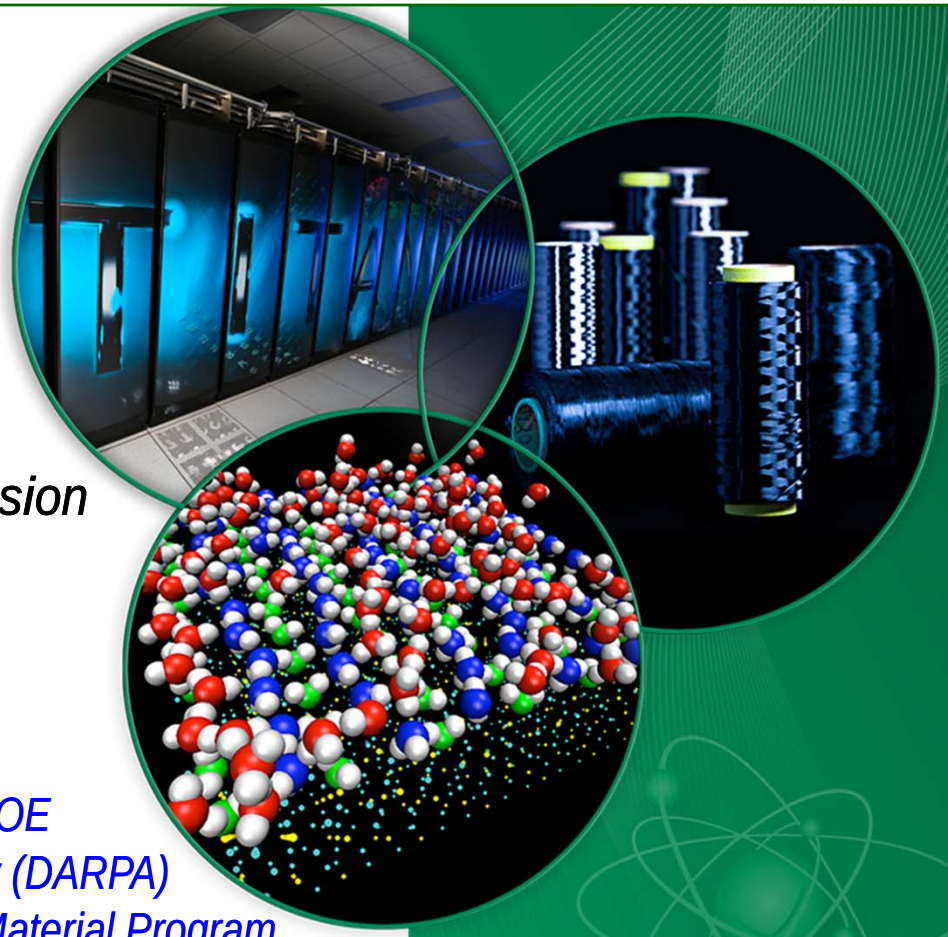
Recent developments in creep-resistant, alumina-forming austenitic stainless steels



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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE U.S. DEPARTMENT OF ENERGY

Outline

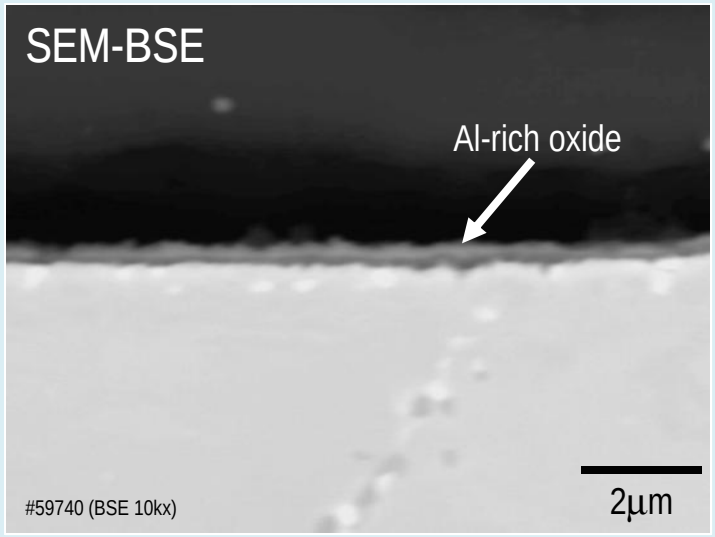
- Introduction: What is alumina-forming austenitic (AFA) stainless steel alloys?
- Recent progress:
  - Commercialization effort
  - New alloy development
    - *Wrought AFA*
    - *Cast AFA*
- Summary

Alumina-forming Austenitic (AFA) Stainless Steel Alloys: A New Class of Alloys

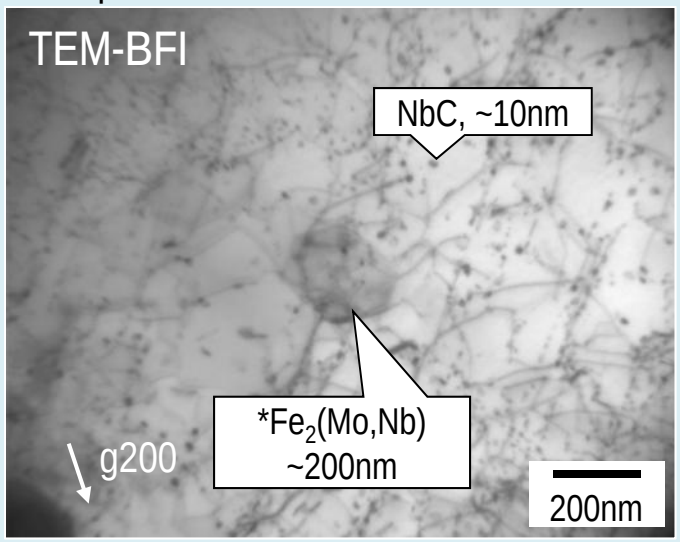
- Combination of good oxidation resistance and good creep resistance
  - Oxidation resistance achieved by the formation of protective, external alumina (Al_2O_3) scale.
  - Austenitic matrix with carbide/intermetallic strengthening

Fe-14Cr-2.5Al-20Ni-0.95Nb-2.5Mo-0.08C base alloy (initial AFA development)

=72h at 800°C in air, cross-sectional view =



=creep tested at 750°C/100MPa for 2200h=

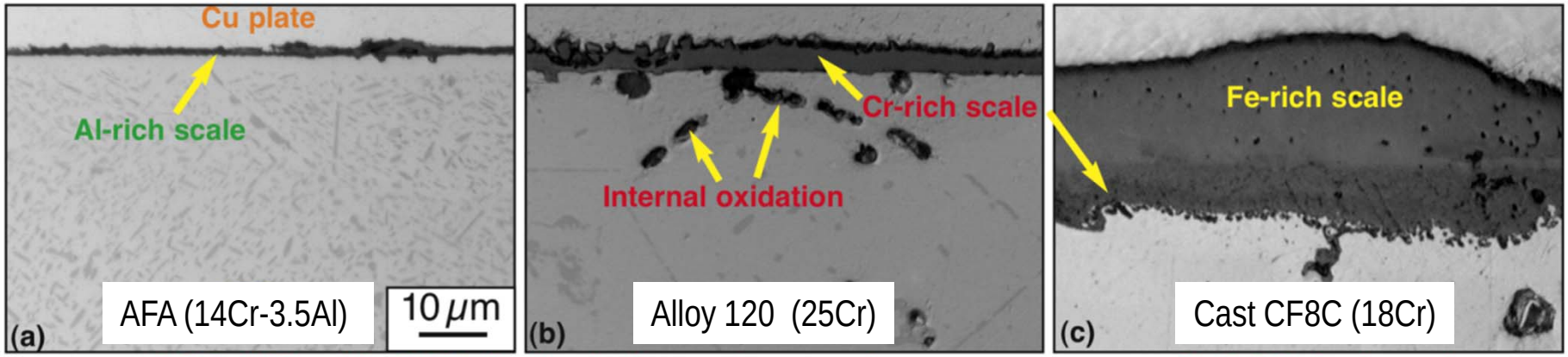


*B2-(Fe,Ni)Al is also observed.

Advantage Compared to Conventional Chromia Scales

Alumina-former

Chromia-former



800 °C, 10,000 h in laboratory air

5,000 h in air

- Continuous, stable alumina layer protects the surface (Promising).
- Protective effect remains even in water-vapor containing environments.
- Careful control of alloy composition is required.

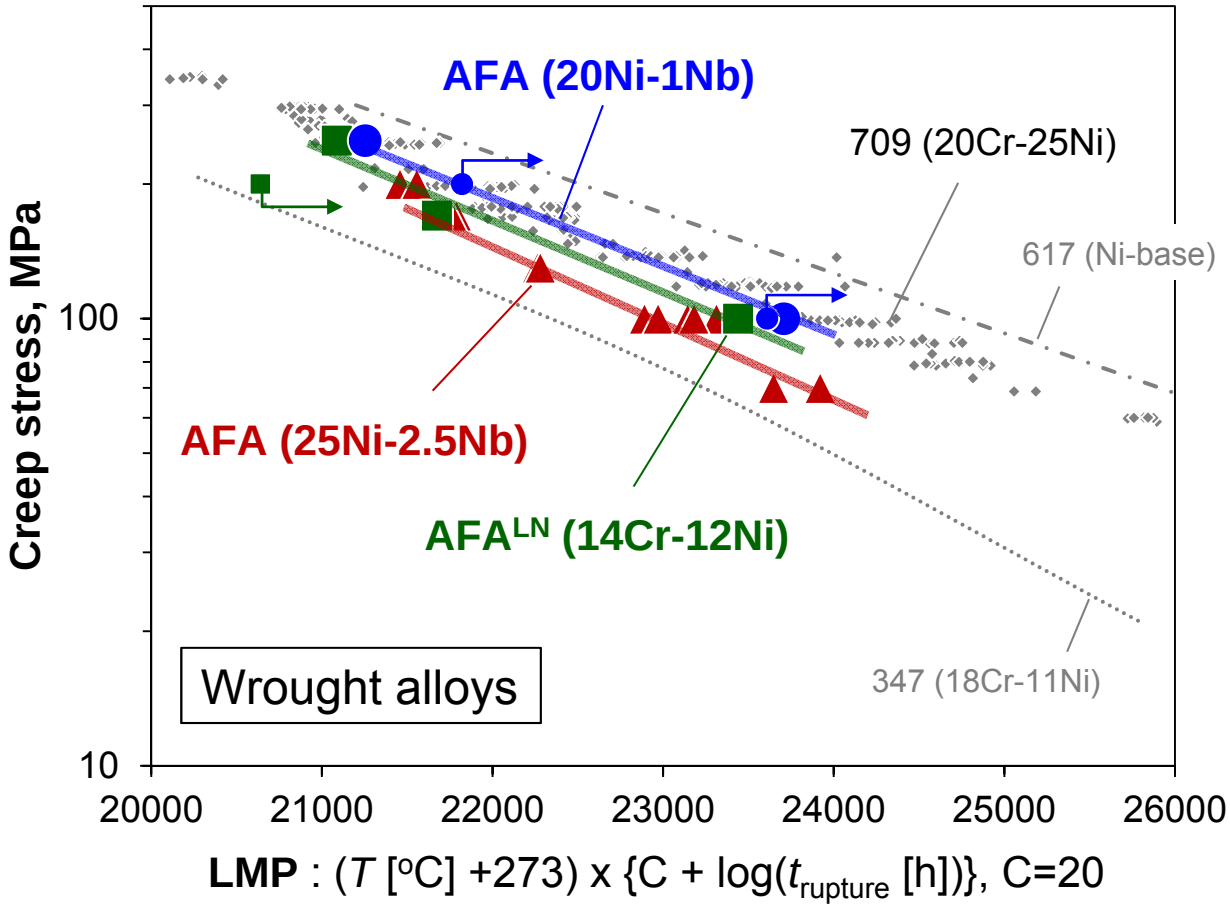
Careful Balancing of Alloy Element Additions Needed to Achieve Combination of Properties

- Additions of sufficient Al essential for development of stable external alumina scale
  - More than 2.5 wt% Al required for alumina scale formation
- Nb additions are key for alumina scale formation
  - More than ~0.6-1.0 wt% Nb is also required for alumina-scale formation
- Too much Al and/or Nb will poison creep properties (δ-Fe, brittle second-phases, etc.)
- Solid solution strengthening and precipitation strengthening is needed
  - How much carbon can be tolerated?
  - Coherent intermetallic phase?
  - Nitrogen is not tolerated due to the formation of stable AlN

Variety of AFA alloys

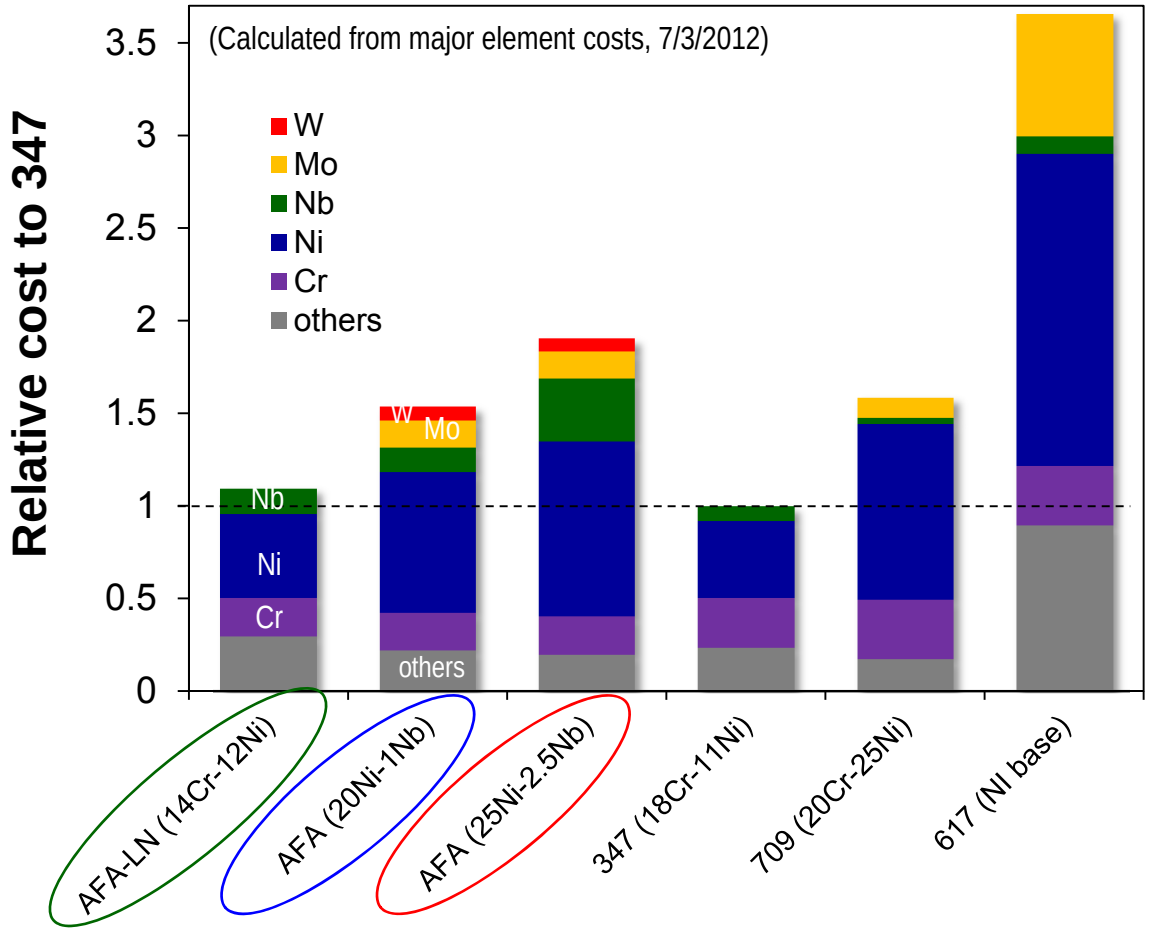
- Three different grades of AFA series (wrought alloys)
  - AFA Grade: Fe- (14-15)Cr-(2.5-4)Al-(20-25)Ni-(1-3)Nb wt.% base
    - *~750-950°C temperature limit for Al_2O_3 formation*
    - *higher temperature ranges need higher Ni and Nb + rare earth additions*
    - *MC and $M_{23}C_6$ strengthening*
  - Low Nickel AFA^{LN} : Fe-14Cr-2.5Al-12Ni-0.6Nb-5Mn-3Cu wt.% base
    - *~ 650-700°C temperature limit for Al_2O_3 formation*
    - *$M_{23}C_6$ strengthening*
  - High Creep resistance γ'-Ni_3Al strengthened AFA: Fe-(14-19)Cr-(2.5-3.5)Al-(30-35)Ni-3Nb + wt.% base
    - *~750-850°C temperature limit for Al_2O_3 formation*
- Cast AFA: *Cast version of AFA alloys*

Comparable Creep Properties to Commercial Heat-resistant Steel Alloys



**Alloy 709: Fe-20Cr-25Ni-Mo-Nb-C-N base, commercially available best creep-resistant austenitic stainless steel.*

Inexpensive Raw Material Cost



Major Elements	USD/KG* (July 2012)
W	43.4
Mo	44.7
Nb	81.9
Ni	23.0
Cr (from Ferro-Cr)	9.0

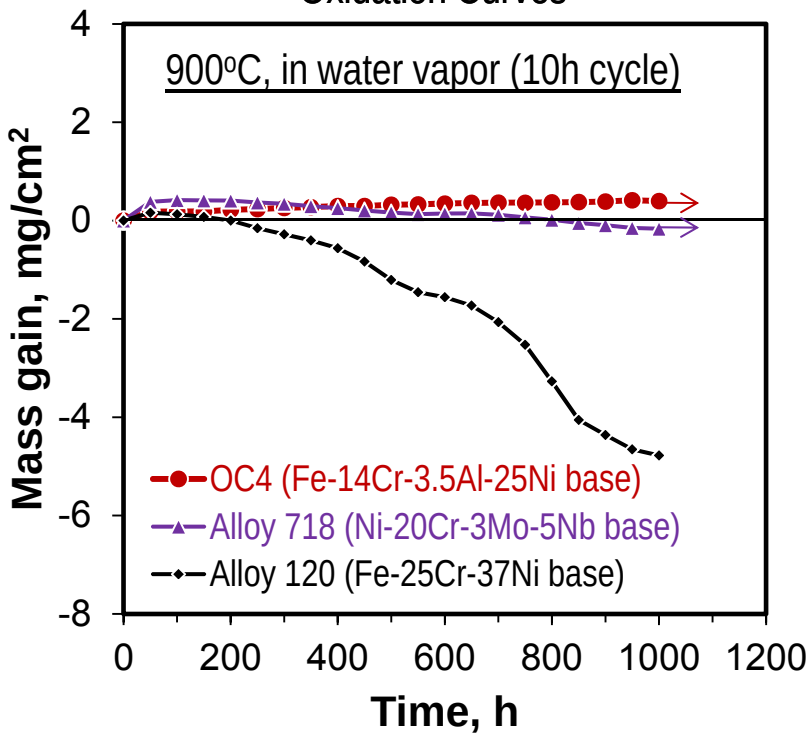
*from http://www.metalprices.com/

- Comparable or even less than the competitors.

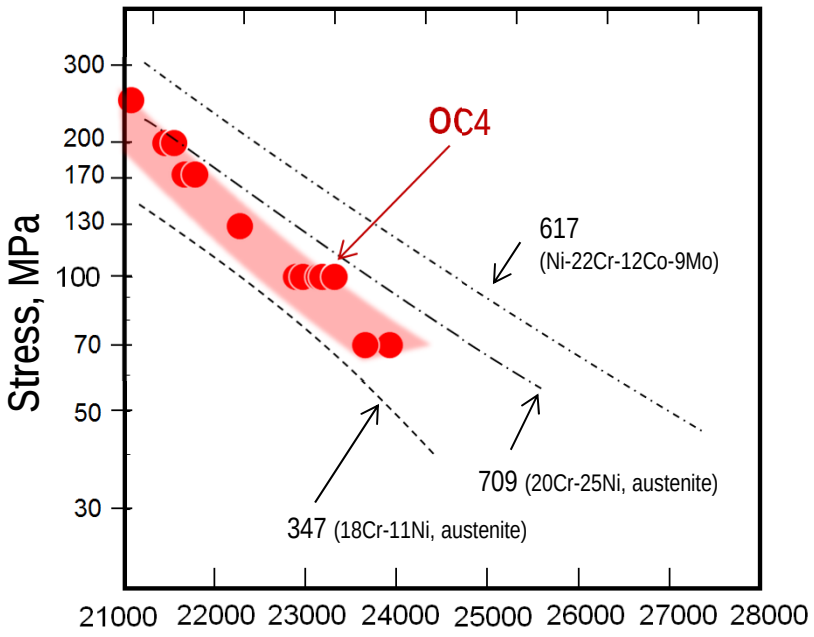
OC4 Has Desired Combination of Properties

- OC4 (Fe-14Cr-3.5Al-25Ni-2.5Nb-2Mo-0.1C base)
  - Promising oxidation resistance up to 900ºC.
  - Moderate creep properties (comparable to advanced austenitic stainless steels).

=Oxidation Curves=



=Larson-Miller Parameter Plot=



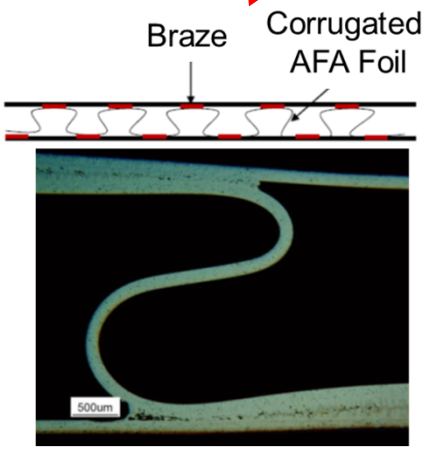
LMP {= T [K] x (20 + log $t_{rupture}$[h])}

AFA Commercialization:

OC4 (14Cr-3.5Al-25Ni-2.5Nb) Products

350 lb wire coil
Elgiloy to Capstone

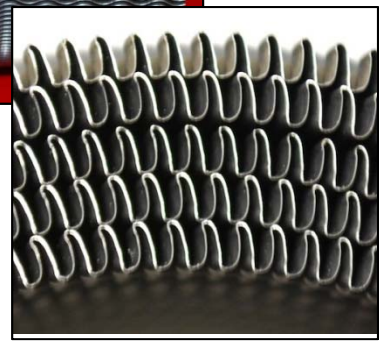
Elgiloy 8" wide, 300 lb,
3.2 mil coil for Capstone



UTRC 6 mil foil subscale
brazed heat exchanger
(foil by Elgiloy)

15" wide, 4 mil AFA foil for **Solar Turbines** recuperator
(Metalwerks 2000lb heat, Haynes, Somers, Elgiloy)

Capstone folded 8" wide 3.2 mil Foil



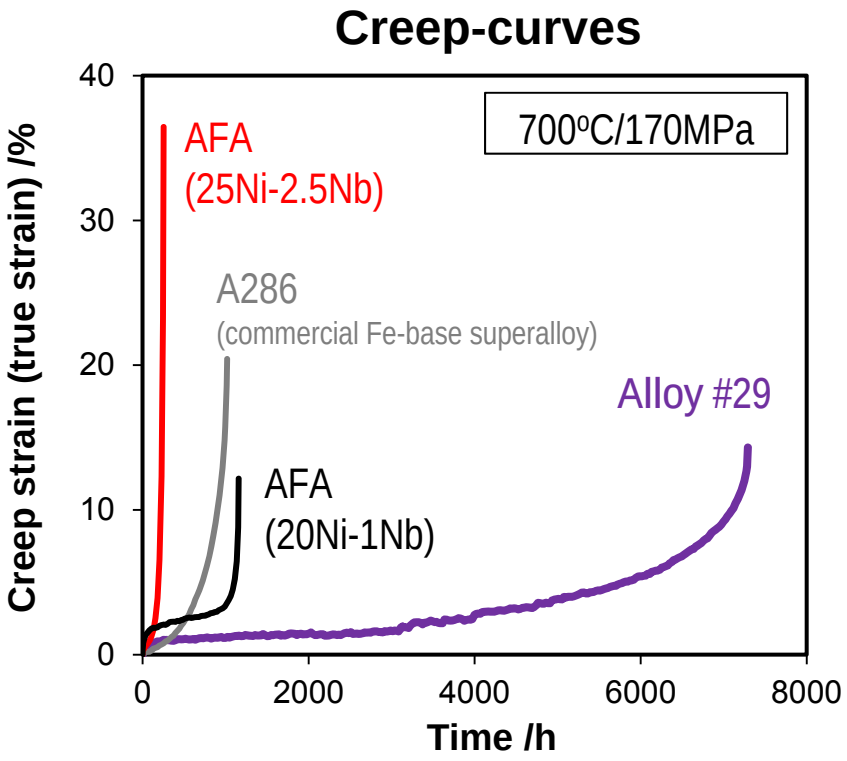
Compatibility Screenings of Environments Currently In Progress

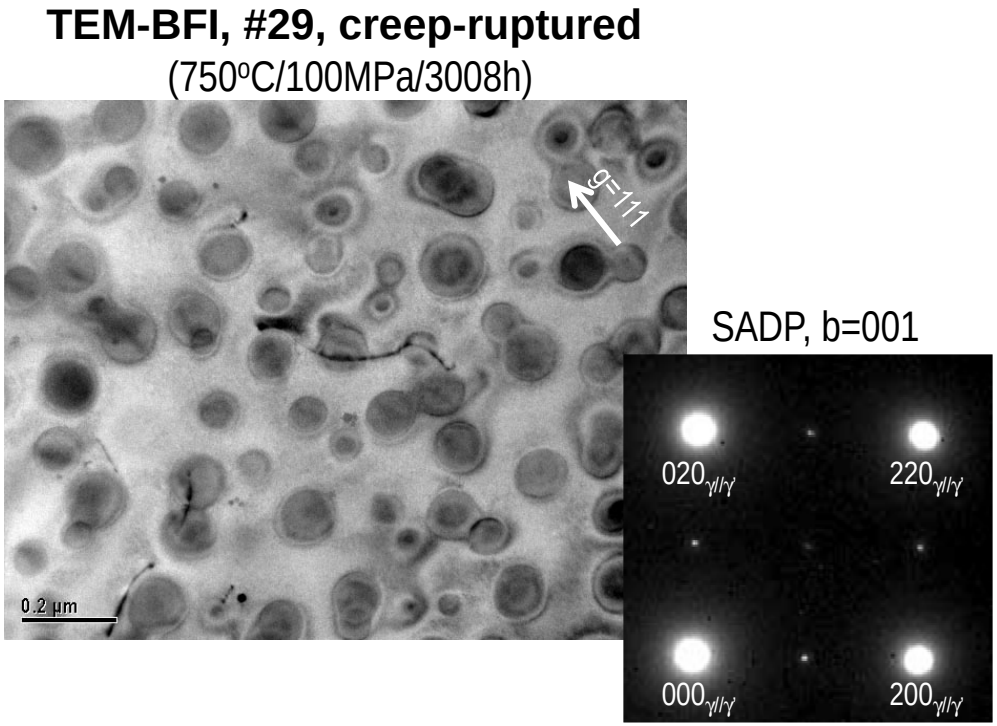
- Fireside boiler and steam
- Supercritical H_2O and supercritical CO_2
- Molten salts/ molten metal
- Solid oxide fuel cell balance of plant
- Aggressive process environments
  - Syngas, sulfidizing, carburizing, and H_2O gases
- Metal Dusting
  - High carbon chemical potential

AFA folded foil specimens for Mercury 50 (4.6MW) engine testing (*courtesy: Solar Turbine*)

Development of Creep-resistant, Fe-base AFA Superalloys

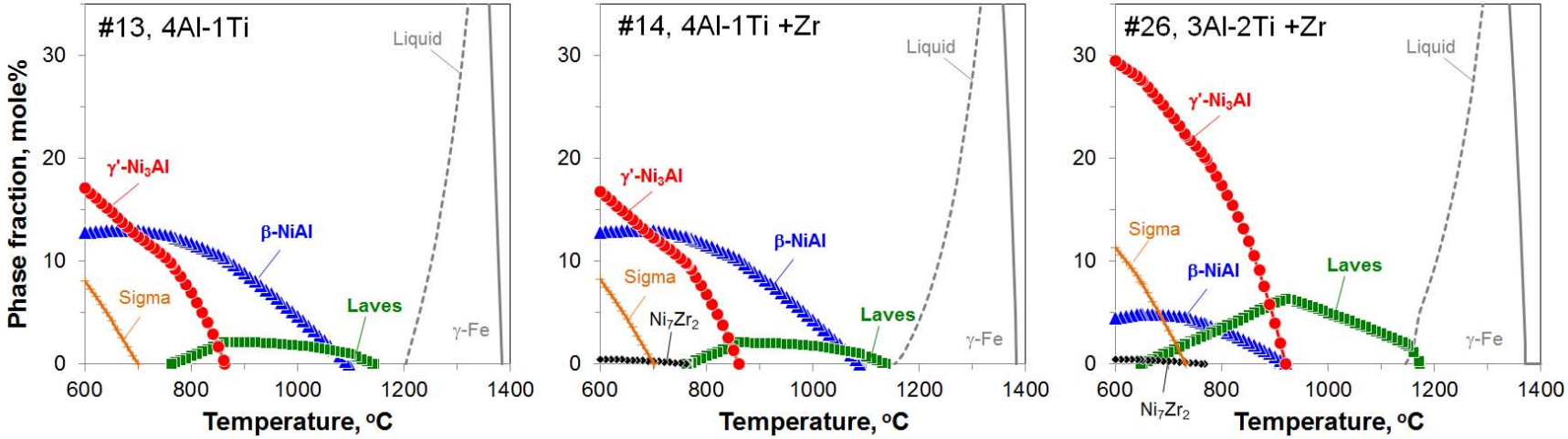
- Optimized AFA alloy compositions to maximize the stability of <u>coherent γ'-Ni_3Al</u> precipitates for strengthening.
- The best alloy showed >7 times longer creep-life (700ºC/170MPa) than A286.





Computational Thermodynamics Support Alloy Design

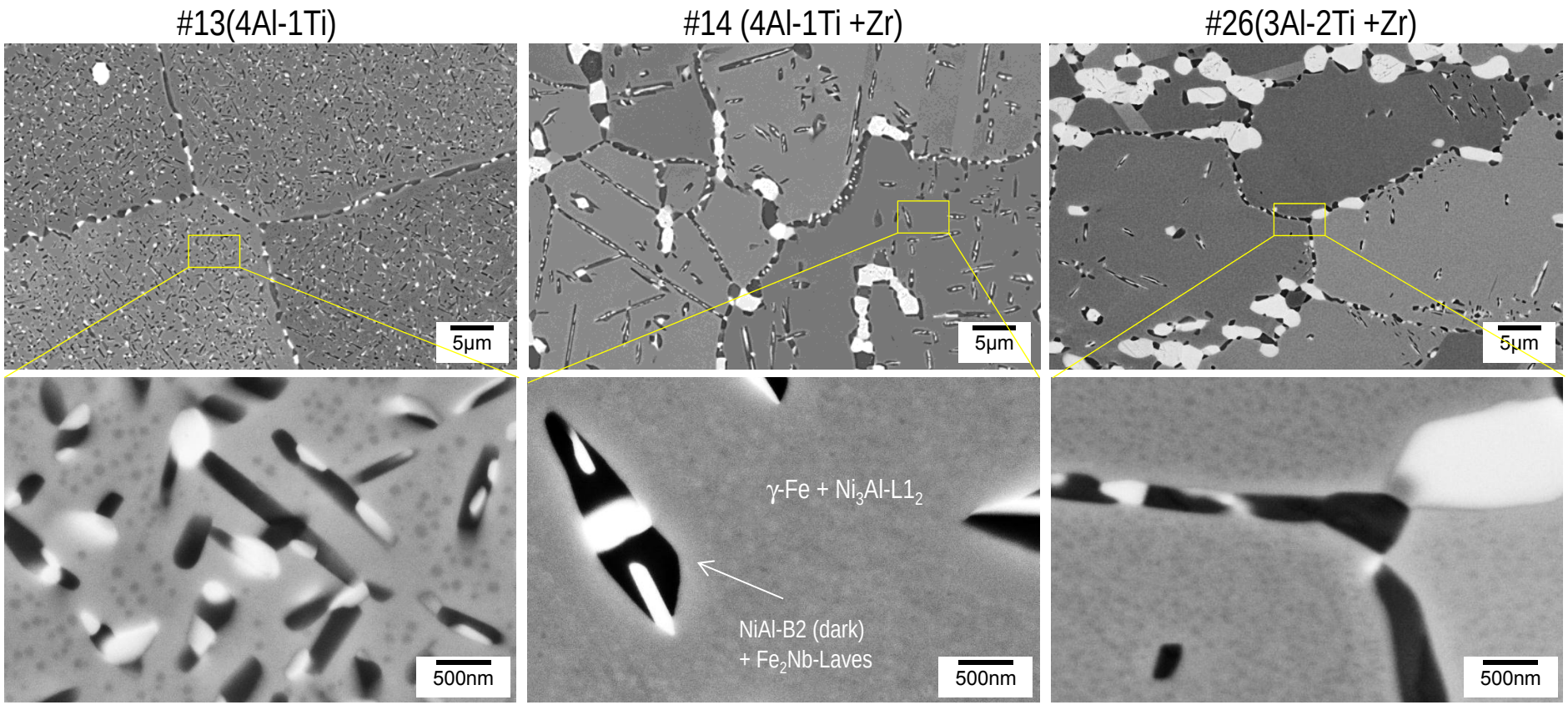
Name	Analyzed composition (wt%)										Remarks
	Fe	Cr	Ni	Al	Si	Nb	Ti	Zr	C	B	
#13	45.73	14.03	32.26	3.96	0.14	2.88	0.98	-	-	-	4Al-1Ti
#14	45.62	14.02	32.23	3.93	0.12	2.81	0.96	0.27	-	-	4Al-1Ti + Zr
#15	45.38	14.03	32.23	3.98	0.14	2.86	0.97	0.29	0.102	-	4Al-1Ti +Zr,C
#26	45.29	14.00	32.47	2.95	0.13	2.93	1.97	0.29	-	-	3Al-2Ti + Zr
#29	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



- Fe-14Cr-32Ni-(3-4)Al-(1-2)Ti-3Nb base, with Zr, C, and B additions.
- JMatPro predicted formation of stable γ'-Ni_3Al below 900°C.

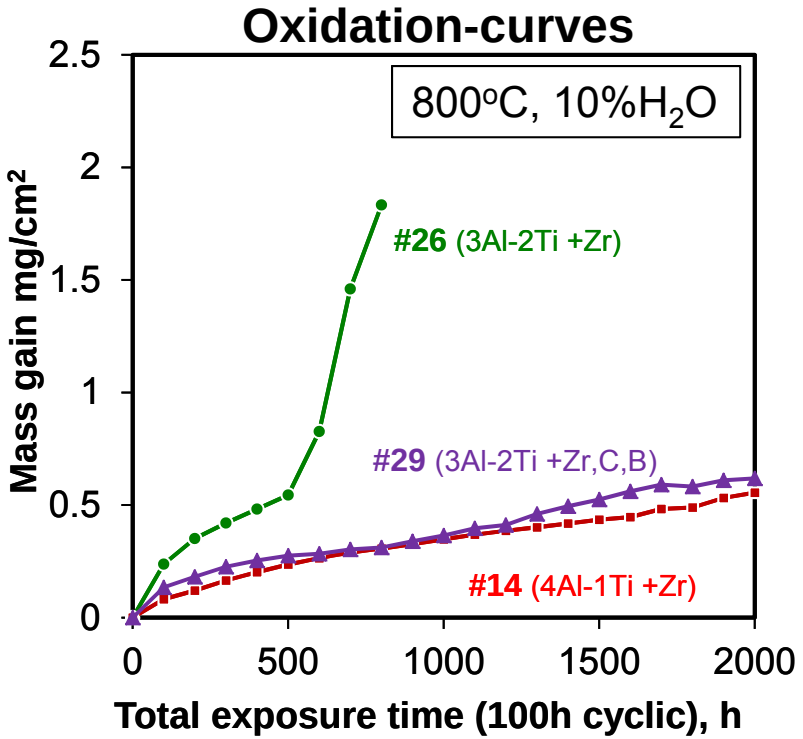
Successful Optimization of γ'-Ni_3Al Dispersion

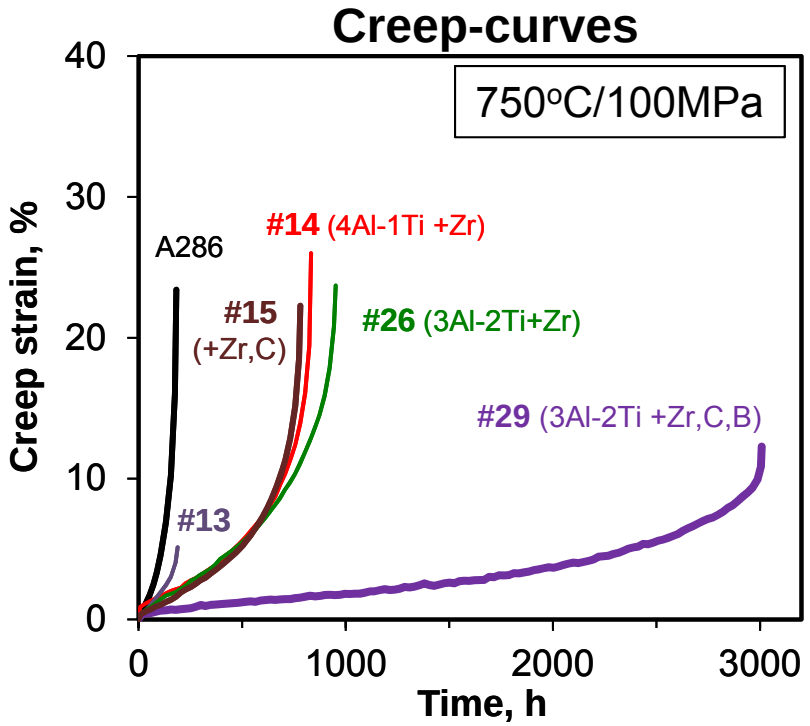
Aged at 750°C for 2,000h



- The Zr addition increases stability of γ'-Ni_3Al relative to β-NiAl.
- High volume fraction of stable γ'-Ni_3Al precipitates can be obtained (3Al-2Ti alloy).

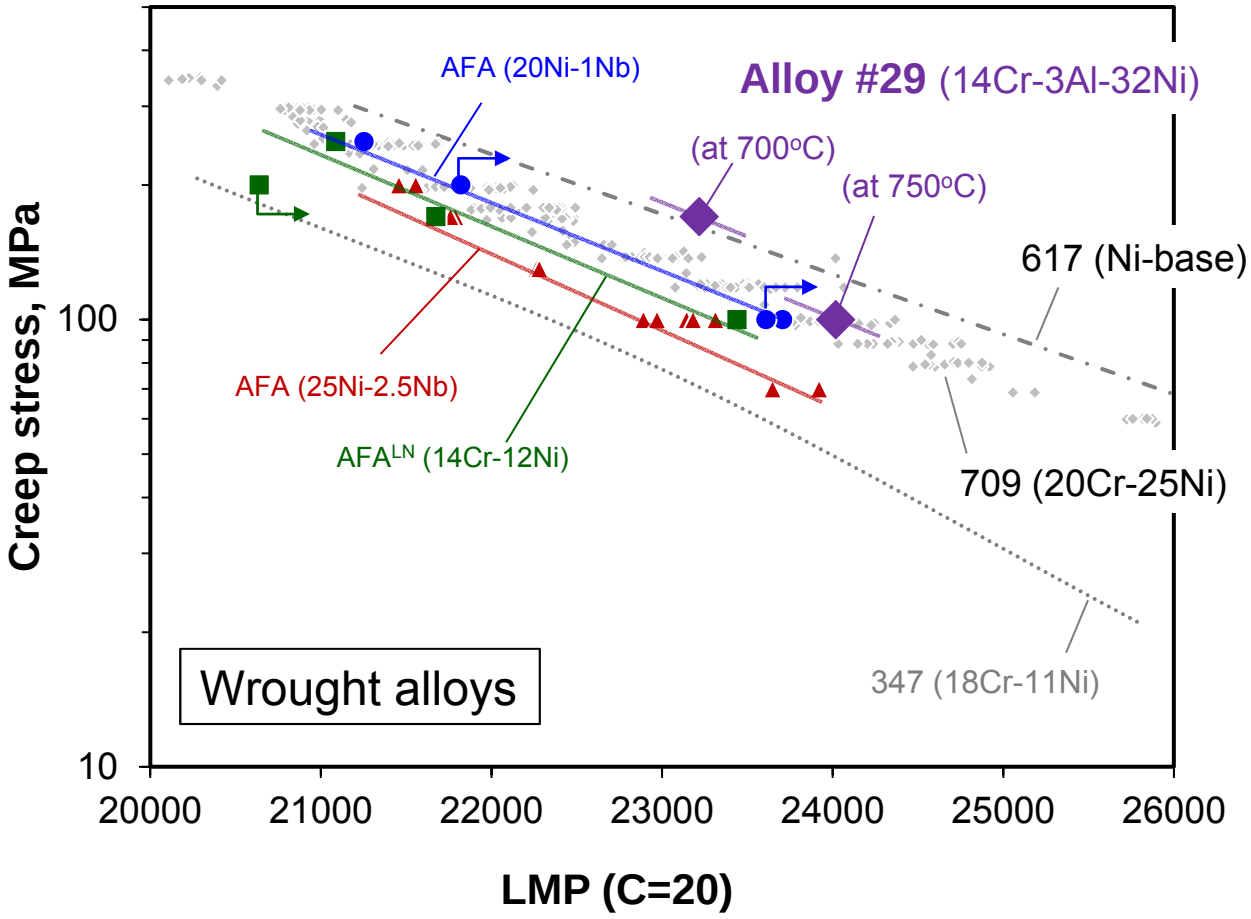
B+C Additions Improves Properties Drastically





- Alloy #29 showed excellent properties of oxidation and creep resistances.
- The B addition increases creep resistance significantly.
- The C addition improves oxidation resistance (as previously reported in different AFA alloys).

Comparable to Ni-base alloy 617 at 700°C

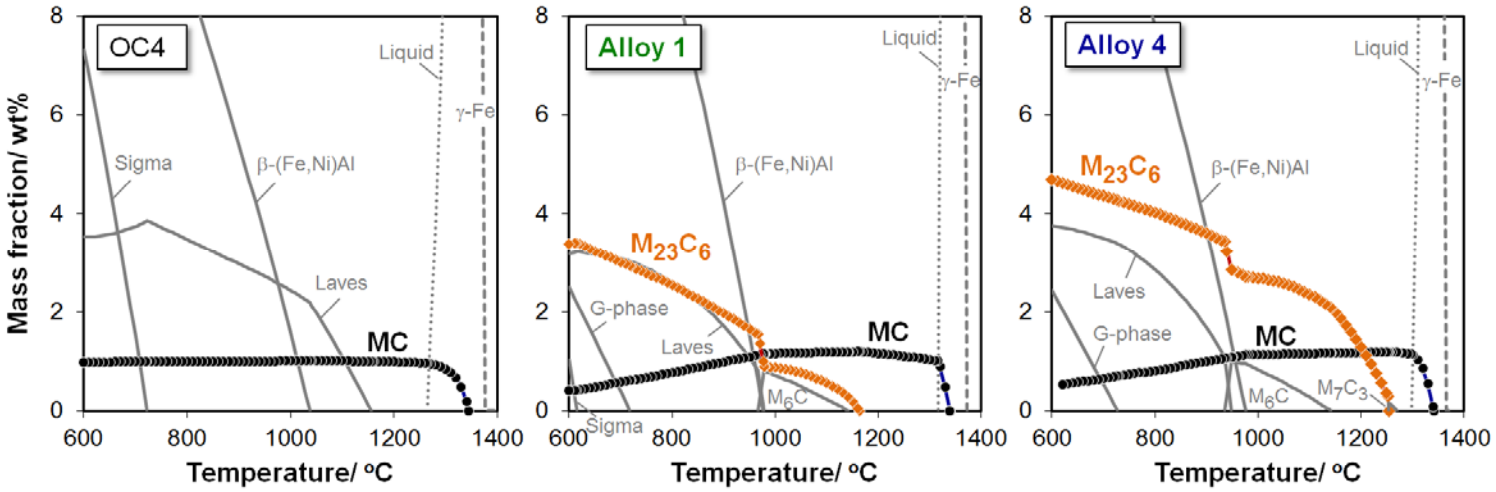


- Strong advantage at relatively lower temperatures (from LMP).

Development of Cast Version of AFA

- Optimized AFA alloy compositions to accommodate castability to the combination of good creep and oxidation resistances.

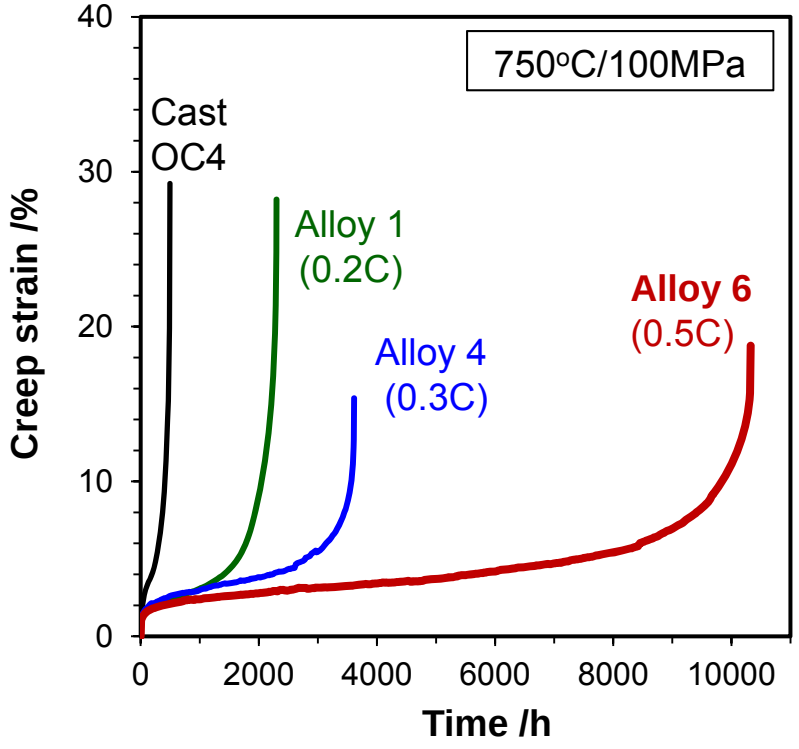
Alloy	Base composition, wt%	Remarks
OC4 (cast)	Fe-14Cr-3.5Al-25Ni-**2.5Nb**-0.15Si-**0.1C**	Baseline
Alloy 1	Fe-14Cr-3.5Al-25Ni-**1.0Nb**-1.0Si-**0.2C**	Low Nb, high C
Alloy 4	Fe-14Cr-3.5Al-25Ni-**1.0Nb**-1.0Si-**0.3C**	Higher C
Alloy 6	Fe-14Cr-3.5Al-25Ni-**1.0Nb**-1.0Si-**0.5C**	Highest C

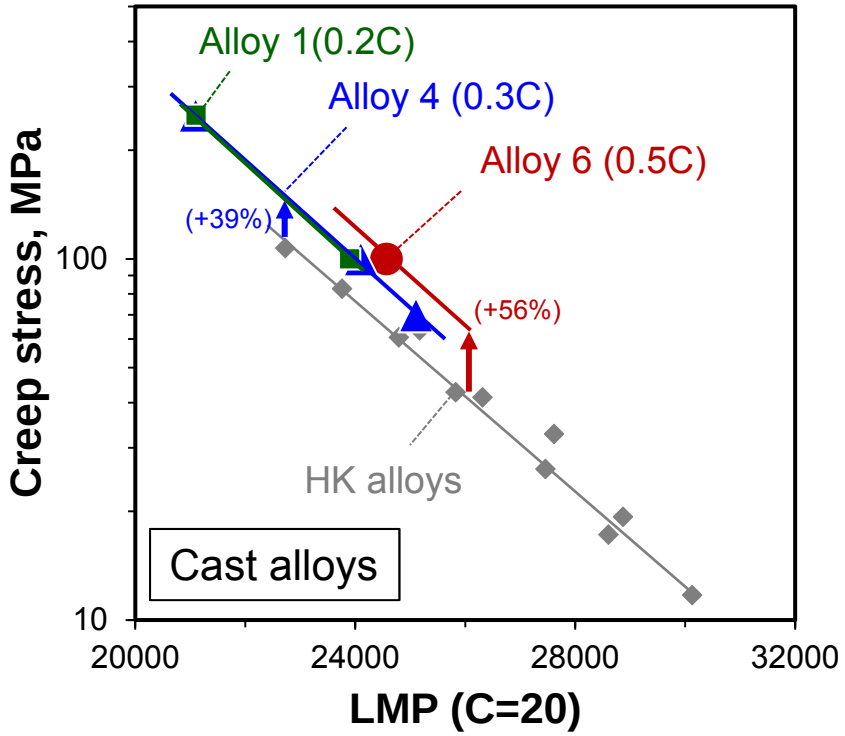


- JMatPro predicted stabilization of $M_{23}C_6$ at elevated temperatures.

Successful Improvement of Creep Properties

- Comparable creep-rupture life to HK series (Fe-25Cr-20Ni base)

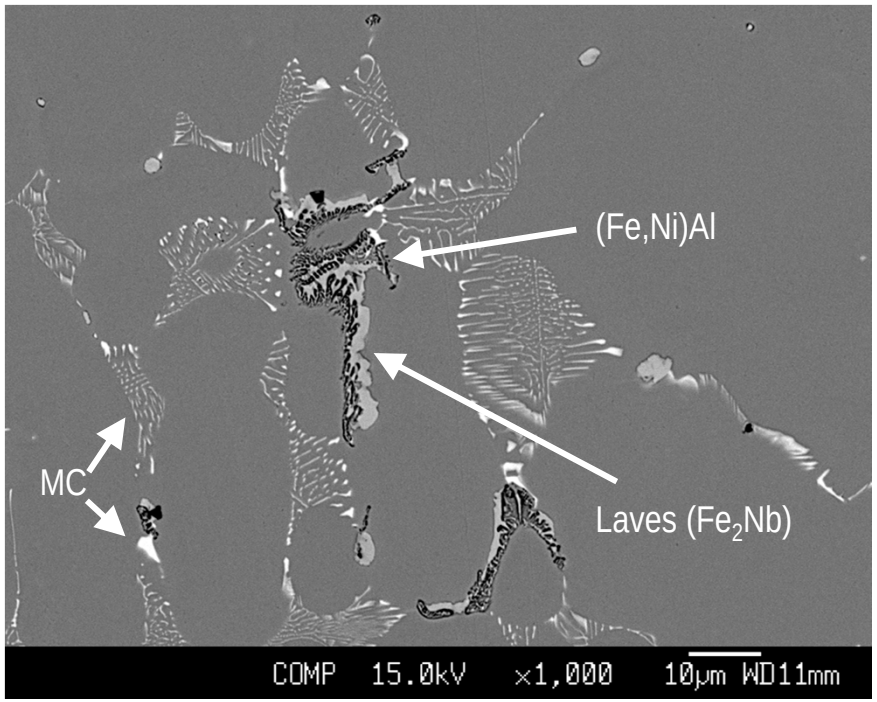




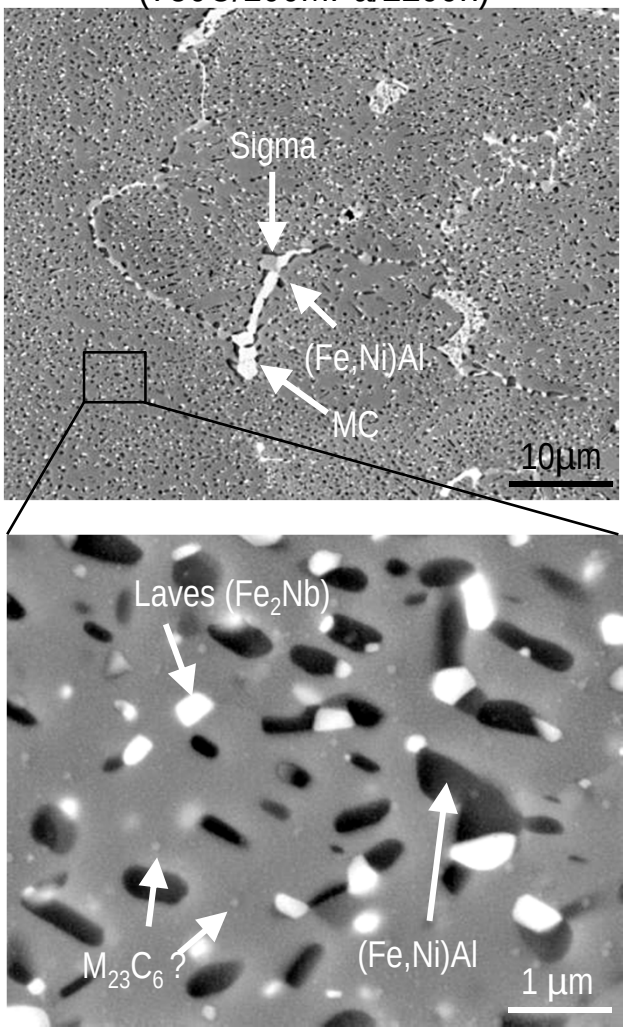
**HK: cast stainless steel, Fe-(24-28)Cr-(18-22)Ni-2Mn-2Si-(0.5-0.6)C base, wt%*

Microstructure Evolution **(Alloy 1, SEM-BSE)**

As-cast

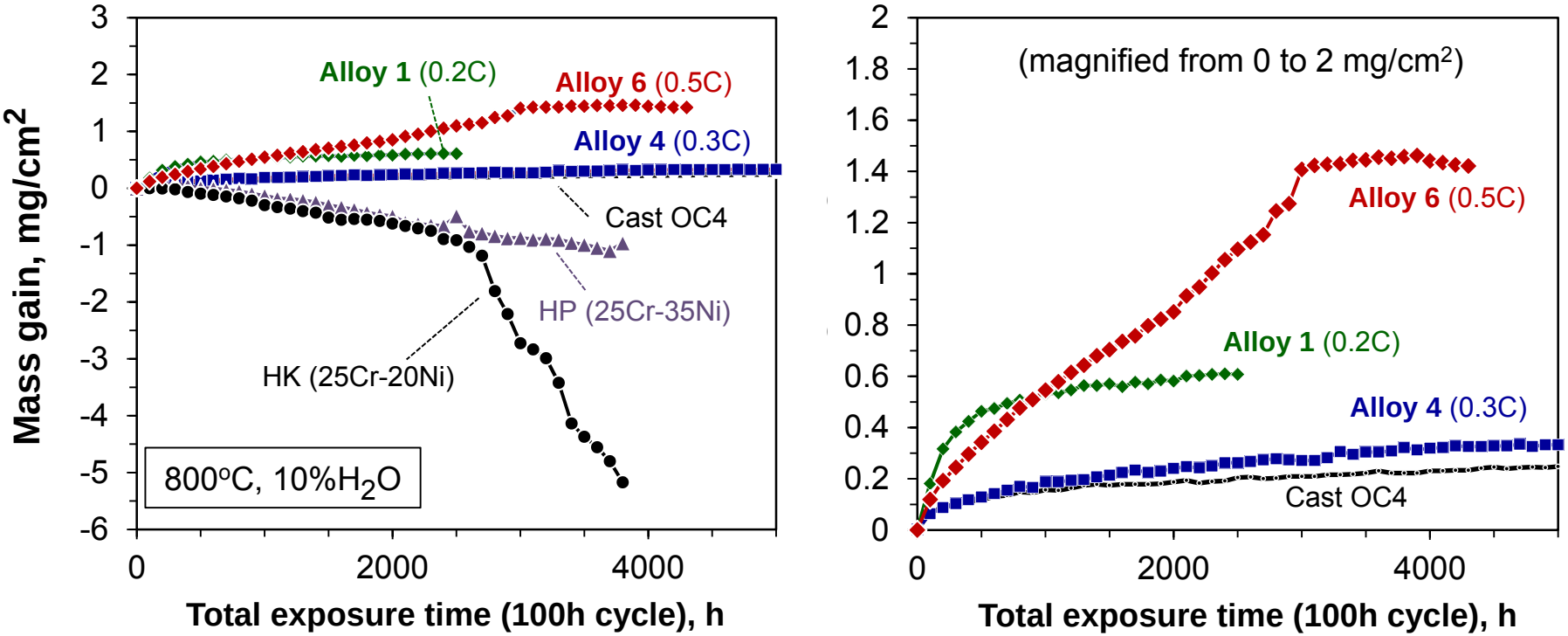


Creep-ruptured
(750C/100MPa/2299h)



- Higher carbon solubility in the matrix than OC4, from Scheil calculation, resulted in higher amounts of strengthening precipitates ($M_{23}C_6$).

Good Oxidation Resistance Comparable to Base Alloy (OC4)



- Better than chromia-forming cast stainless steels (HK, HP).
- 0.3-0.5C range is target for best balanced properties.

Scale-up Efforts with A Commercial Partner

- Two cast AFA tubes (centrifugal casting, ~3.8” OD x 2.4” ID x 185” L) were made by a commercial manufacturer.
  - No significant defect (crack, etc.) was observed.
  - Mechanical property screening is in progress.

(*courtesy: Duraloy*)

Summary

- AFA development for commercialization in progress.
  - Foil products for heat-exchanger is one of potential applications.
  - Seeking other potential applications (steam tubing, petro-chemical piping, etc.)
- New product form:
  - Development of Fe-base AFA superalloy exhibited a potential breakthrough concept of a new heat-resistant steel alloy.
  - Cast AFA showed comparable creep properties/ superior oxidation resistance to HK series.