High temperature steels in conventional thermal plants
– views on trends

Pertti Auerkari
VTT, Espoo, Finland

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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?

European best coal fired plants (adapted from Mayer & Masuyama, 2008)
New materials: e.g. 9-12% Cr steels

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)

Potential loss in strength by failed fabrication or repair

P22 = 1
Experience on materials in service

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/560°C/200 kh

Creep damage at saddle point HAZ after 135 000 h at 535°C
X20 after > 200 kh at ~530°C
Experience on materials in service

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 ≥ 580°C
- Established steel, less long term experience

Specific features:
- 0.1%C, easier to weld than X20
- Rupture strength ~97 MPa/590°C/200 kh
Experience on materials in testing & service

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 (>600°C)
- 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/600°C/200 kh

Kimura & Sawada 2015
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, Al₂O₃)
- Suggested remedies: reduction of impurities, adjusting composition, heat treatment
Further evolution: 9Cr-3W-3Co-0.02Nd (P93?)

<table>
<thead>
<tr>
<th>Element</th>
<th>Target</th>
<th>Improvement</th>
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<tbody>
<tr>
<td>9Cr</td>
<td>• Long-term creep strength</td>
<td>Creep strength of base metal</td>
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<tr>
<td></td>
<td>• Solution strengthening</td>
<td></td>
</tr>
<tr>
<td>3W</td>
<td>• Laves phase precipitation strengthening</td>
<td></td>
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<tr>
<td>0.01B</td>
<td>• Suppression of coarsening of M23C6 on G.B.</td>
<td></td>
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<tr>
<td>0.01N</td>
<td>(low-N) • Suppression of Z-phase and BN precipitation</td>
<td></td>
</tr>
<tr>
<td>0.02Nd</td>
<td>• Suppression of S segregation</td>
<td>Creep ductility</td>
</tr>
<tr>
<td>3Co</td>
<td>• Stability of martensite</td>
<td>Toughness</td>
</tr>
<tr>
<td>0.01B</td>
<td>• Suppression of fine HAZ</td>
<td>Creep strength of welded joint</td>
</tr>
</tbody>
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Hamaguchi et al. 2015
9Cr-3W-3Co-0.02Nd (P93?) welded

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

Hamaguchi et al. 2015
Materials / solutions for cycling (CF) service

Challenges:

- Early CF methods developed for aerospace Ni alloys with design life $\sim 10^4$ h $\rightarrow$ 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 $\rightarrow$ 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

- 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

![Composition-based phase diagram](image)
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