VTT TECHNICAL RESEARCH CENTRE OF FINLAND LTD

High temperature steels in conventional thermal plants

– views on trends

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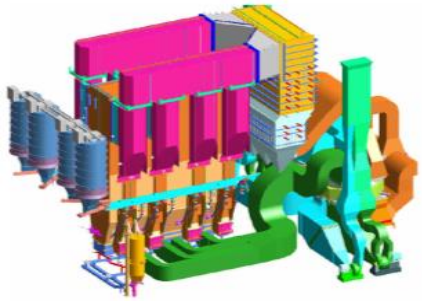
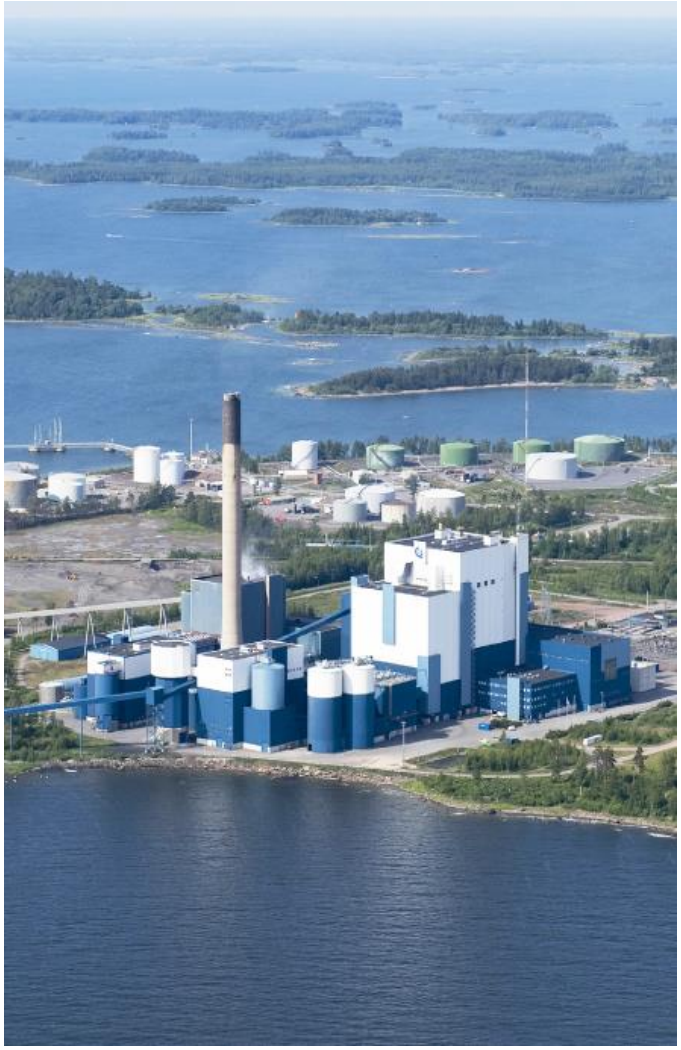


MatISSE Workshop on Structural Materials for future Energy Systems
25-26 November 2015



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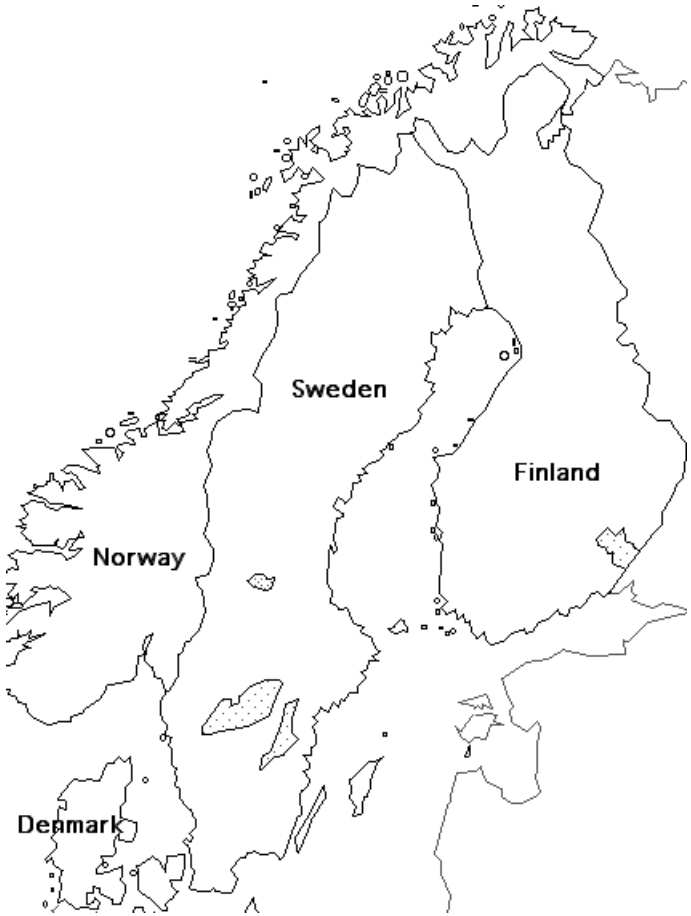
Introduction: background



- **Finland**
  - fossil (decreasing)+biomass, nuclear (~25%, increasing), hydro (15-20%), import
  - not very lucky
- **Sweden**
  - mostly hydro + nuclear, some fossil+biomass
  - quite lucky
- **Norway**
  - mostly hydro, also for export
  - very lucky (hydro undercuts subsidised wind)
- **Denmark**
  - wind (>30%), fossil, biomass + waste, import
  - not very lucky
- **Nordic countries (with Iceland) in general**
  - common legislation/free borders before EU
  - common spot market since 1996
  - district heating common

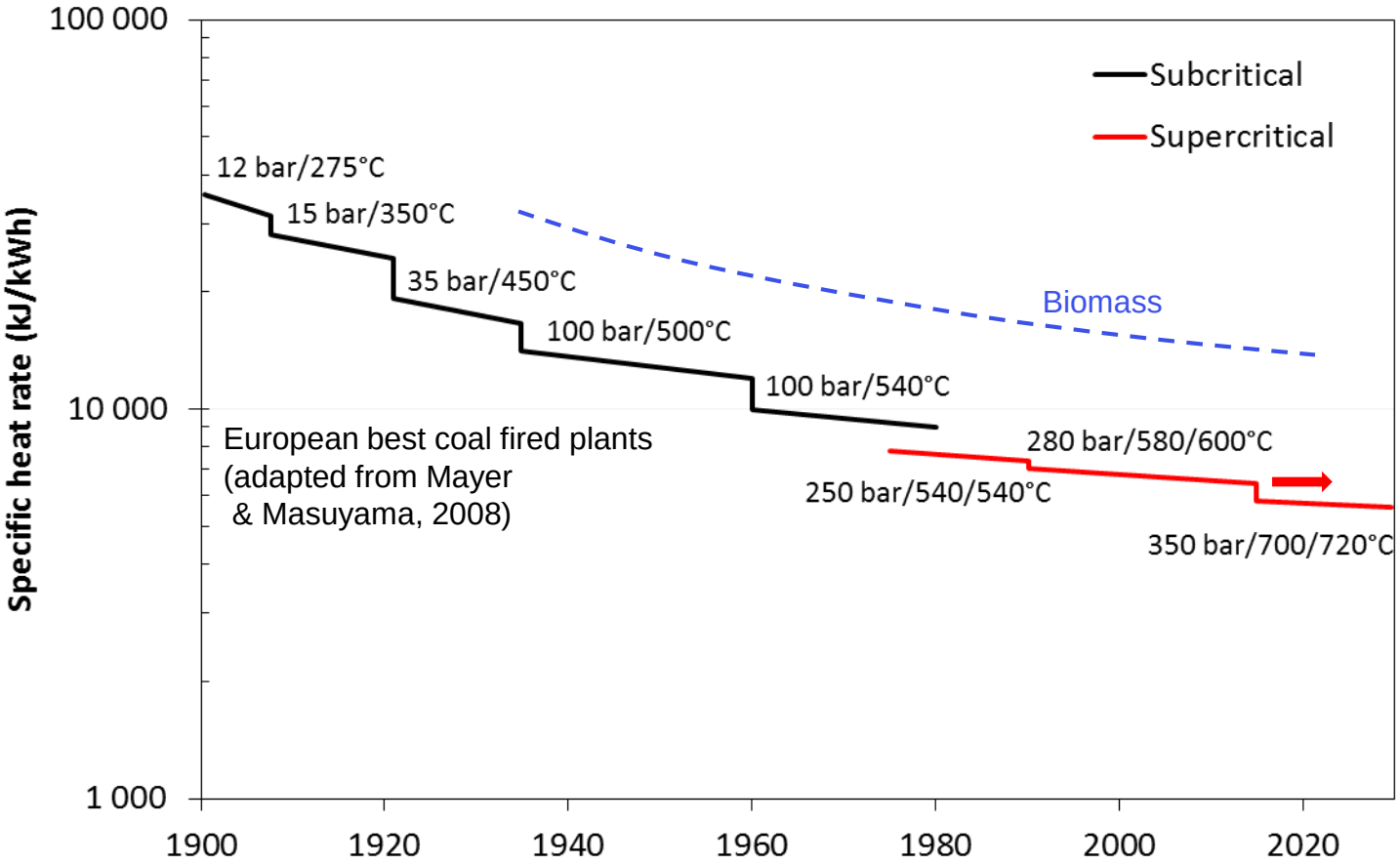
Introduction: drivers and responses

- **Cost / economy:**
  - (disregarding nuclear here)
  - fuel advantages/limitations
    - fossil (heat value/climate policies)
    - biomass (credits/availability)
    - waste (cheap or paid for/corrosive)
  - co-firing, flexible fuels → BFB/CFB boilers
  - alternatively, higher efficiency with fossil
    → less specific emissions
- **Environment:**
  - dirty boilers for cleaner world
  → corrosion, fouling
  → reduced acceptable temperatures
  → high alloy, ceramic or sacrificial surfaces

Material selection and development

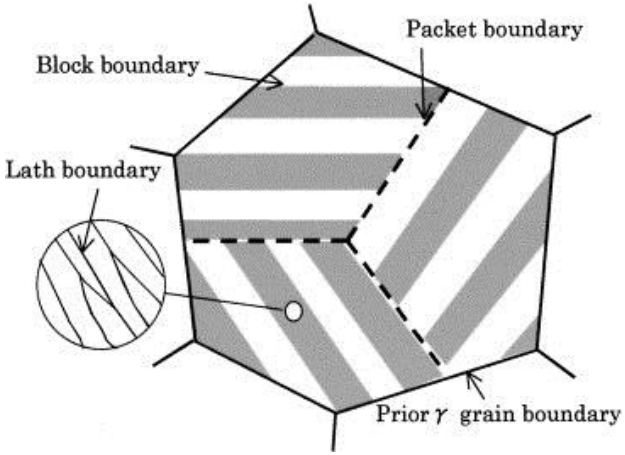
- **Cost related design issues**
  - processes to minimise physical size/volume
  - fuels with good and even heating values (you wish)
  - simple cheap materials used as much as possible
  - minimal volume of costly high-end materials
- **Predictability for (large long term) investment**
  - known materials, yet performing & competitive
  - reliability for “design” life
  - no surprises (regulation, technical, other)
  - modifications expected over plant life e.g. in controls, instrumentation and monitoring, but generally avoided in major choices of structural materials
- **Development?**
  - avoid change beyond design if possible (cf. T24)
  - R&D = parallel process for new plants & processes

Operating environments: history and future

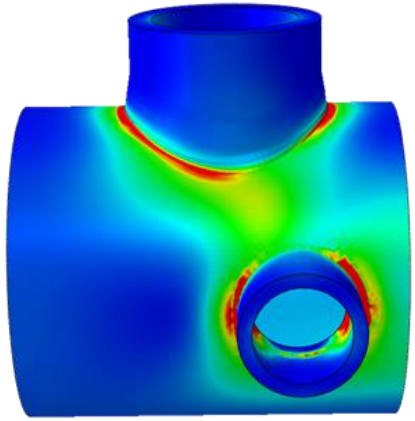


- **Increasing efficiency = decreasing heat rate**
- **Development of technology**
- **Reduce fossil fuels - then what?**

New materials: e.g. 9-12% Cr steels



Multiscale microstructure of tempered martensitic steel (Hayakawa 2000, Kimura et al. 2006)



X20 header section

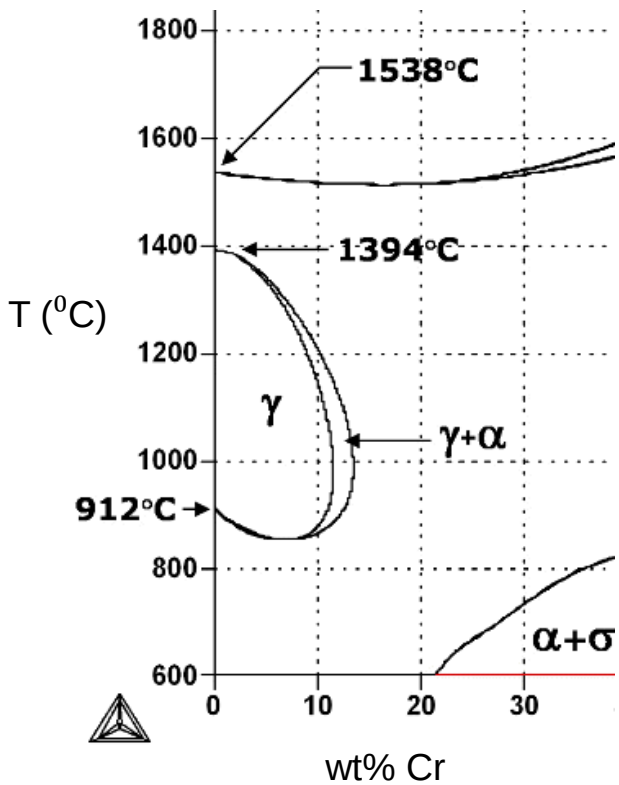
Steels for tubes & pipes:

- 1960's - : X20 (DE), not so new anymore
- 80's to '90's- : P91 (US), P92 (JP)
- 2016? - : P93
- Numerous predecessors & sidesteps, parallel alloys for castings, forgings, …

Characteristics:

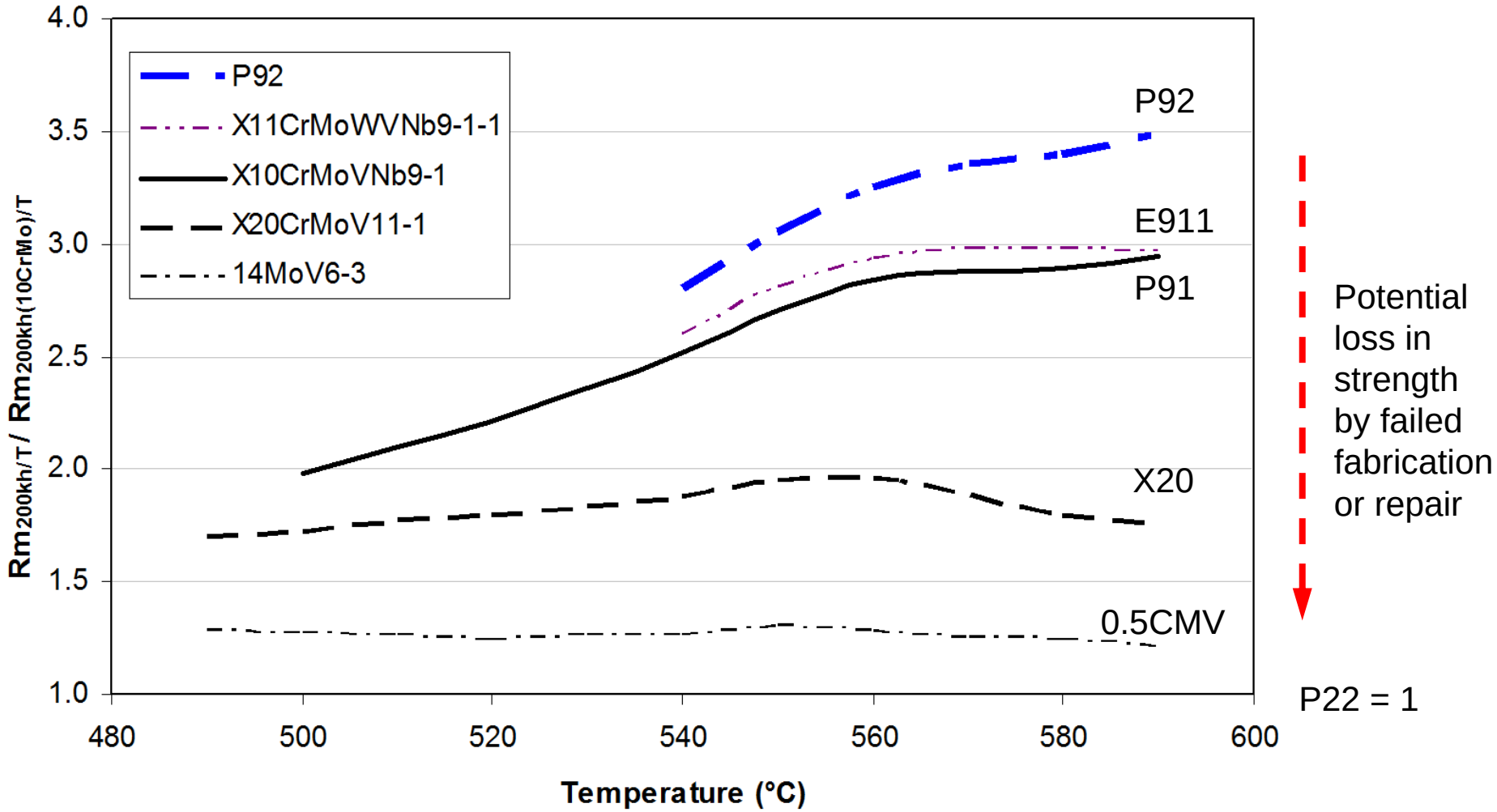
- tempered martensitic microstructure
- multiscale internal boundaries, precipitates, solid solution elements → strength, ductility
- fair oxidation resistance (Cr), compatibility in thermal cycles of operation
- strong influence by errors in heat treatments
- *new until full range of service experience*

Ferritic/martensitic Cr steels – HT applications

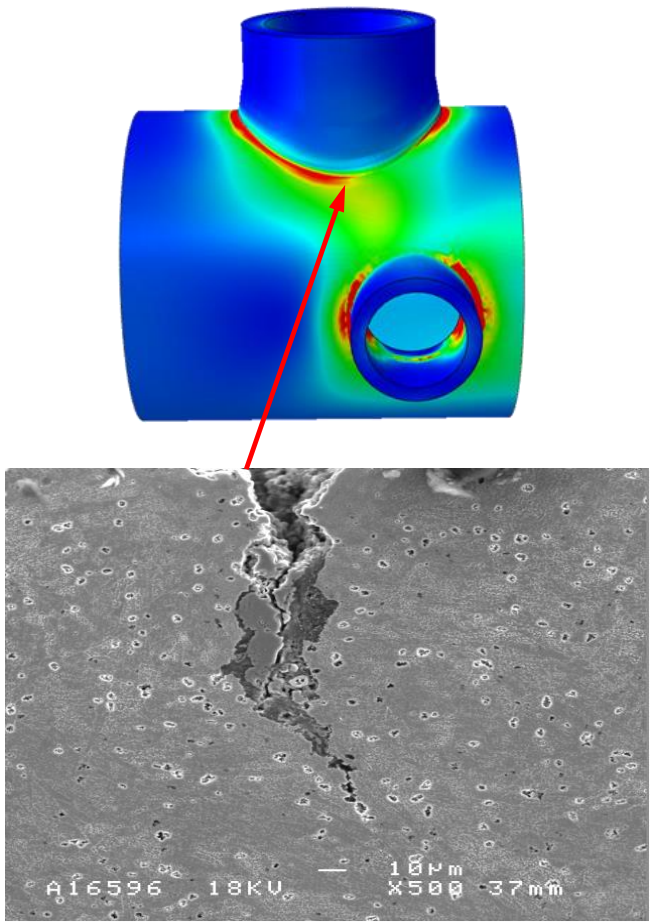


- QT: martensitic from air quench ≥ 5%Cr (P5); Cr increases hardenability and provides resistance to oxidation and hydrogen attack
- +Mo for tempering and creep strength (also W, solid solution strengthening)
- Strengthening precipitates:
  - MX
  - $M_{23}C_6$
  - intermetallics such as Laves phase
- Balancing the details for strength/ductility: C, N, B, V, Nb, Al, Ni, Co, …
- About 100 y evolution from steels of general machinery, power & process industry

Creep strength (EN 10216-2, 200 kh) compared to 10CrMo9-10 (P22)



Experience on materials in service



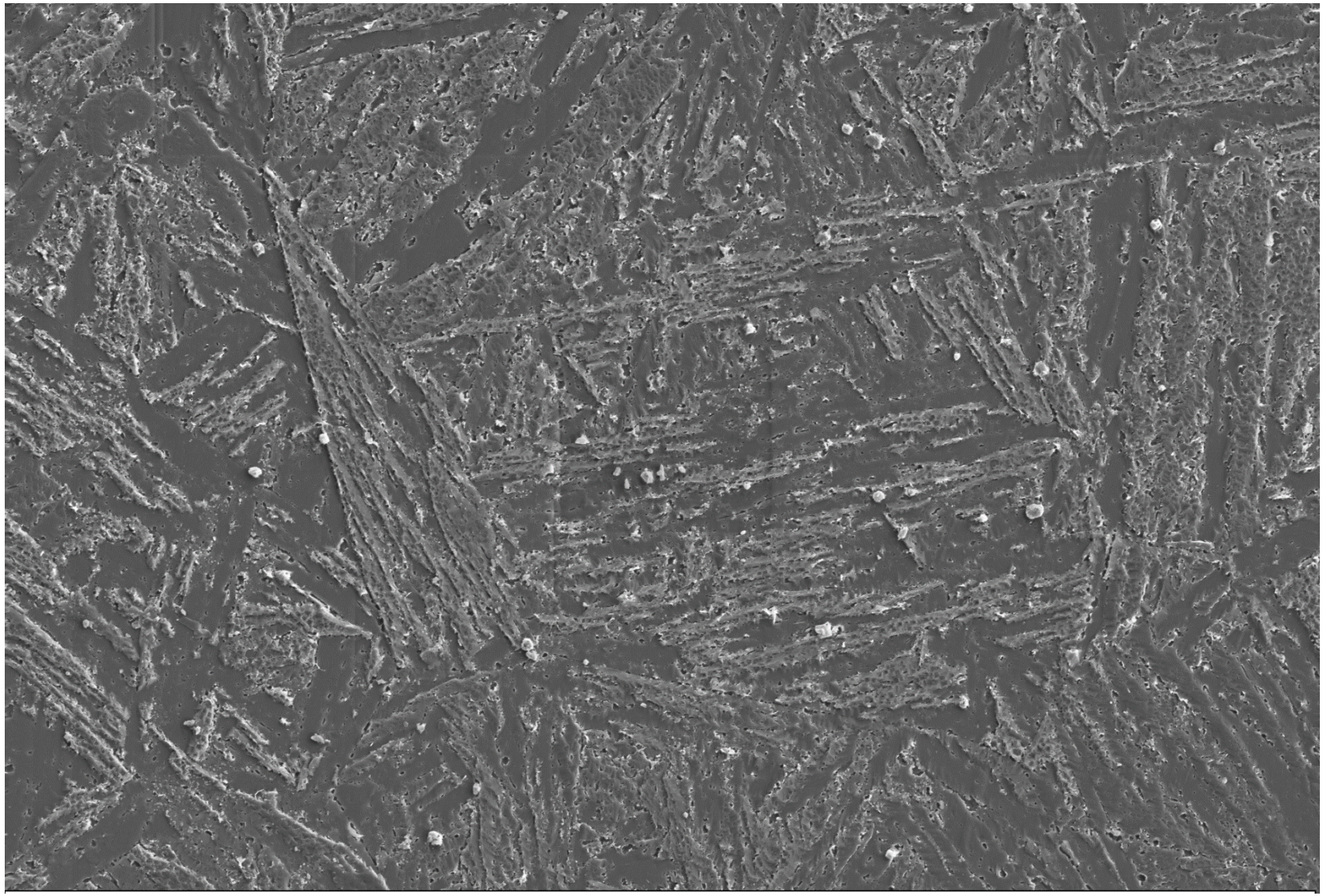
Creep damage at saddle point HAZ after 135 000 h at 535ºC

X20CrMoV11-1 (EN 10216-2):

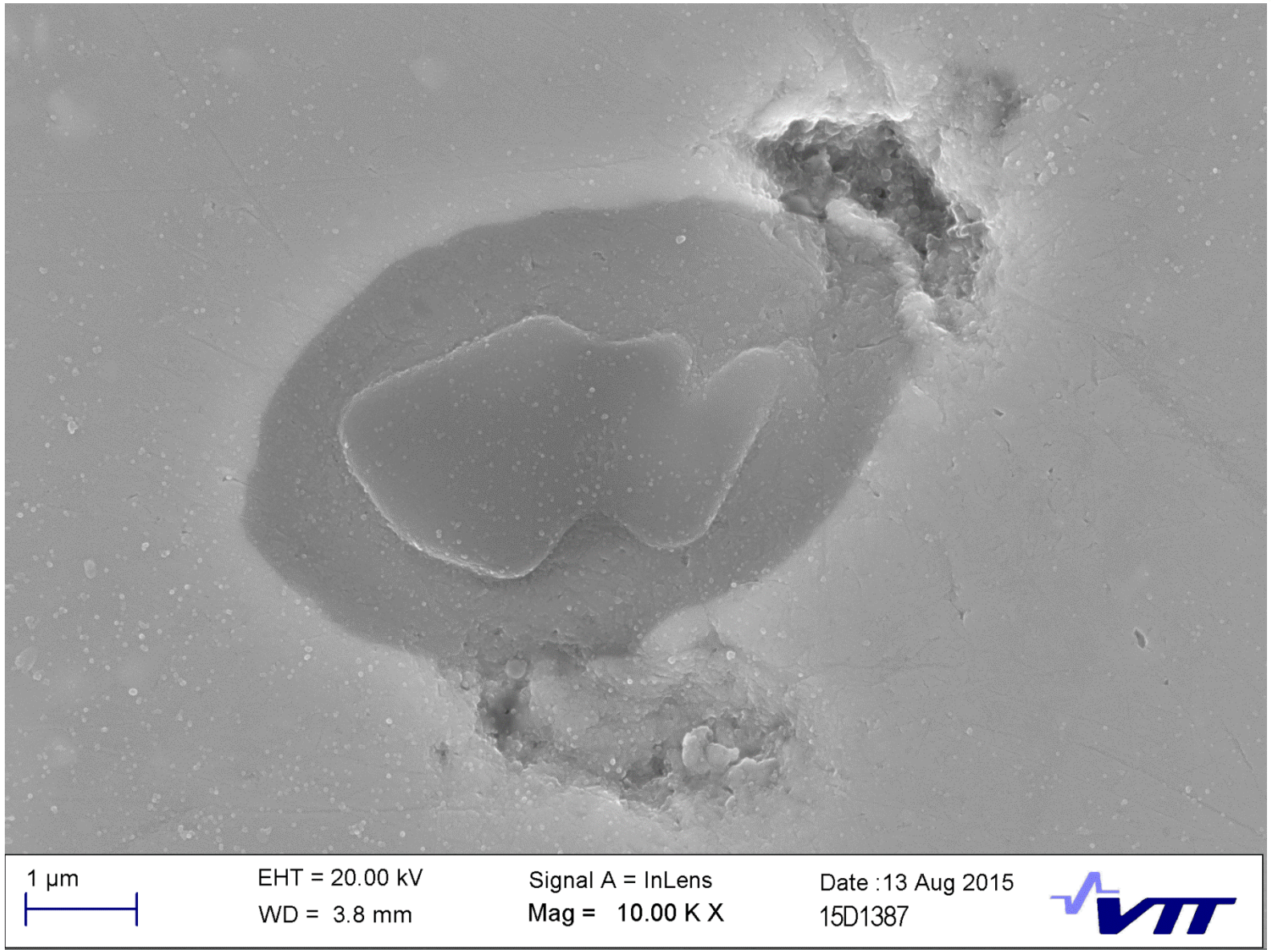
- In widespread use since 1970's, also for superheaters/reheaters, not in ASME code < short-term toughness (welded)
- Generally good indicated long term performance in Europe, > 200 kh in plant
- No systematic indications of low ductility, suggested relatively late emergence of creep cavitation damage in inspections
- Established steel ☺ - to be replaced ☹

Specific features:
- 0.2%C, to be noted for welding
- Rupture strength ~96 MPa/560ºC/200 kh

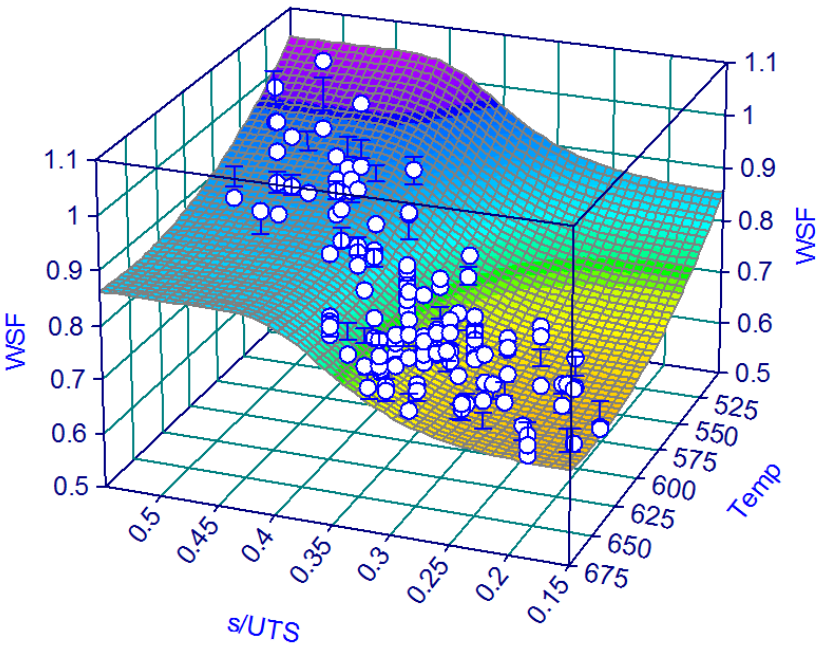
X20 after > 200 kh at ~530ºC



10 µm


1 µm
EHT = 20.00 kV
WD = 3.8 mm
Signal A = InLens
Mag = 10.00 K X
Date :13 Aug 2015
15D1387

Experience on materials in service



s/UTS = stress/ tensile strength

WSF < 0.8 at high temperatures

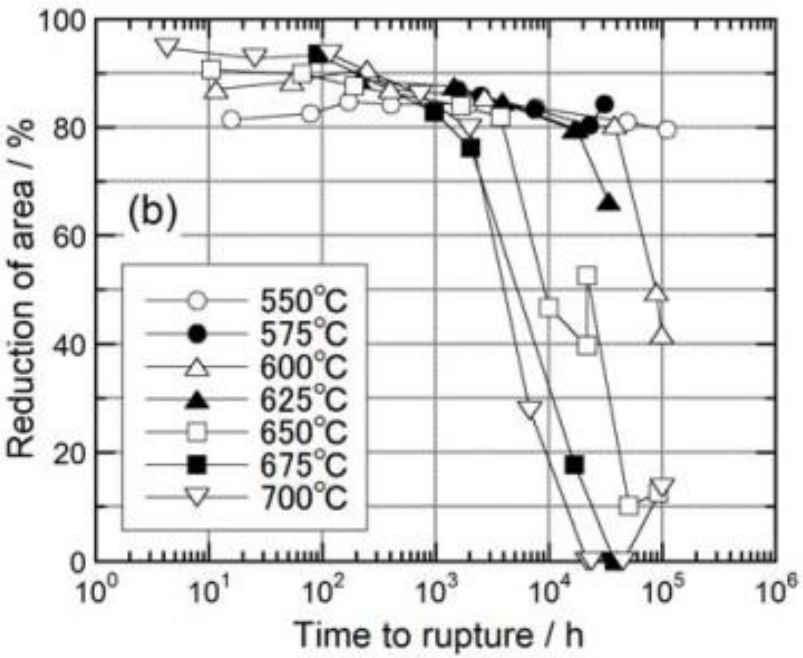
P91 (X10CrMoVNb9-1 EN 10216-2):

- In widespread use since 1990's, less for boiler internals than X20 (T91, lower Cr)
- Reported cases of early creep damage with high Al (Al:N), high operating temperatures
- No systematic indications of trouble when avoiding upper operating range ≥ 580ºC
- Established steel, less long term experience

Specific features:

- 0.1%C, easier to weld than X20
- Rupture strength ~97 MPa/590ºC/200 kh

Experience on materials in testing & service



Kimura & Sawada 2015

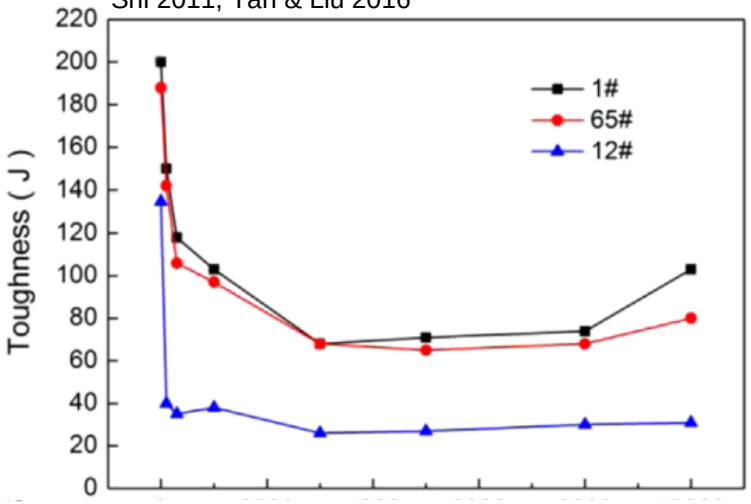
P92 (X10CrWMoVNb9-2 EN 10216-2):

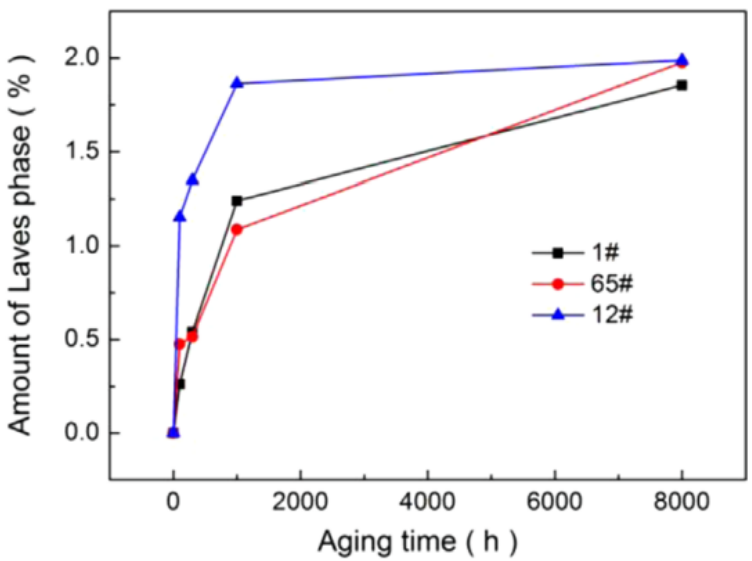
- Used since 1990's, mostly for heavy sections of large plants
- Suggested cases of low creep ductility (composition, fabrication) for upper range of operating temperatures (>600ºC)
- Mostly short to medium term operating experience, not yet a fully established steel

Specific features:
- 0.1%C, much more Laves phase than in P91 or X20
- Rupture strength ~101 MPa/600ºC/200 kh

Experience on materials in testing & service

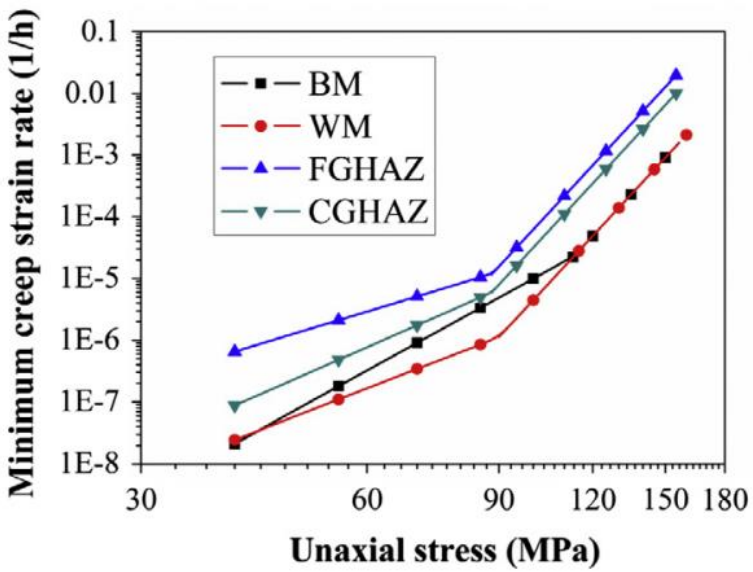
Shi 2011, Yan & Liu 2016



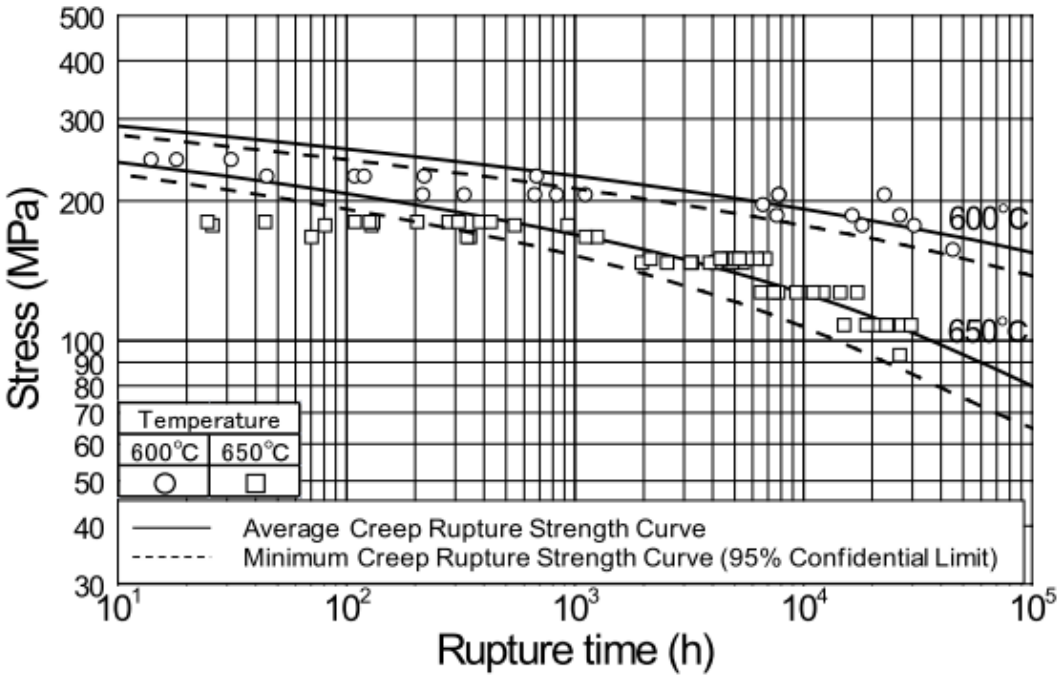


P92

- Toughness can also be low (cf. X20)
- Suggested reasons for low ductility: local strain near prior austenite gb's, cavitation at particle surfaces (MnS, Laves, BN, Al_2O_3)
- Suggested remedies: reduction of impurities, adjusting composition, heat treatment



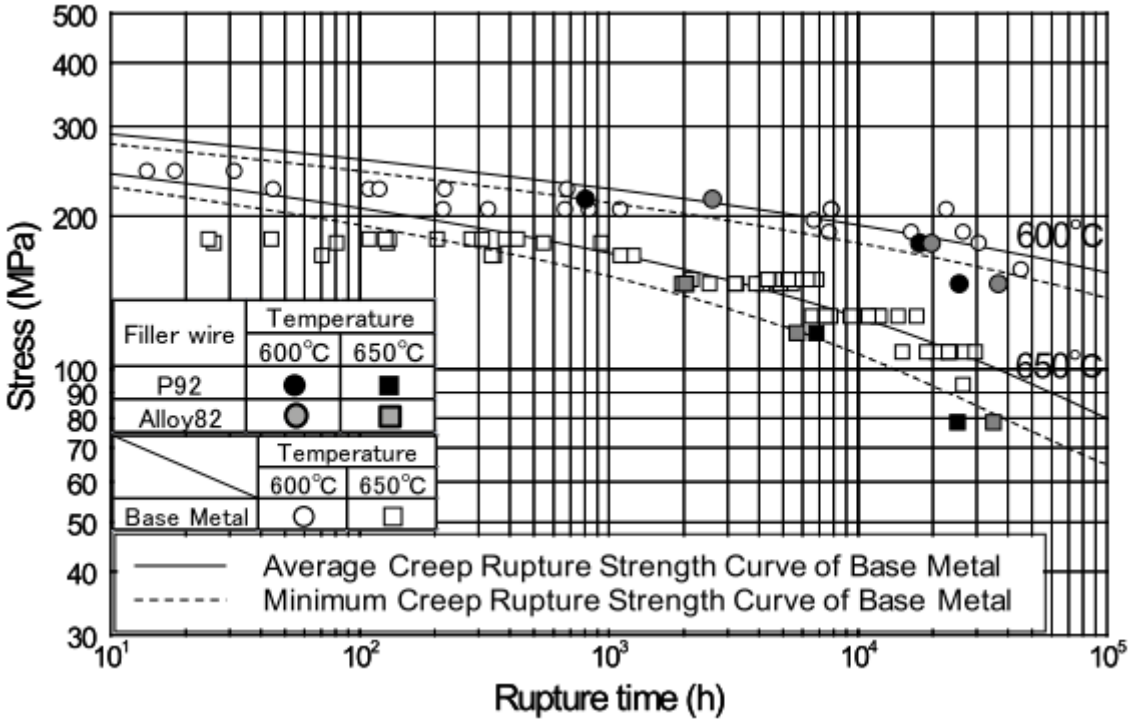
Further evolution: 9Cr-3W-3Co-0.02Nd (P93?)



Hamaguchi et al. 2015

Element	Target	Improvement
9Cr	・Long-term creep strength	Creep strength of base metal
3W	・Solution strengthening ・Laves phase precipitation strengthening	
0.01B	・Suppression of coarsening of $M_{23}C_6$ on G.B.	
0.01N (low-N)	・Suppression of Z-phase and BN precipitation	
0.02Nd	Suppression of S segregation	Creep ductility
3Co	Stability of martensite	Toughness
0.01B	Suppression of fine HAZ	Creep strength of welded joint

9Cr-3W-3Co-0.02Nd (P93?) welded

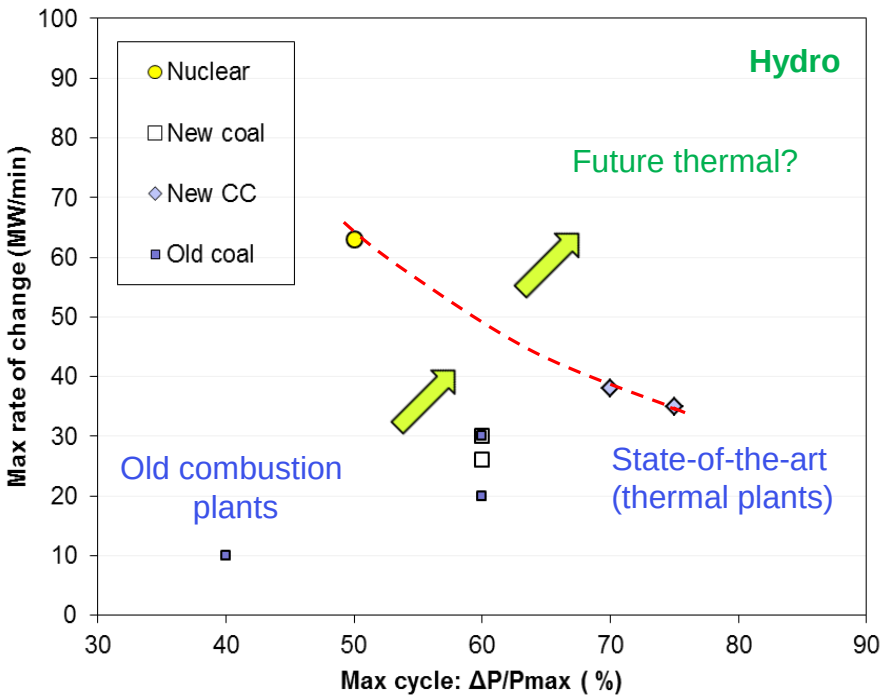


Hamaguchi et al. 2015

Observations:

- testing up to about 45 000 h, downward trend accommodated in the fitting model?
- P92 under- and Alloy82 over-matching?
- failure positions in longest tests: type IV avoided?
- often poor correlation in short term (creep) testing

Materials / solutions for cycling (CF) service



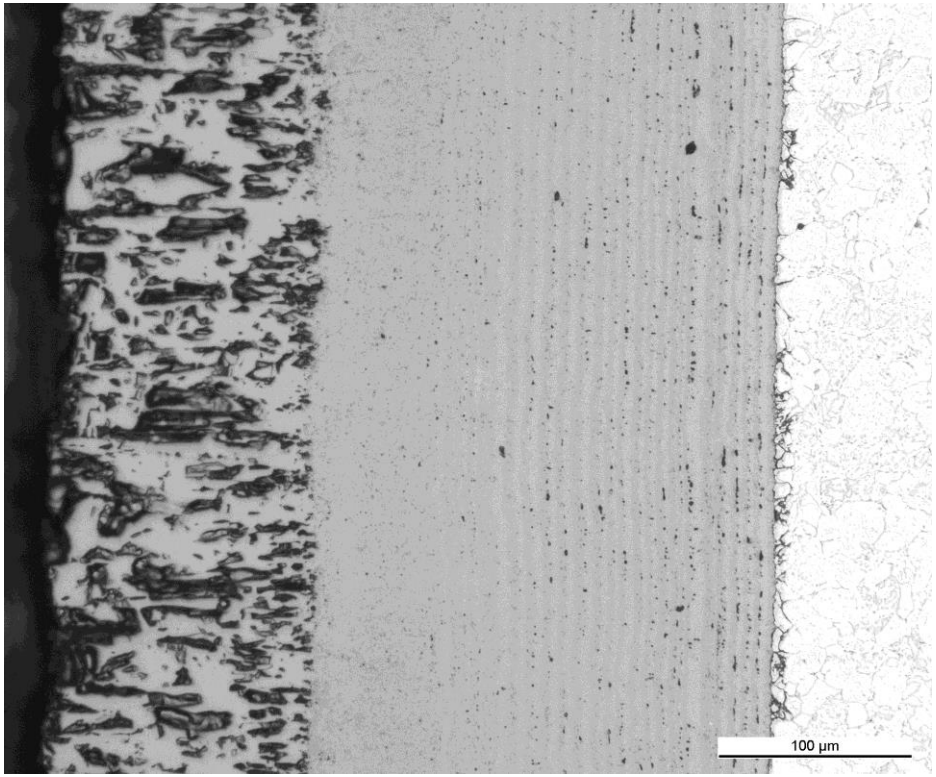
Challenges:

- Early CF methods developed for aerospace Ni alloys with design life ~10^4 h → HT but no long tests
- For land-based equipment with design life of more than $2 \cdot 10^5$ h, long holds make slow testing of both conventional & new materials

→ more emphasis on modelling and monitoring of equipment condition

- Improved resistance to more extensive cycling, reduced minimum loads (not only a materials issue)

Impact of evolving operating environments



steam

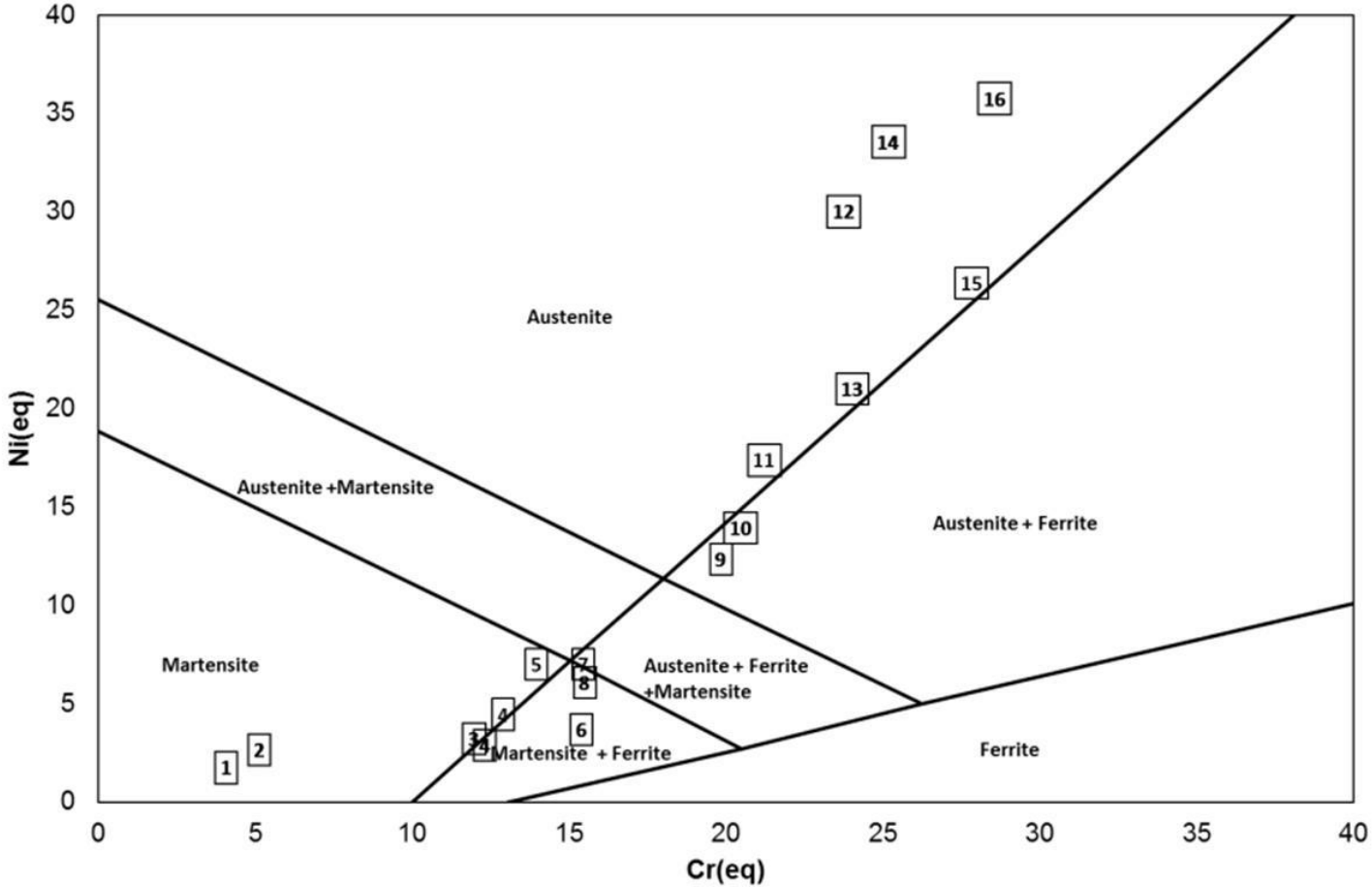
metal
(T22)

- **Biomass/waste/co-fired plants**
  - corrosion sets limits
  - austenitics, other high alloy materials

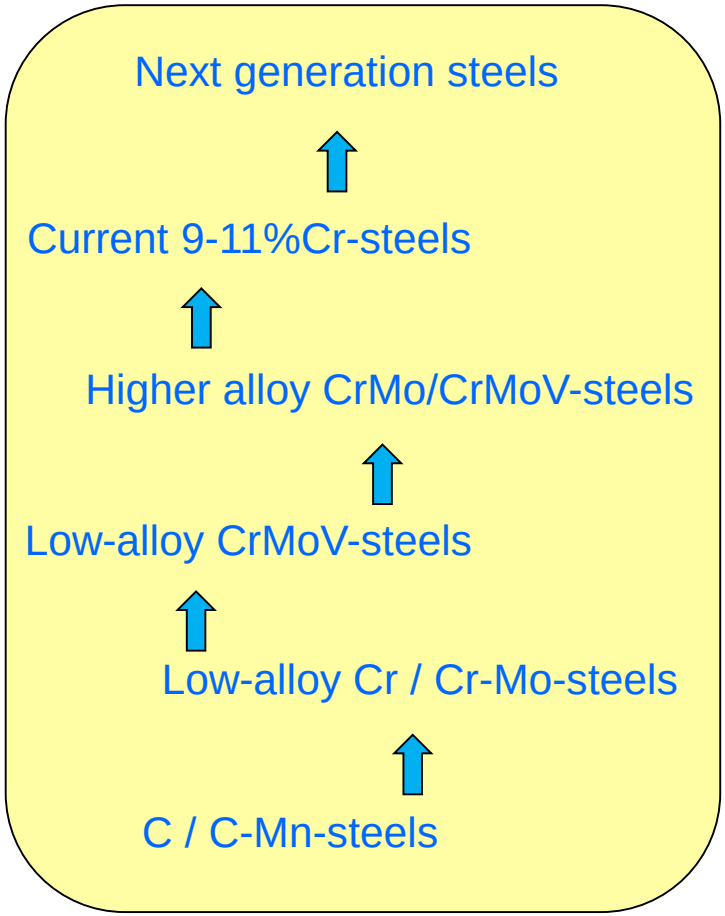
- **High efficiency (SC) plants**
  → thick walls, alloy steels
  → stiffness, constraint
  → water side oxidation possibly life-limiting
  → HT austenitic steels

- **Cycling, ramping, low minimum load:**
  - large/fast strain cycles
  - spalling, blockage, erosion
  - austenitics sensitive

Composition-based phase diagram



Conclusions - summary



- **HT steel evolution for pressure equipment** is gradual and requires

  - long term qualification for first introduction

  - status of new material until initial adjustments and further evidence have accumulated to show trusted limits of application

  - dealing also with new challenges like those from cyclic/intermittent service, cost bias from subsidies, etc.

- **Each new generation** of successful steels provides

  - sufficient thermal/resource/cost efficiency

  - advantages for equipment & service conditions (temperature, loads, chemical environment)


Thank you