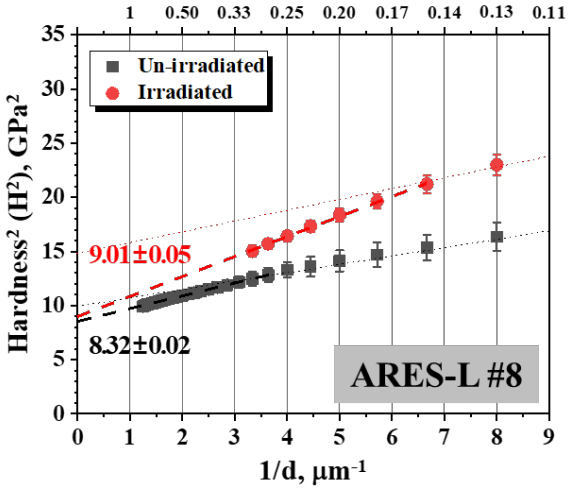


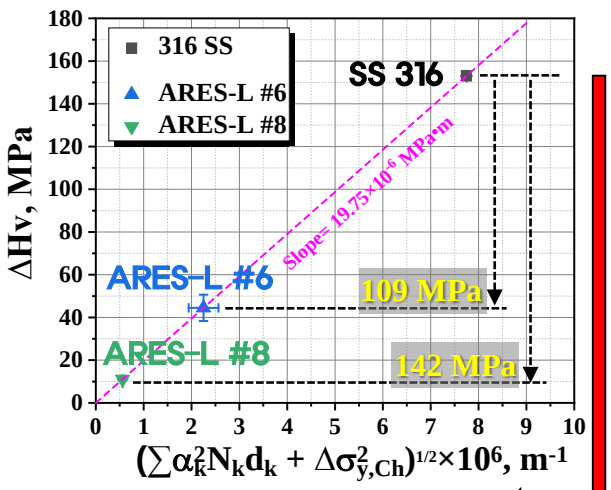










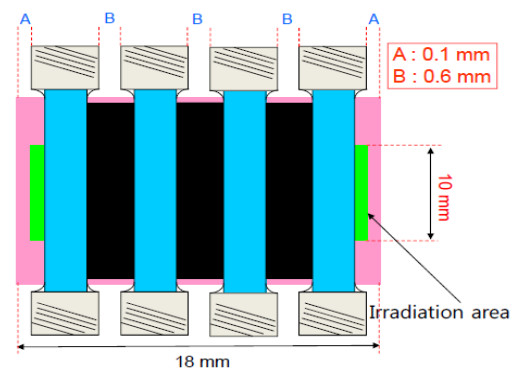


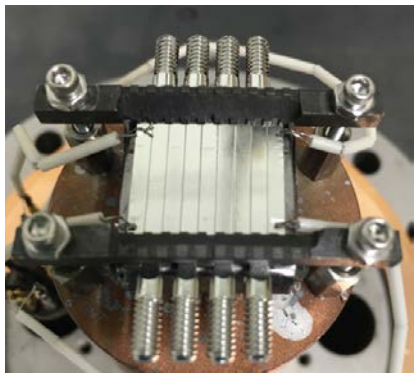
Higher radiation hardening resistance

ARES – IASCC resistance

❑ Irradiation-assisted stress corrosion cracking resistance

- Proton irradiation by MIBL (Michigan Univ., prof. G. Was)
- Test condition:
  - Damage (5 dpa), Energy (2 MeV), dose rate (~10^{-5} dpa/s), Temp. (360℃)

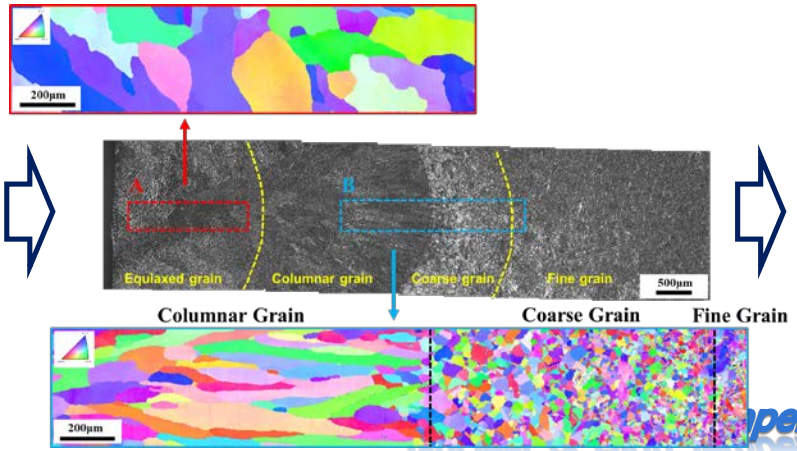




MIBL

Nu_Html

❑ Development of welding procedure for ARES



TEM

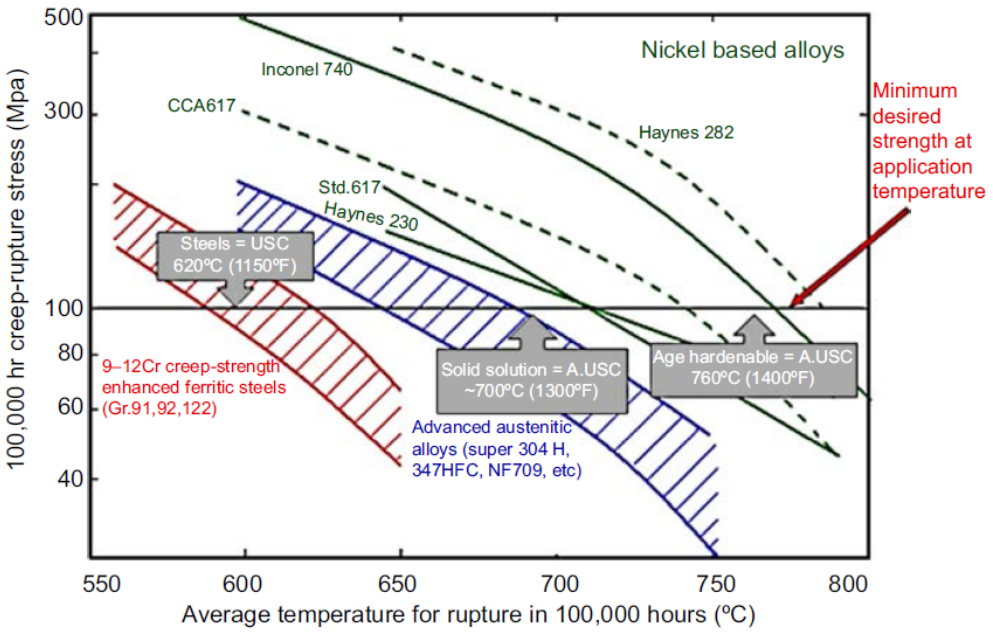
III. ACES
for HTR & Non-Nuclear

ACES - Motivation

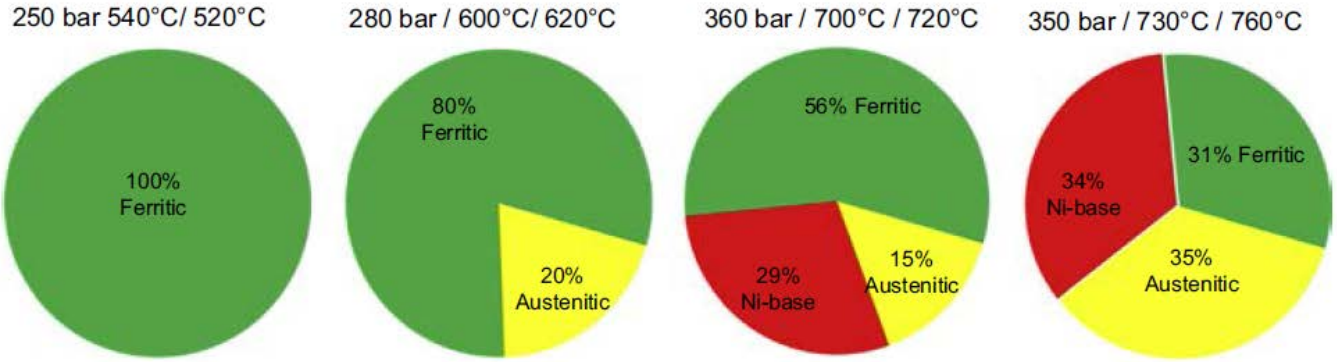
[1] A.D. Gianfrancesco, The fossil fuel power plants technology (2016)
[2] F. Kluger et al, 2nd IEA CCC Conference (2014)

HT materials

- Design temperature criterion: creep rupture life of >10^5 h for 100 MPa
- Advanced austenitic SS are catching up Ni-based solid solution strengthened (SSS) alloys



▲ Relative creep rupture strength of steels and nickel alloys [1]



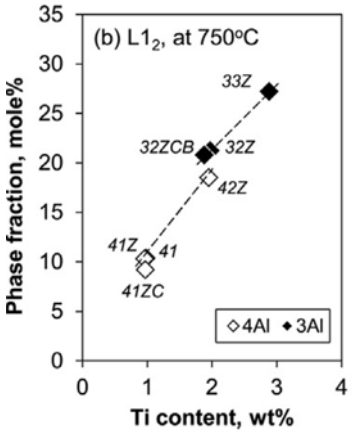
▲ Material fraction in subcritical, supercritical, ultra-supercritical and advanced ultra-supercritical power plants [2]

ACES - Motivation

[1] Y. Yamamoto et al, Scr. Mater. (2013)

❑ Alumina-forming alloys (ORNL)

- Typical composition: Fe-(20~32)Ni-14Cr-(2.5~3.5)Al
  - Increasing Ti → increased γ'-Ni_3(Al,Ti) fraction → higher creep life
  - Ti degrades corrosion resistance; minor elements (ZCB) improve

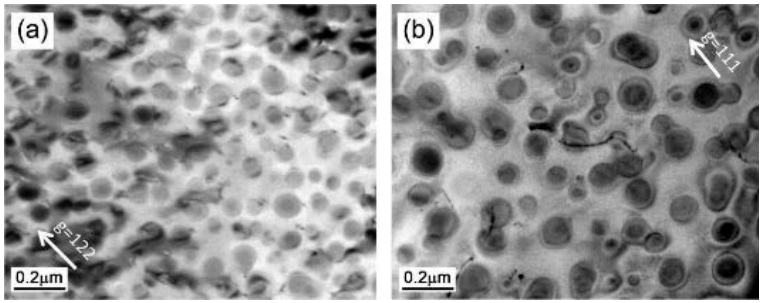


▲ Phase stability of γ' precipitates with Ti content[1]

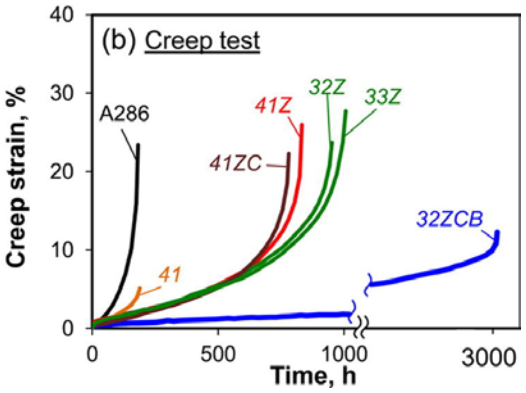
Table 1. Chemical compositions of the alloys studied.

Name	Analyzed composition (wt%)										Remarks
	Fe	Cr	Ni	Al	Si	Nb	Ti	Zr	C	B	
41	45.73	14.03	32.26	3.96	0.14	2.88	0.98	–	–	–	4Al – 1Ti
41Z	45.62	14.02	32.23	3.93	0.12	2.81	0.96	0.27	–	–	4Al – 1Ti + Zr
41ZC	45.38	14.03	32.23	3.98	0.14	2.86	0.97	0.29	0.102	–	4Al – 1Ti + Zr,C
42Z	44.32	13.97	32.45	3.91	0.13	2.95	1.95	0.30	–	–	4Al – 2Ti + Zr
32Z	45.29	14.00	32.47	2.95	0.13	2.93	1.97	0.29	–	–	3Al – 2Ti + Zr
33Z	44.23	14.02	32.46	2.98	0.14	2.96	2.88	0.29	–	–	3Al – 3Ti + Zr
32ZCB	45.36	13.99	32.46	2.97	0.14	2.80	1.88	0.29	0.065	0.005	3Al – 2Ti + Zr,C,B
A286	56.2	14.5	25	0.15	0.2	–	2.1	–	0.04	0.006	1.25Mo, 0.3V, 0.2Mn, 0.015P

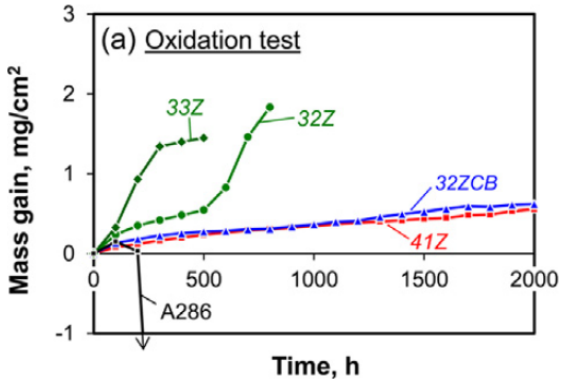
▲ Composition of alumina-forming alloys studied in Ref. [1]



▲ γ' precipitates after creep testing of (a) 32Z and (b) 32ZCB at 750 °C [1]



▲ Creep test at 750°C and 100MPa [1]



▲ Oxidation in air + 10% H_2O at 800°C [1]

ACES - Approach

High Ti for γ'-$Ni_3(Al,Ti)$

High Al for Al_2O_3

Balanced creep & corrosion resistance

Alumina forming alloys (AFA)

Fe-(20-32Ni)-(14-16Cr)-(2-4Al)-(<2 Ti)-(2-3Nb)+ZCB

Al↑

Ti↑

High Al-Ti alloys

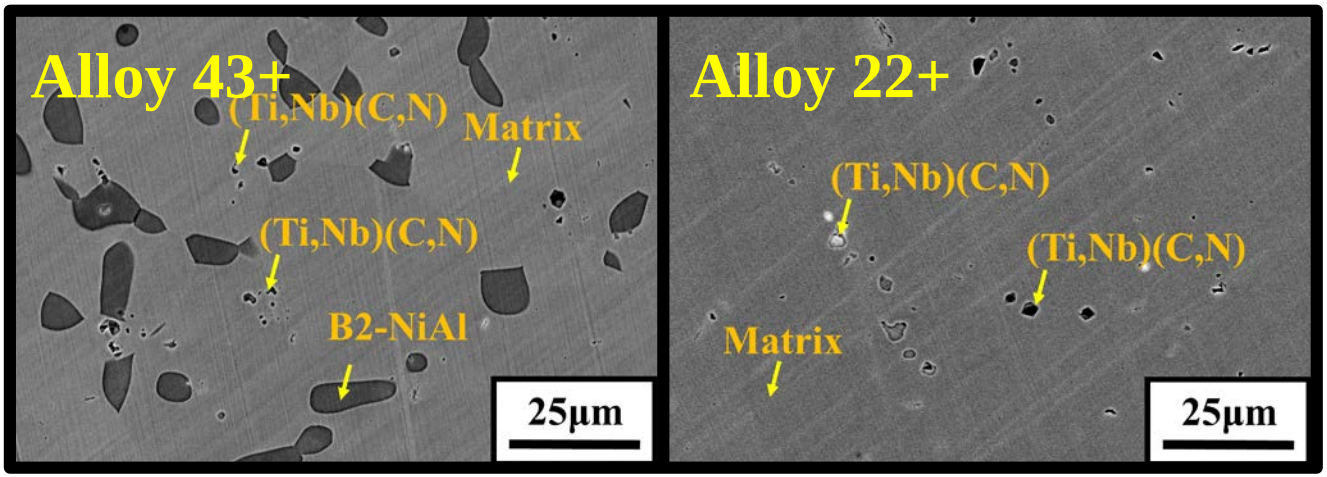
Fe-(30-35Ni)-(16-18Cr)-**4.5Al-(2-4Ti)**-1Nb+ZCB

ACES – Compositio/Microstructure

G. Obulan Subramania, Corr. Sci. (2021)

SEM analysis

- Coarse B2-NiAl phases with fraction, size and composition similar to cast alloy 43+ SA



▲ SEM-BSE images showing the microstructure of the model alloys

Alloy	Phase	Fe	Ni	Cr	Al	Ti	Nb	Si	Zr
43+	Matrix	Bal.	28.7	18.9	7.9	3.2	0.3	0.4	0.01
	B2-NiAl phase	Bal.	40.3	7.5	23.5	6.6	0.3	0.3	0.04

▲ Average composition in at.% of the phases in alloy 43+

ACES - Creep life comparison

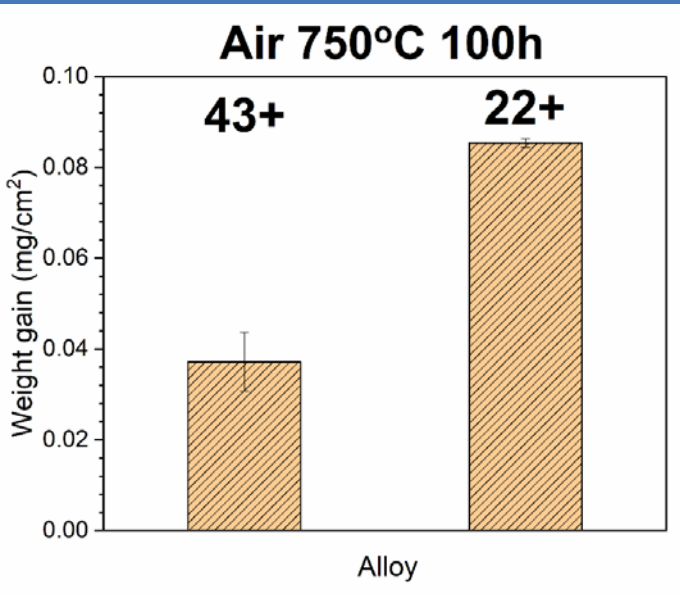
Data provided in PhD thesis, G. Obulan Subramania (2021)

Creep condition	Alloys	Creep rupture time (h)
750 °C and 150 MPa	**43 SA (cast condition)**	**270 h**
	43+ SA (cast condition)	**525 h**
	43+ AR (wrought condition)	**478 h**
	Alumina-forming alloys (with Laves, carbide and γ'-Ni_3(Al,Ti) precipitates) – calculated from LMP plot	~ 100 – 300 h
	Alloy HR6W	~ 100 h
	Sanicro 25	~ 1000 h
750 °C and 100 MPa	**43 SA (cast condition)**	**1510 h**
	Alumina-forming alloys (with Laves and carbide precipitates)	~ 200 – 2000 h
	Alumina-forming alloys without Ti (with Laves, carbide and γ'-Ni_3(Al,Ti) precipitates)	867 h
	Alumina-forming alloys with Ti and beneficial minor elements Zr, C and B (with Laves, carbide and γ'-Ni_3(Al,Ti) precipitates)	~ 3000 h
	Alloy HR6W (22Cr-22Fe-7W)	~ 2000 h
	Alloy HR120 (25Cr-37Ni-MWCo)	~3000 h
	Alloy NF709 (20Cr-25Ni-1.5MoNbTiN)	~ 5000 h
	Sanicro 25 (22-Cr-25Ni-4W)	~ 8000 h

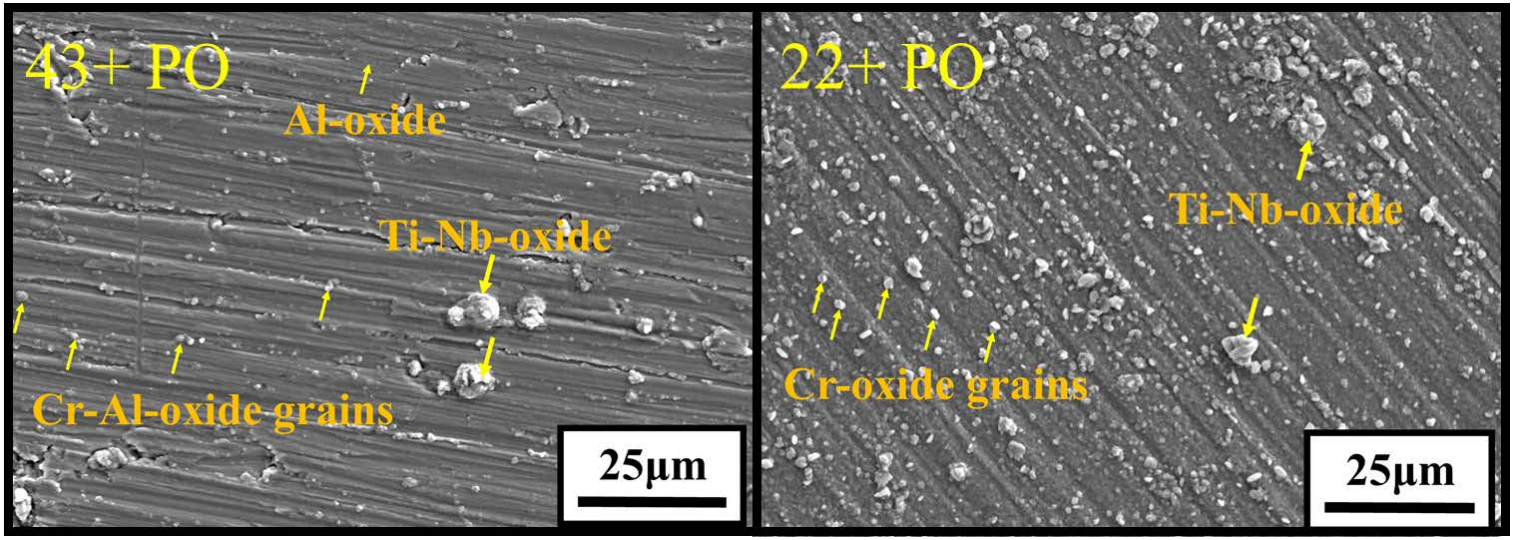
ACES - High temperature oxidation

Air oxidation 750ºC 100h

- Alloy 43+ → Lower weight gain and Al-oxides on surface
- Alloy 22+ → Cr-rich oxide
- Ti-Nb-oxides from previously Ti-Nb-carbonitrides



▲ Weight gain after oxidation in air at 750ºC for 100h



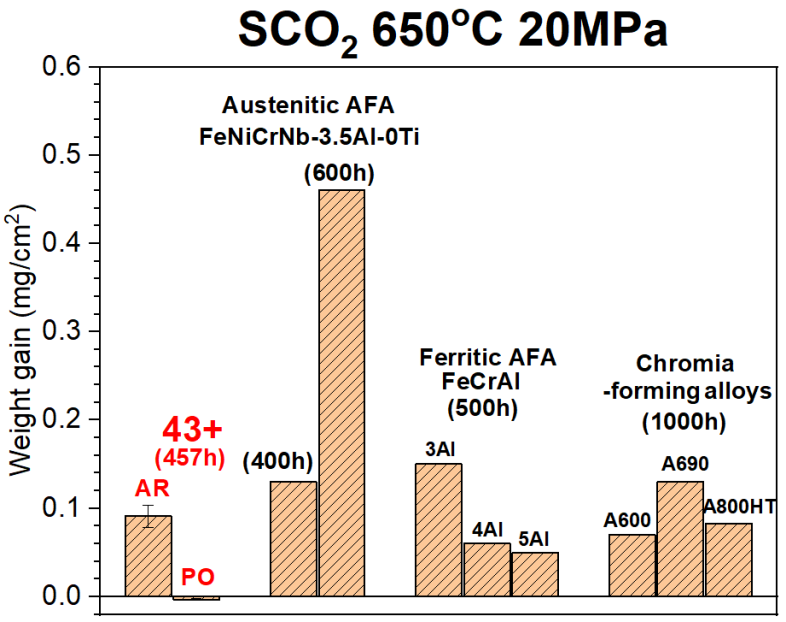
▲ SEM-SE surface images after oxidation in air at 750ºC for 100h

ACES - High temperature oxidation

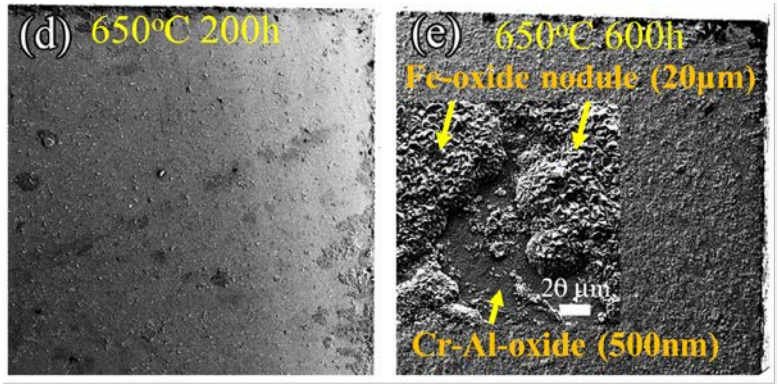
[1] L.F. He et al, Corr. Sci. (2014)
[2] V. Firouzdor et al, Corr. Sci. (2013)

Compared with other alloys

- AFA (3.5Al-3Nb-0Ti) in S-CO_2 → breakaway corrosion (Cr & Al depletion)
- Protective Cr_2O_3 → Higher Cr-content beneficial

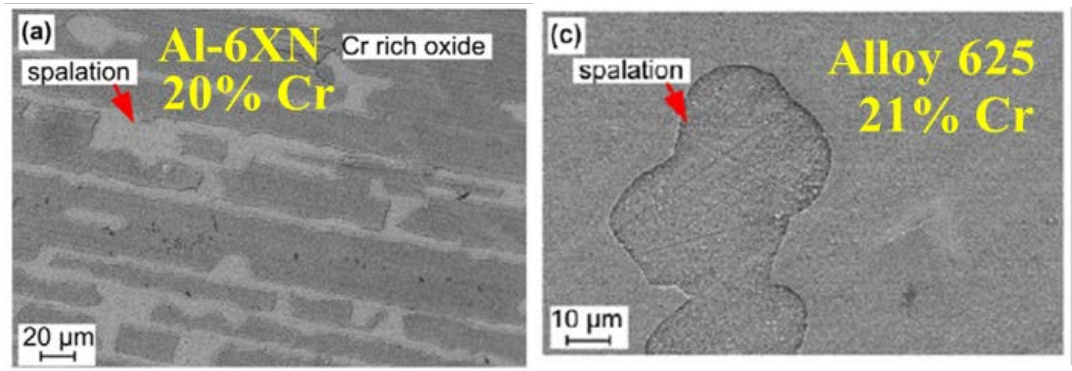


Alumina-forming alloys



▲ Weight gain and surface morphology of AFA (3.5Al-2.5Nb-0Ti) in S-CO_2 environment at 650°C [1]

Chromia-forming alloys



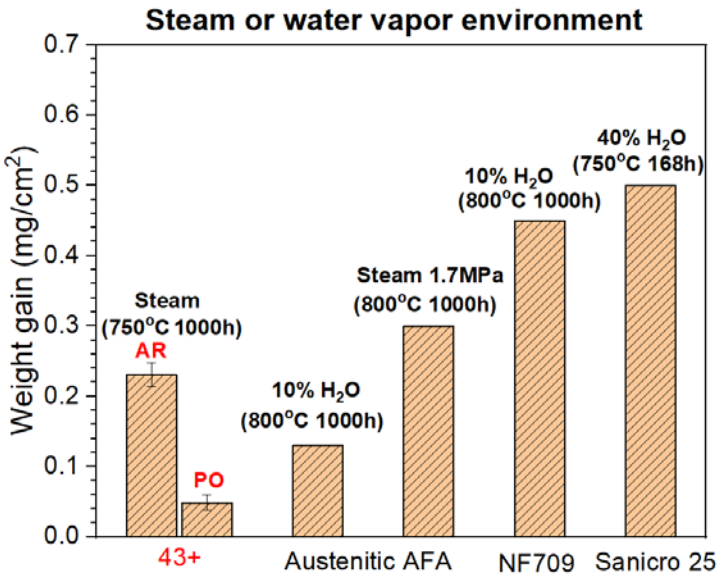
▲ Surface morphology of Al-6XN (Fe-24Ni-20.5Cr) and Alloy 625 (Ni-21.5Cr) alloys in S-CO_2 environment at 650°C [2]

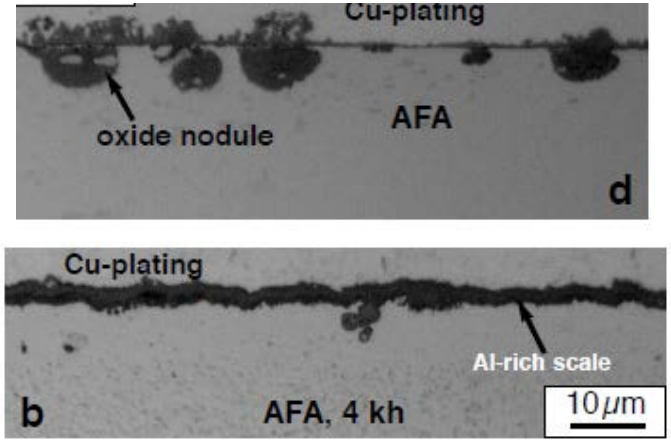
ACES - High temperature oxidation

[1] K.A. Unocic et al, Corrosion 2013 Conference
[2] L. Intiso et al, Oxid. Met. (2015)
G. Obulan Subramania, sub to Corr. Sci. (2021)

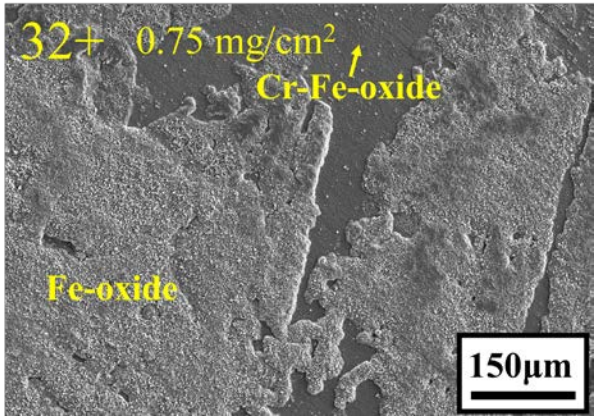
Compared with other alloys

- Alumina forming alloys offer better protection in H_2O environments
- Chromia-forming alloys susceptible to breakaway corrosion

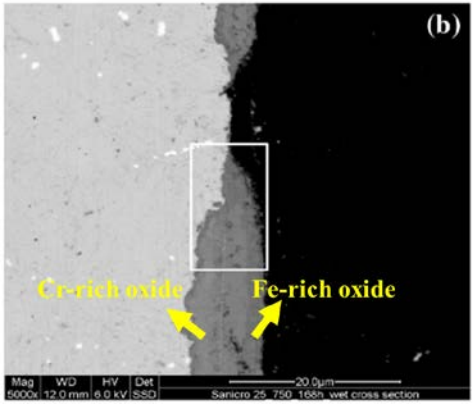




▲ Cross-section of an austenitic AFA after corrosion in steam environment at 550°C and 800°C [1]



▲ Alloy Fe-32Ni-14Cr-3Al-2Ti-1Nb-0.075Zr-0.075C-0.01B in steam at 750°C for 1000h



▲ Cross-section of Sanicro 25 after corrosion in H_2O environment at 750°C for 168h [2]

Summary

- **ADSS**
  - Excellent high temperature steam oxidation resistance with large strengthening by B2 phase
  - Affordable thermal ageing embrittlement
  - Thin tube of t ~ 0.3 mm successfully fabricated by cold-pilgering
- **ARES-L**
  - High-Cr, High-Ni austenitic SS with large quantity of nanosized NbC precipitates in austenite matrix
  - Excellent corrosion resistance in LWR environment
  - Excellent swelling resistance up to 200 dpa confirmed by ion irradiation
- **ACES**
  - Al and Ti were increased for better oxidation creep resistance compared to ORNL-AFA
  - Pre-oxidation of alumina forming alloy(43+) further improved oxidation resistance in air, S-CO2, and steam.

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Thank you!