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Ron Munson Associates

The Challenge of Introducing New Materials into Boiler-based Power Generation Applications

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ELECTRIC GENERATION
ISSUES, TRENDS, and PRACTICAL SOLUTIONS

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Presentation Outline

- Drivers for materials development
- Classic materials and limitations
- Approaches to enhanced materials for advanced technology such as ultra-supercritical boilers
- New materials issues and case studies

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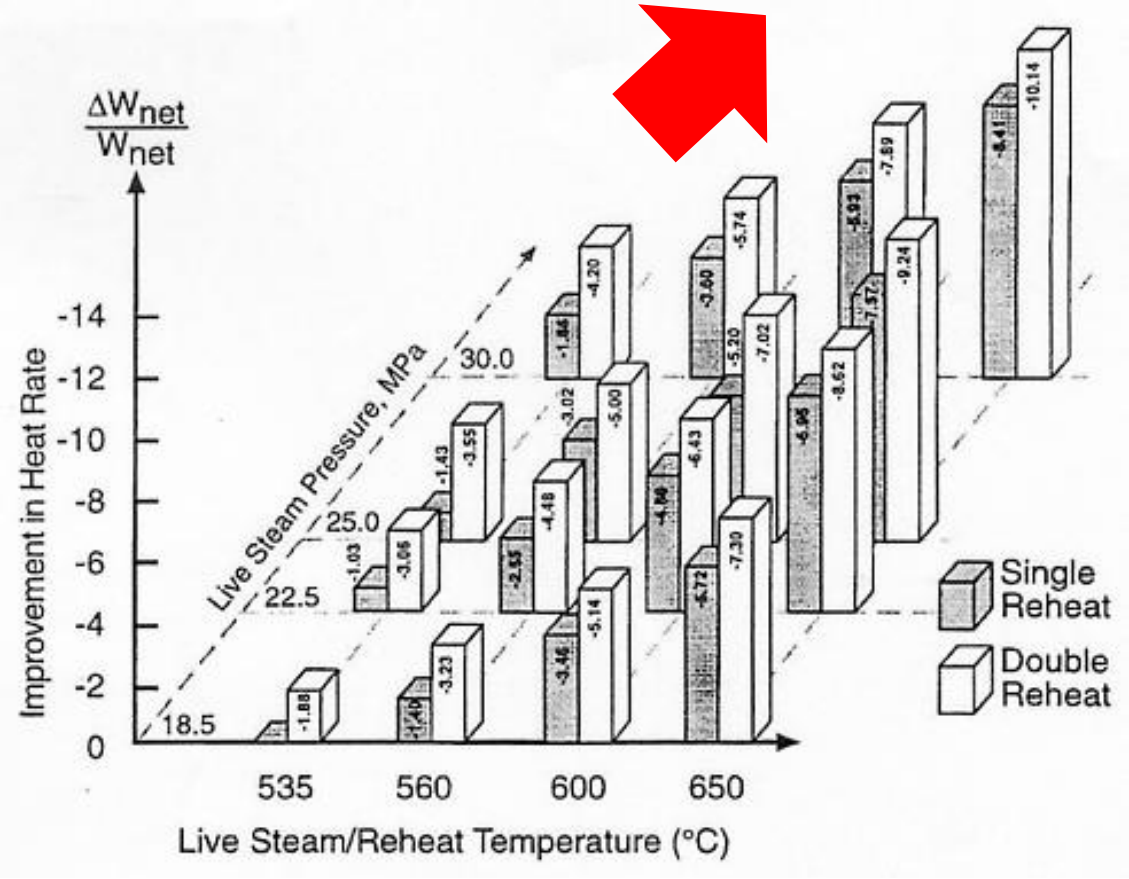
Drivers for Materials Development

Motivators

- Higher steam pressure and temperatures
- Ability to cycle run at lower loads
- Smaller footprint - less mass for pressure containment and support structure
- Environmental considerations - cleaner (hotter) burn and less fuel (efficient)
- Lower Cost - shorter ROI times for investors

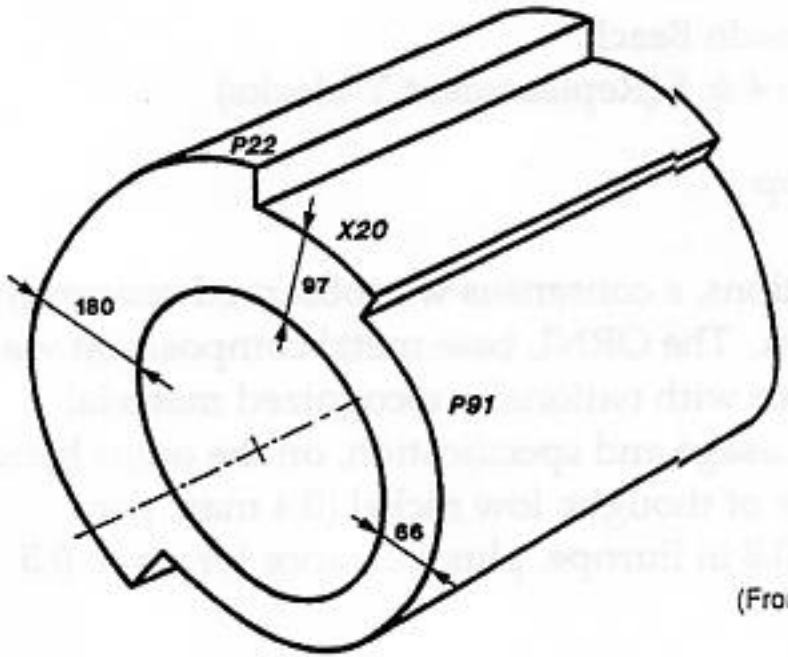
Representation of the Heat Rate Improvement by Increasing Steam Temperatures



Weight Savings by Using P91 or X20 Alloy versus T22

COMPARISON OF W/ALL THICKNESS

12CrMoV (X20) - mod. 9CrMoV (P91) - 2.25CrMo (P22)



Pressure: 300 bar
Temperature: 580°C
Pipe internal diameter: 255 mm

(From J. Hald, Technical University of Denmark)

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Drivers for Enhanced Materials

- *Creep-oxidation capability* - Higher Steam Temperatures lead to greater turbine efficiency
- *Creep*- tensile strength- Higher Steam Pressures lead to greater turbine efficiency
- *Cycling capability* - Thinner Boiler Components – Better cycling performance, less mass and support requirements
- *Environmental* - More efficiency means burn less fuel – environmental benefit
- *Reliability* – Materials with higher alloy content have more insidious/unpredictable failure mechanisms

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REMEMBER!!

Munson's Axiom - *The more sophisticated the alloy the more insidious and unpredictable the damage mechanism!*

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Steam Review 101

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Steam / Water

- Water can exist in FOUR states:
  - Solid - Ice 1 ATM Pressure- temp less 32°F
  - Liquid- @ 1 ATM pressure – 32-212°F at higher pressures it can be stable at much higher temperatures e.g. 2940 Psi (~690°F)- the co-existence temperature is the “saturation temperature”
    - At saturation some energy is used to create the phase change- Latent heat of Vaporization

Steam / Water (Cont'd)

- Vapor (steam) - Can be modeled as "an ideal gas"- any temp/pressure beyond the saturation temp. As the temp/pressure increase the latent heat of vaporization decreases
- Supercritical Fluid (plasma) - What is this??

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A Few Key Points

- You cannot pump steam, only water
- You cannot increase the pressure of steam in a boiler, only add heat
- Turbines do not like water
- One cubic foot of water becomes 1760 ft^3 of steam
- Superheated steam acts as an ideal gas
  - $P_1 * V_1 = P_2 * V_2$
  - Thus 1 ft^3 steam at 100 Atm. equals 100 ft^3 of steam at 1 Atm.

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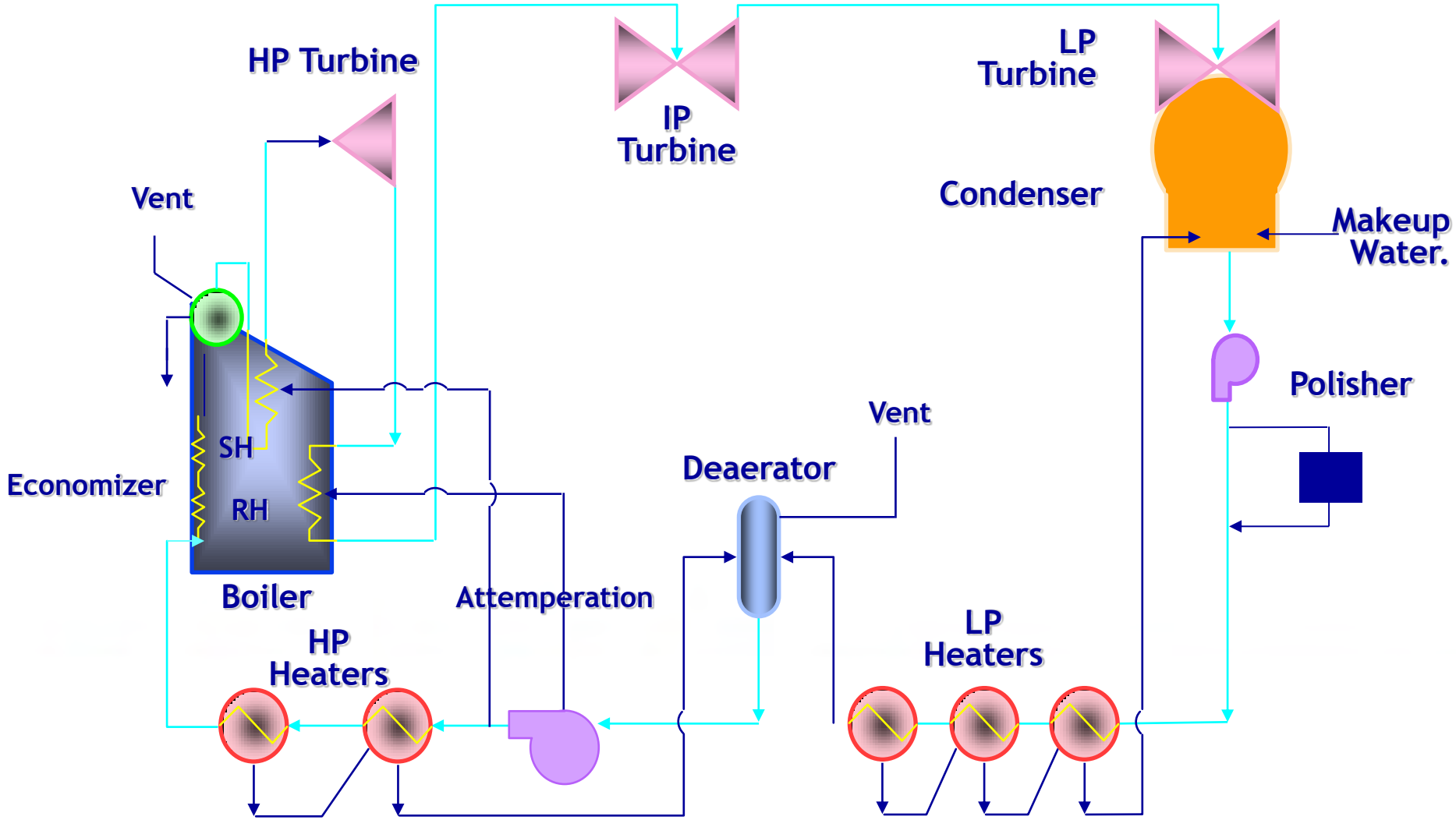
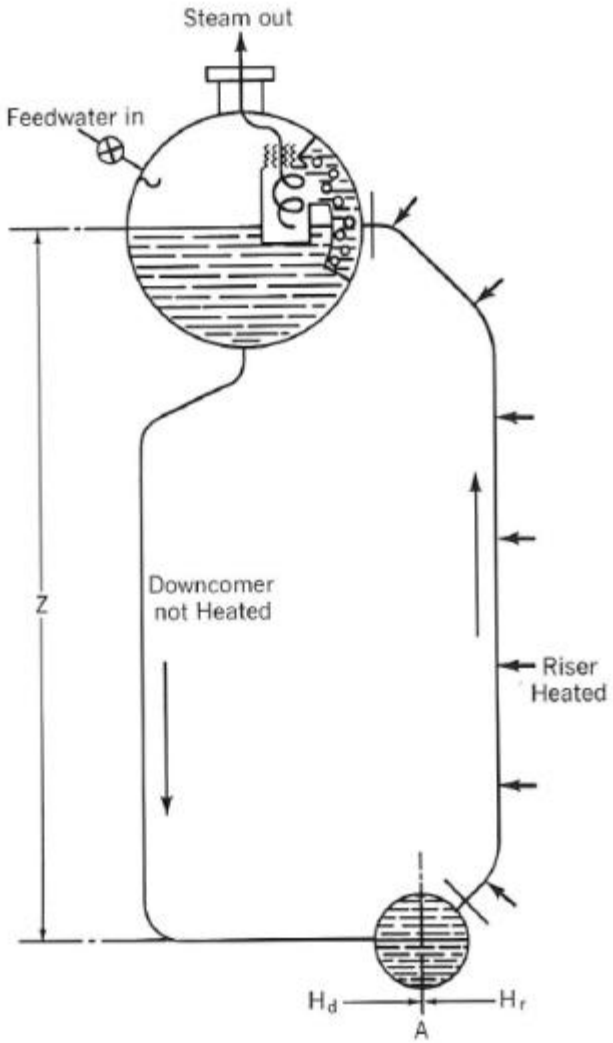
Typical Utility Steam Cycle



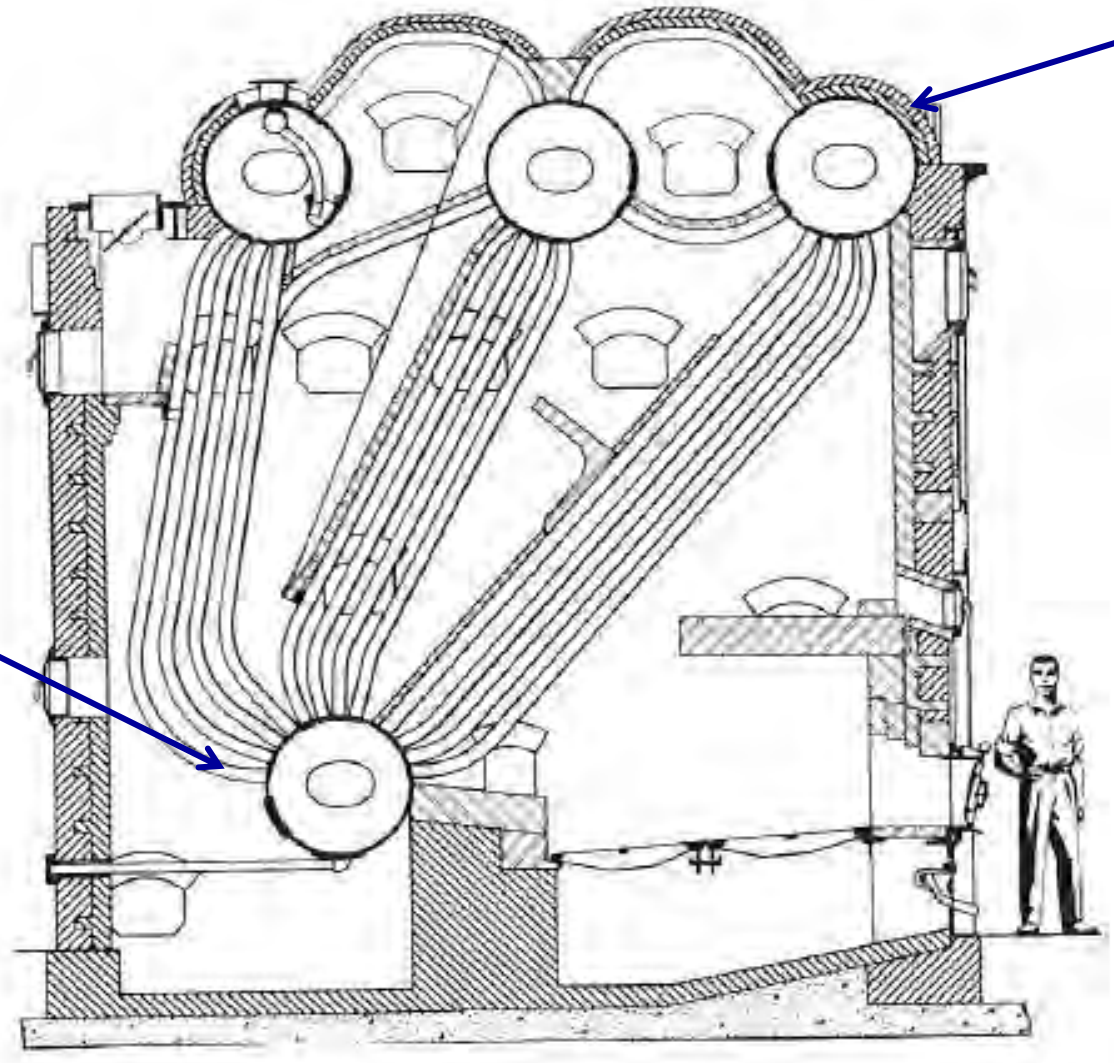
Basic Steam Generation



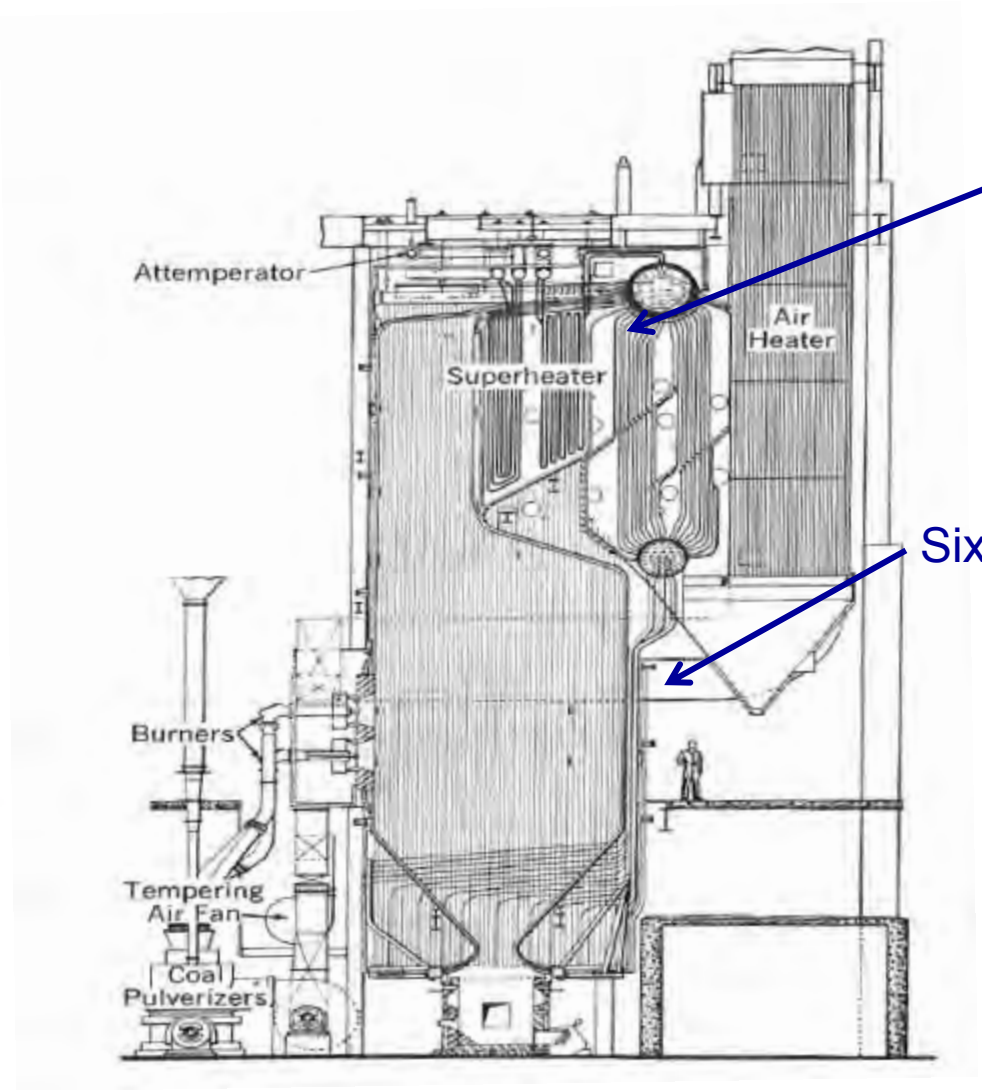
Sub-Critical Boilers

- Steam is separated from the water in a mechanical vessel
- Steam is superheated usually 700-1050°F
- Materials limitations at 1050°F
  - Oxidation limit
  - Creep limit

Very Basic Water-Tube Boiler



Slightly Larger Water-Tube Boiler



Supercritical Boiler Conditions

- As the pressure increases the boiling temperature increases and the latent heat of vaporization decreases
- A further increase in pressure and temperature leads us to a point at which the latent heat of vaporization is zero, or there is no boiling. Water directly becomes supercritical fluid. This is the Critical Pressure and the Critical Temperature. For water this occurs at 705°F and 3242.8 psi
- Thus if you can maintain operating conditions above these you do not ever have to worry about water/steam separation

Supercritical Boilers

- Generally operates at 3680 psi @ 1050-1100^{0}F
- Older technology
- Upper limit on pressure and temperature by the available materials for high temperature components (finishing superheaters and reheaters)
- Design not suitable for reduced load operation

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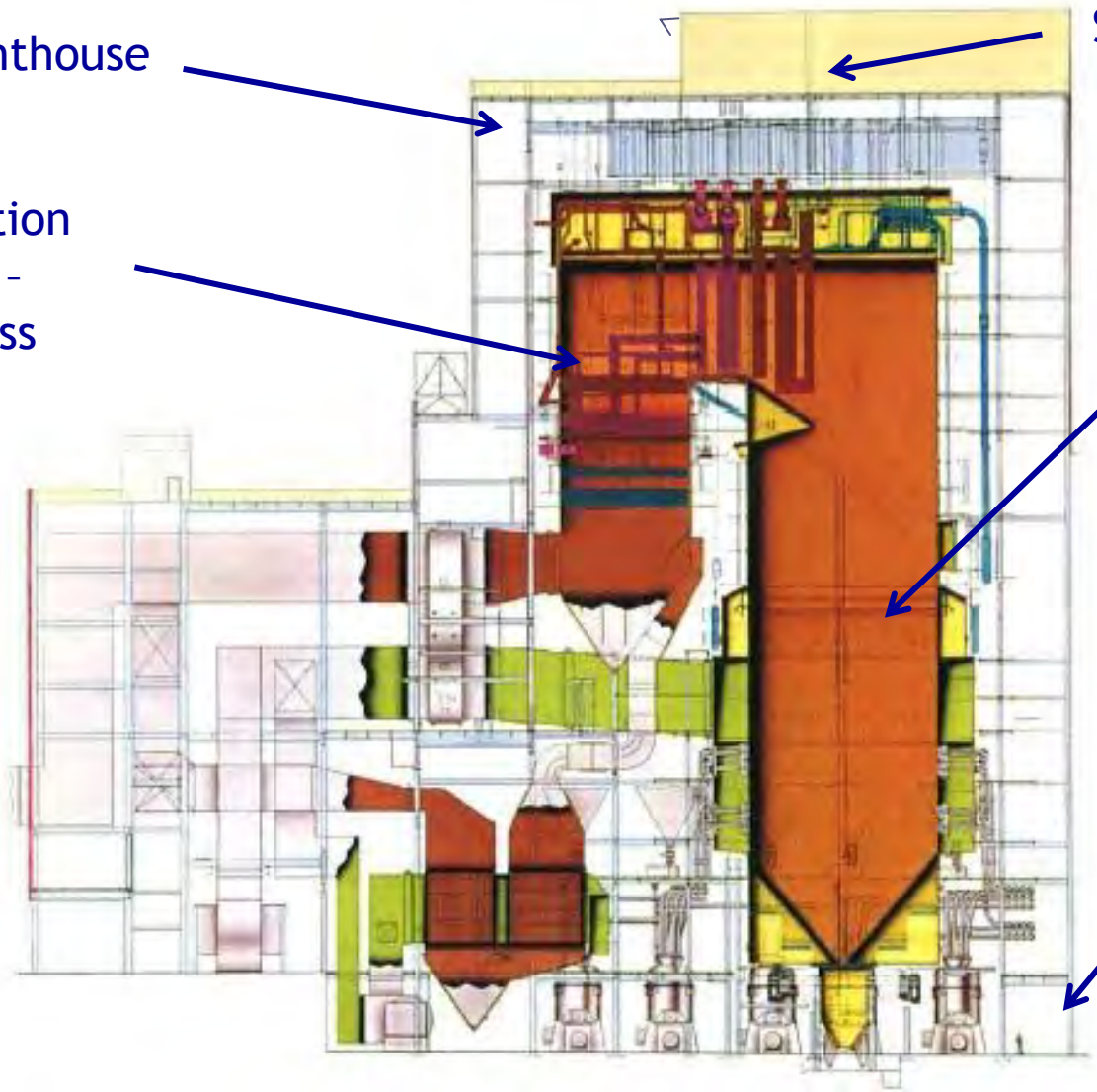
Typical Supercritical Boiler



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Ultra Supercritical Boilers (USC)

- Pressures at or above 4500 psi
- Temperatures of 1100°F - 1175°F
- Very good heat rate and thermal efficiency
- Upper limit on pressure and temperature by the available materials for high temperature components (finishing superheaters and reheaters)
- Design not suitable for reduced load operation
- Fuel is Pulverized Coal - Very prevalent in Europe and the Pacific where Coal is much cheaper and more available than natural gas - Several in the US

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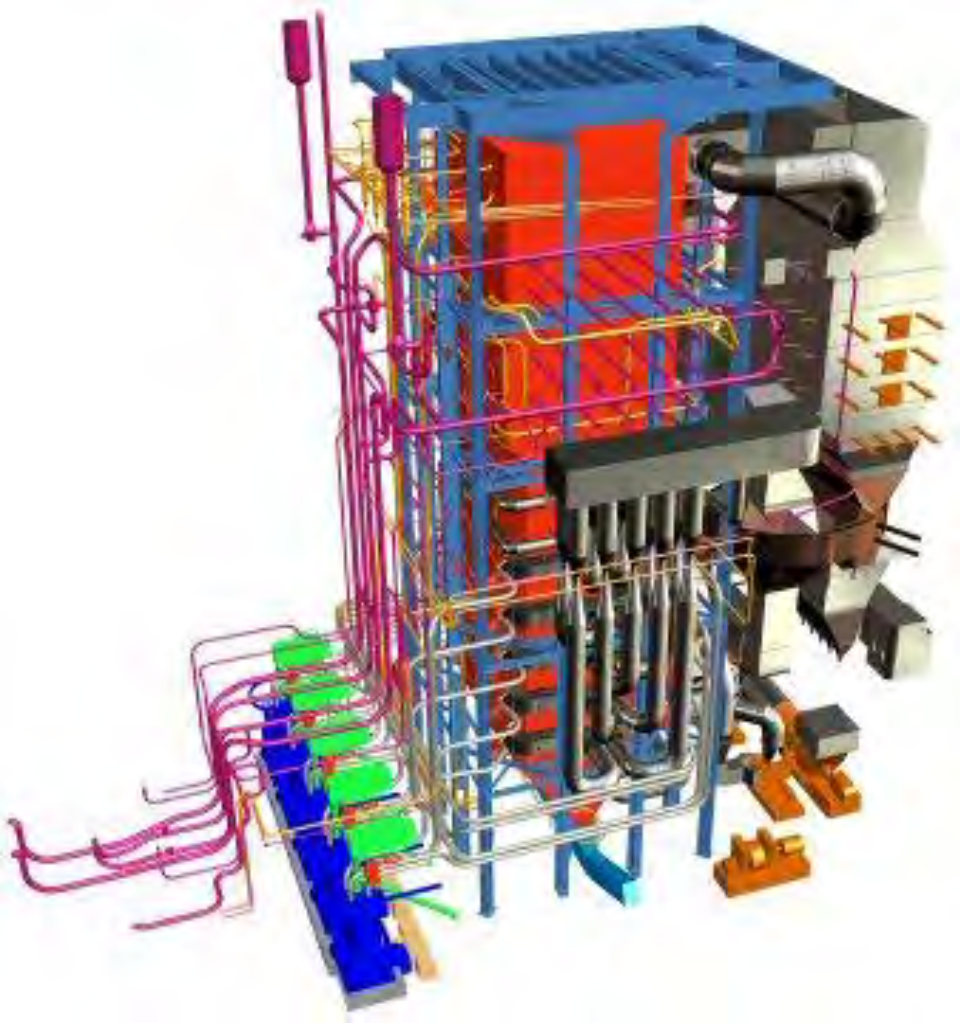
Typical Ultra Supercritical Boiler



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Issues with Ultra Supercritical Boilers

It is all about the Materials!!!

or Lack thereof

Classic Materials and Limitations

General Classes of Steels (Classic)

- Mild Carbon Steels - SA 178 Class A
- Medium Content Carbon Steels -
  SA 178 Class C, SA 210 C, SA 192
- Low Alloy Steels -
  CrMo - SA 213 Grades P2-P22, CMO SA 209 T1a
- Austenitic Stainless Steels -
  SA 213 TP 316, 347 etc.

Carbon Steels

- Little or No Creep Resistance above 1050°F
- Poor Oxidation Resistance above 1050°F
- Not Thermodynamically Stable (graphitization, spheroidization) above 700°F
- Poor Choice for high temperature service - even in waterwall applications
- Excellent for fabrication and welding

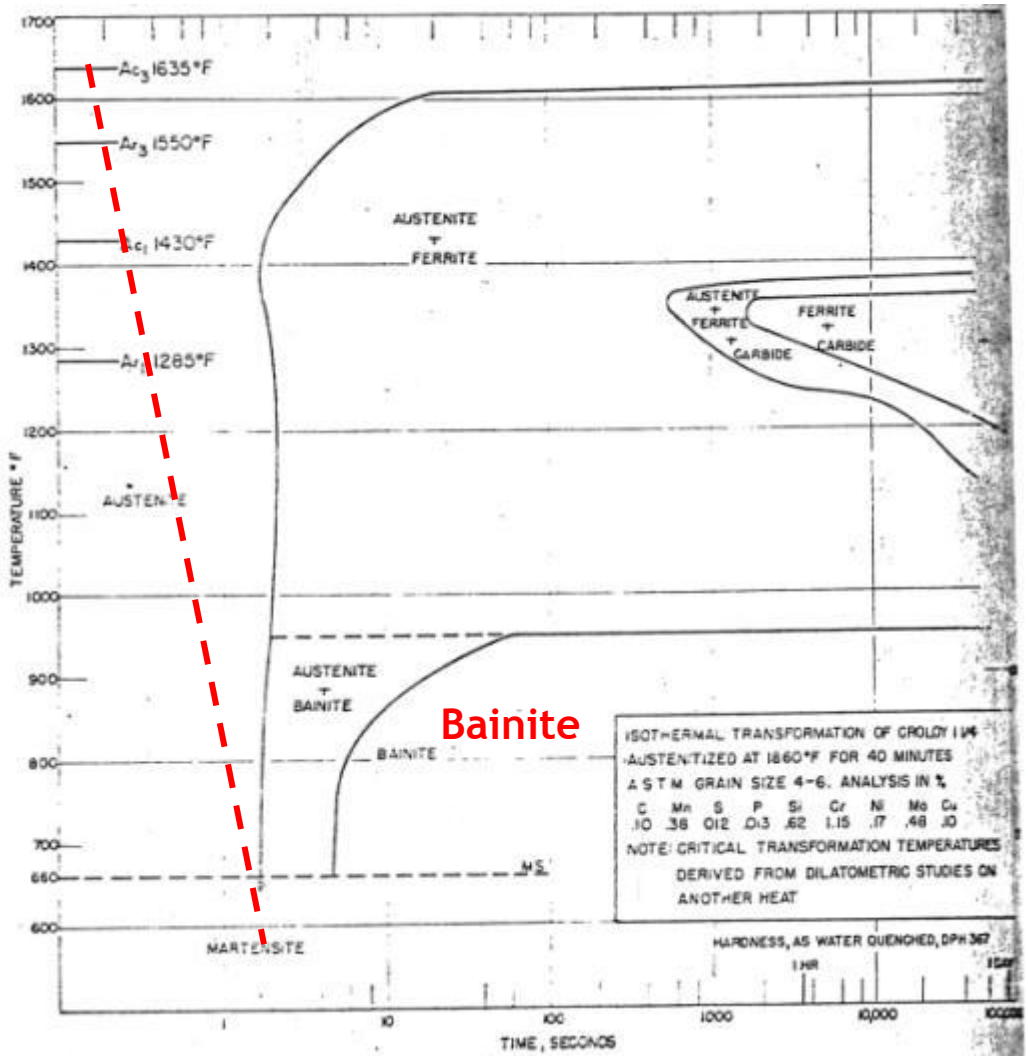
Low Alloy Steels

- Alloyed with Chromium, Molybdenum, Vanadium, Nickel, Tungsten, etc.
- Tolerable creep resistance below 1050°F; no margin for abuse
- Poor oxidation resistance above 1050°F; tracks Chromium content
- Strength depends on the transformation hardening to Bainite or Martensite; some creep resistance benefit of solid solution strengthening

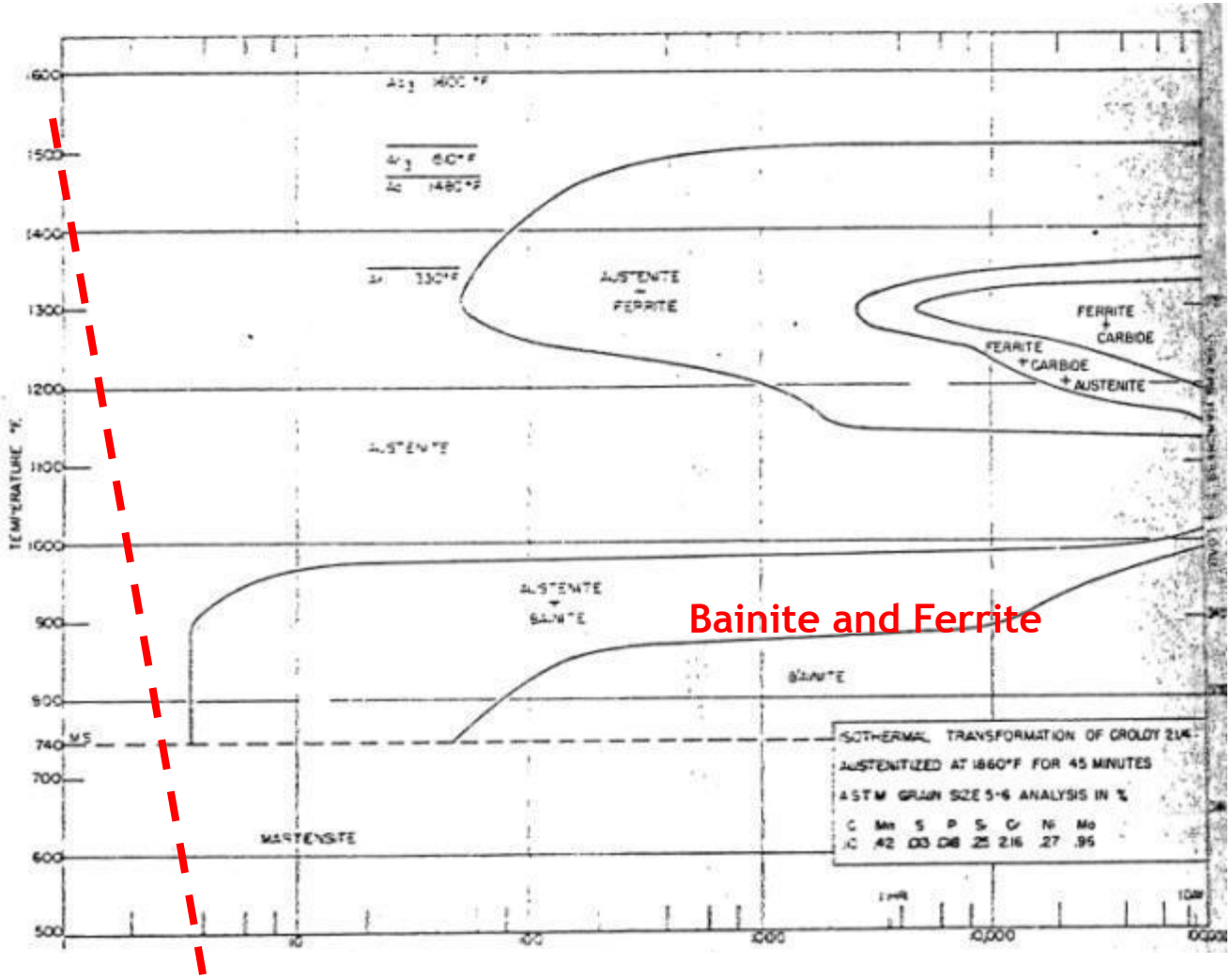
Low Alloy Steels (Cont'd)

- Bainite / Ferrite is the "normal" structure that develops by conventional thermal processing, good strength and toughness (creep resistance poor above 1050°F)
  - Will degrade over time to a ferrite/carbide mixture
- Forgiving in welding in that as-welded structure is a martensite or bainite that can be directly tempered
- Can be used in waterwall panels in lower part of furnace in supercritical boilers
- Can be used in low temperature superheater positions

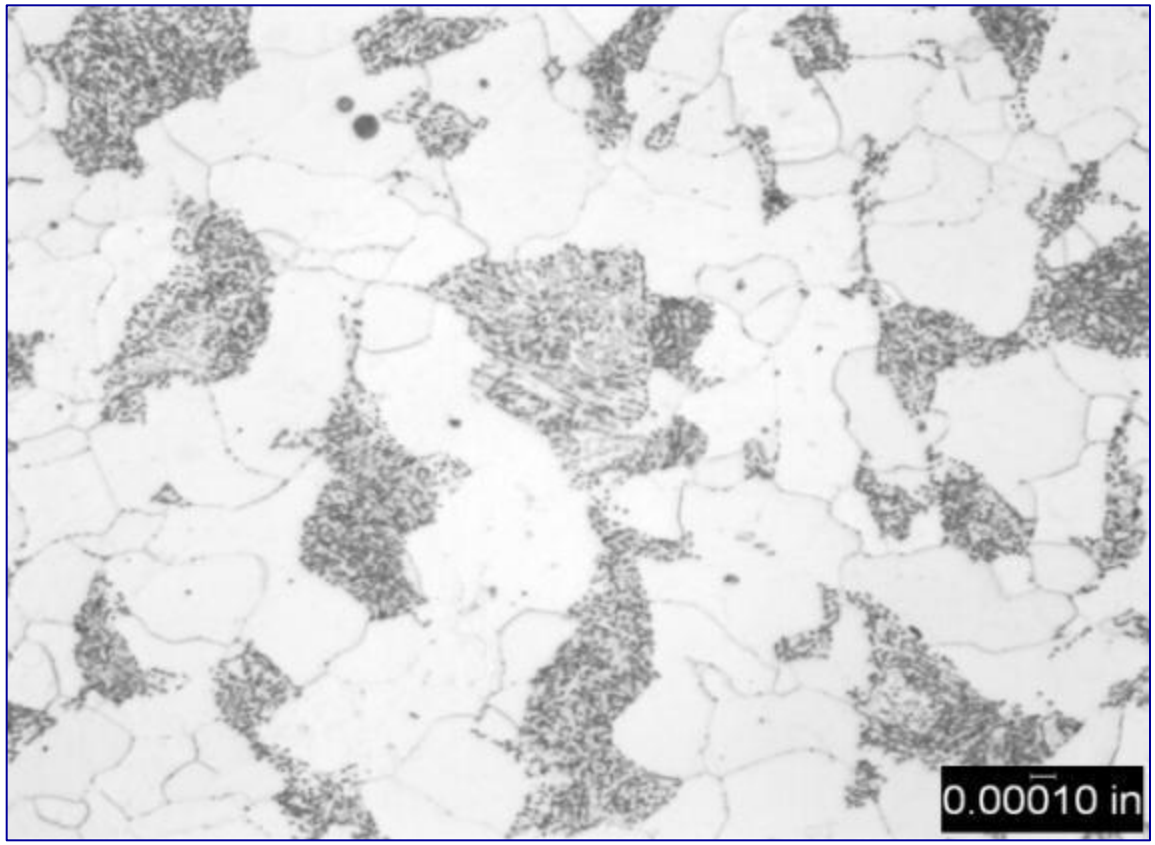
TTT Curve for SA 213 Grade T11



TTT Curve for SA 213 Grade T22



SA 213 Grade T11 Steel Microstructure Moderate Aging – Ferrite / Bainite



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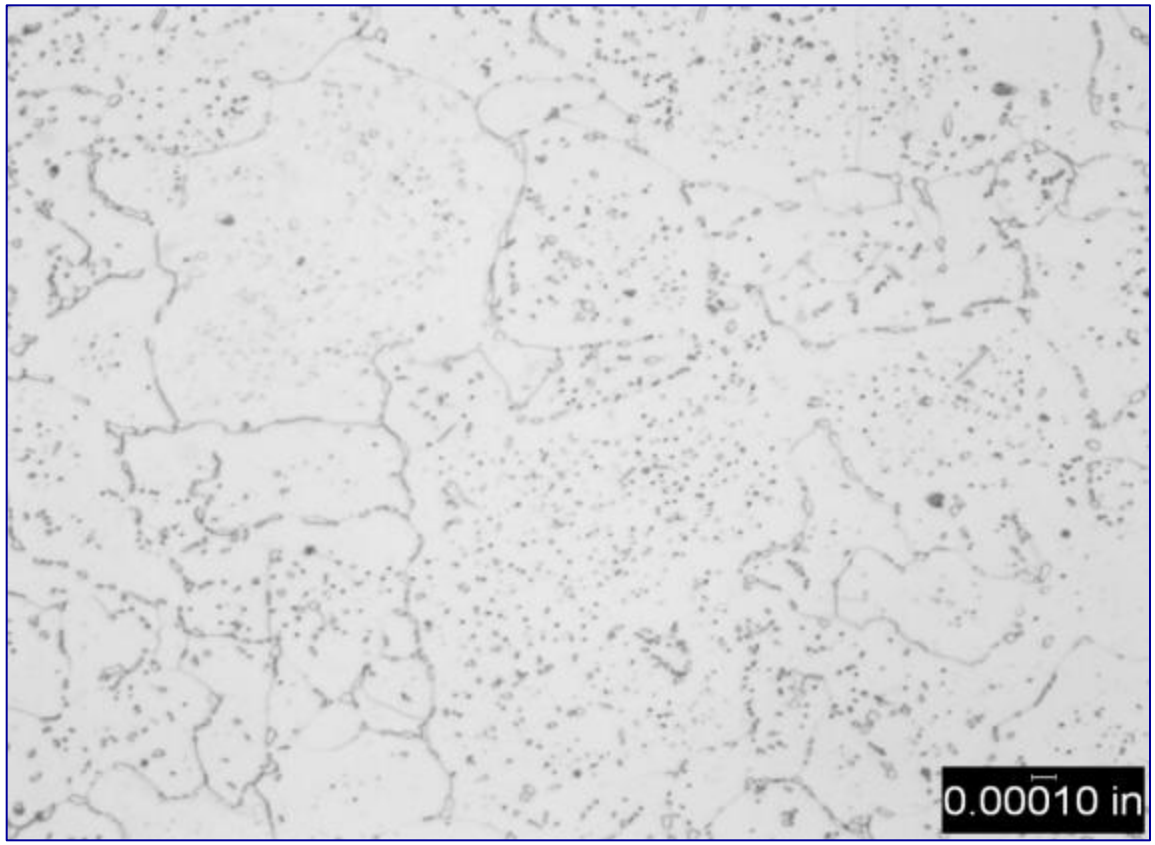
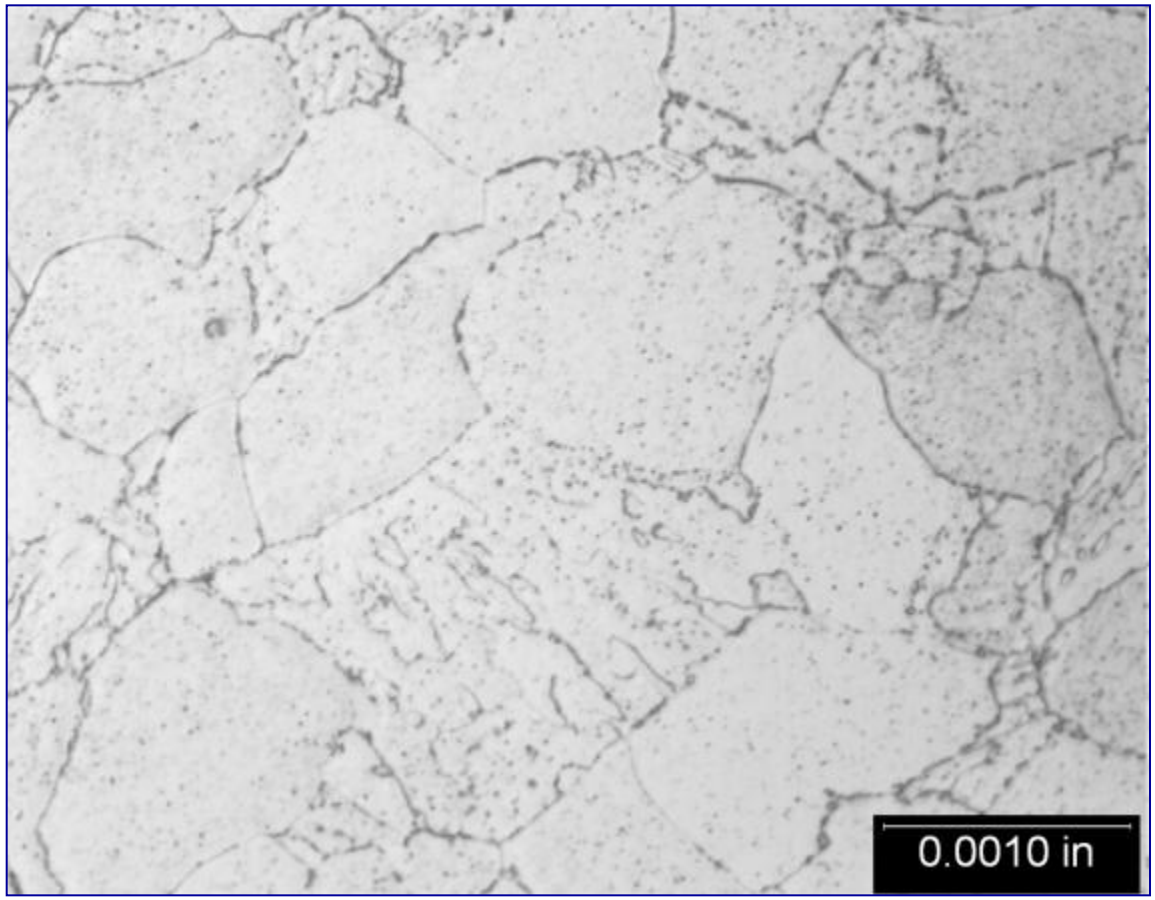
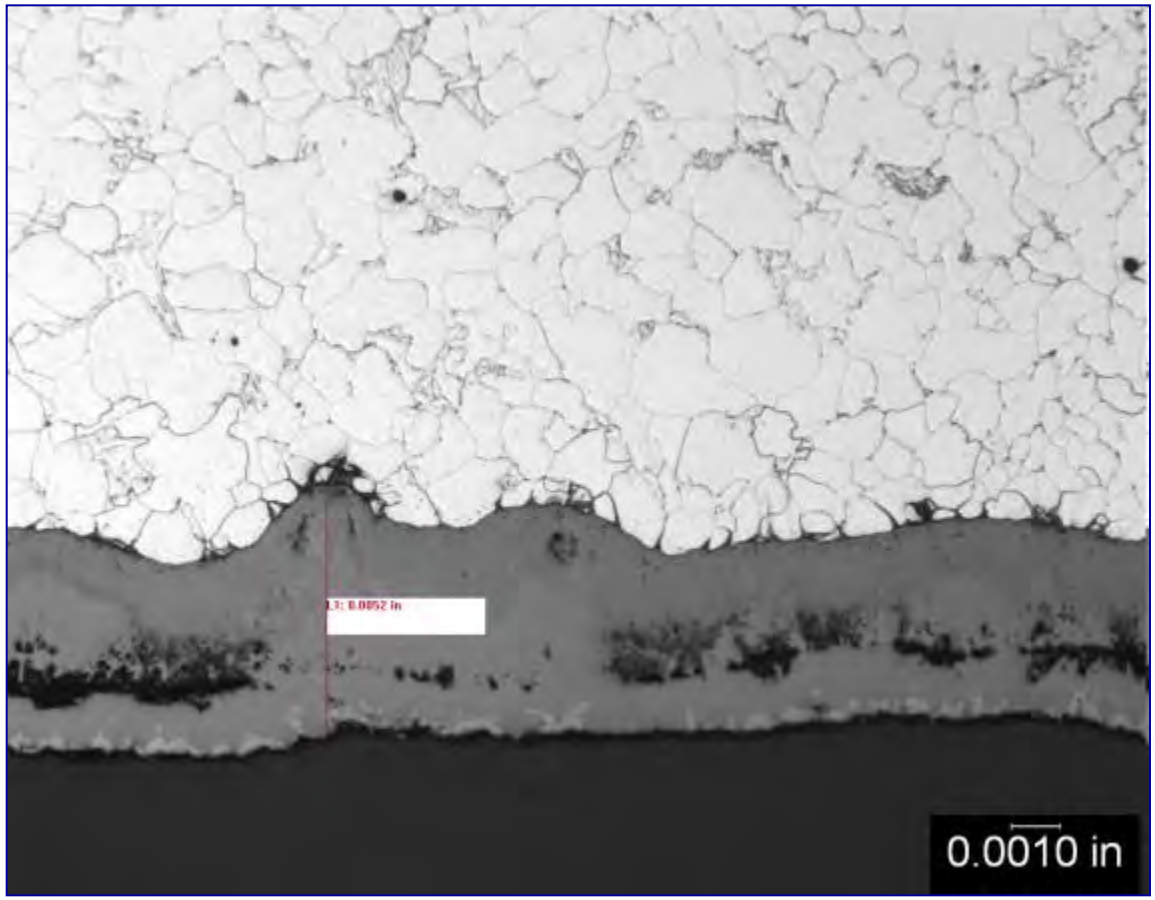
SA 213 Grade T11 Steel Microstructure Significant Aging



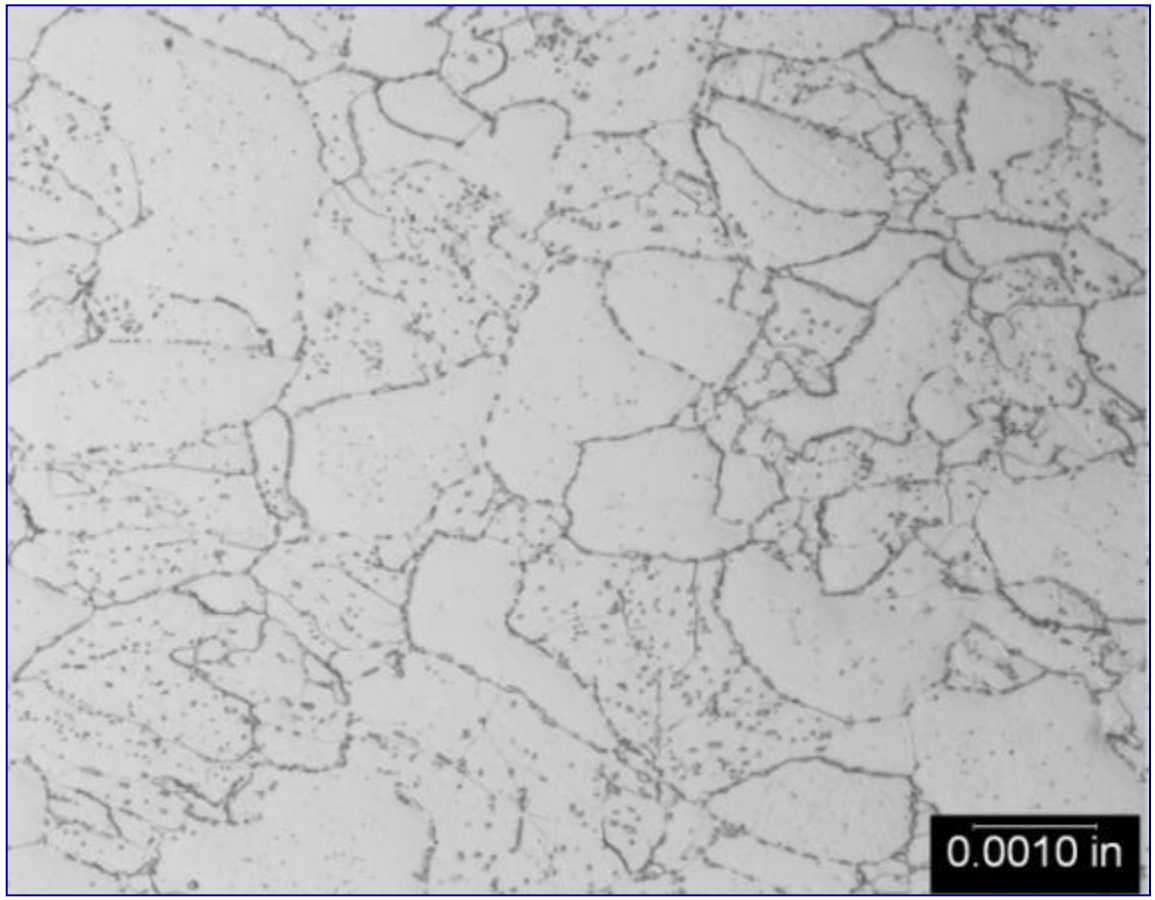
SA 213 T22 Microstructure 8000 Hours at 1050ºF (Ferrite with Carbide)



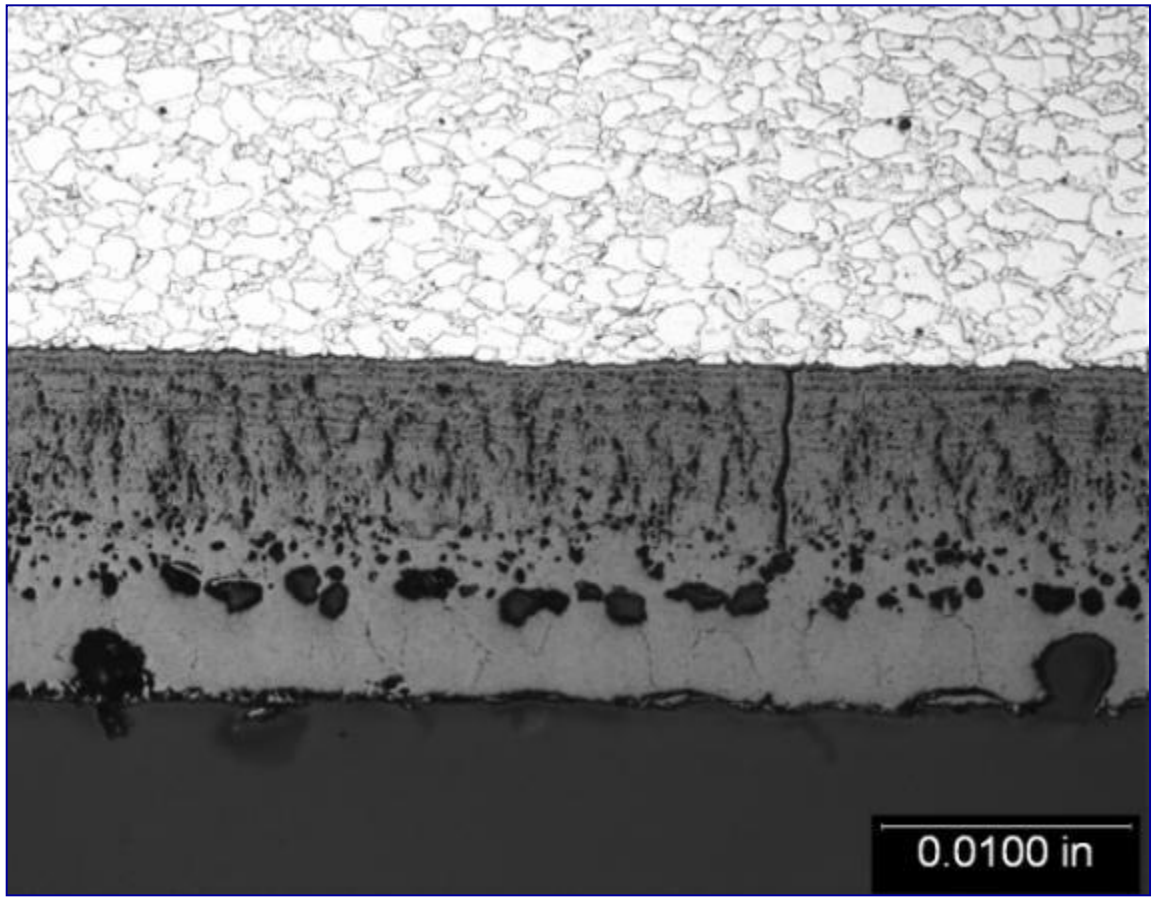
SA 213 T22 Oxide Growth 8000 Hours at 1050ºF



SA 213 T22 Microstructure 8000 Hours at 1130ºF



SA 213 T22 Oxide Growth 8000 Hours at 1130ºF



Summary on Low Alloy Steels

- Well used and understood
- Reliable over the years
- Forgiving in processing, fabrication, repair
- Inadequate above 1050°F

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Approaches to Enhanced Materials for Advanced Technology Such as Ultra-Supercritical Boilers

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Criteria for Alloy Deployment for USC

- Tolerable creep resistance above 1050°F
- Oxidation resistance above 1050°F
- Good tensile and rupture strength at all temperatures
- Good toughness (hot and cold)
- Workability for processing
- Good weldability
- Ferrous based
- Long-term metallurgical stability

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Solution Path for Advanced Boiler Materials

- Enhance what you have already
  - Low alloy with new or different elements
  - Adjust interstitials
- Use Stainless Steels (with modifications)
  - Ferritic/Martensitic
  - Austenitics
  - Duplex
- Nickel Based alloys

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“New” Materials Issues and Case Studies

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Next Generation Alloys

- Ferritic / Martensitic stainless steels (nominally 12% chromium and above)
- Austenitic stainless steels SA 213 TP 316, 347 etc.
- Super Ferritics-Low alloys (**C**reep **S**trength **E**nhanced **F**erritics) (**CSEF**) SA 213 grade T/P91/ T23/T24
- Nickel based alloys

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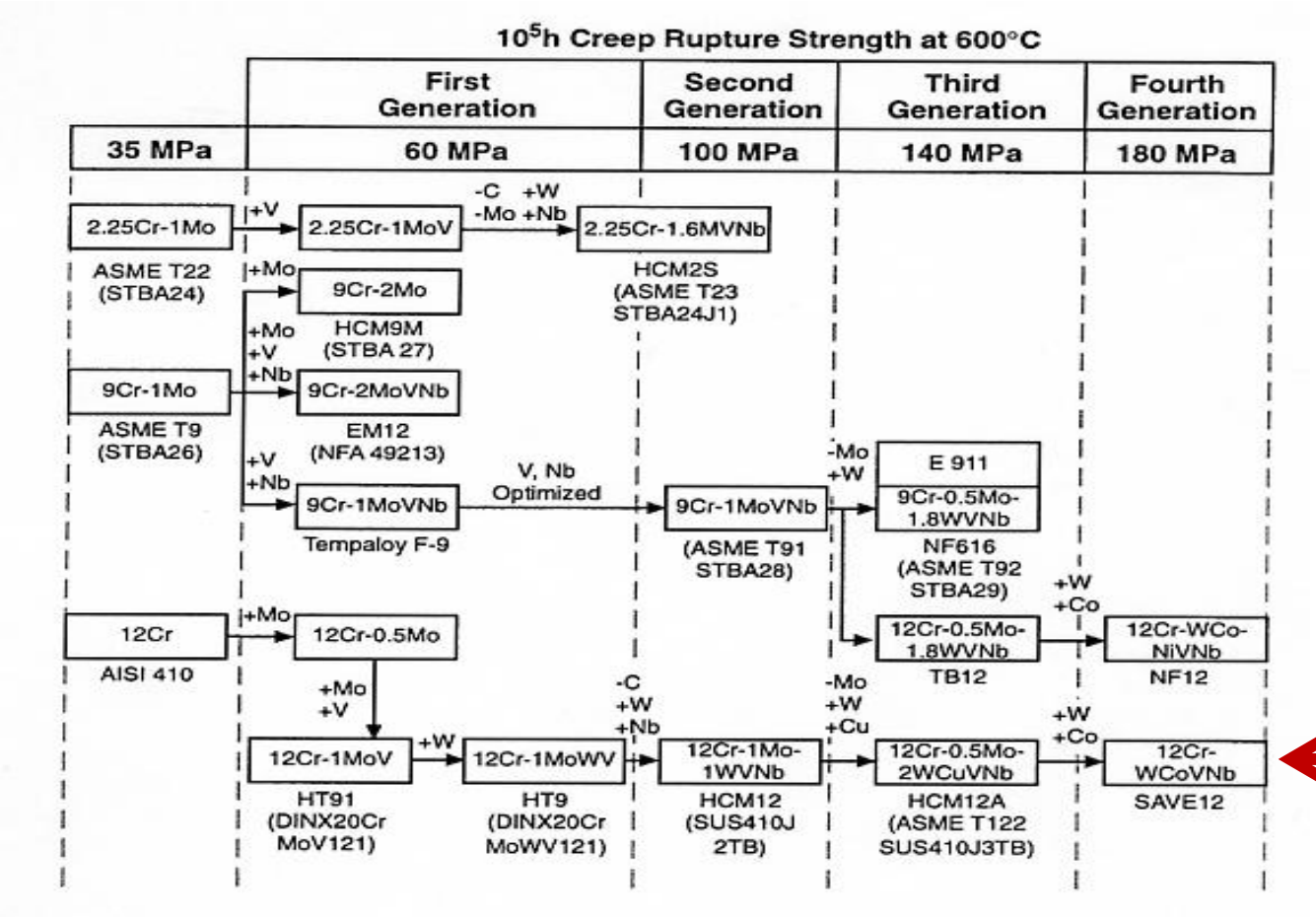
Ferritic / Martensitic Stainless Steels

- High chromium (>11%) allows good oxidation resistance
- Very difficult to weld - requires PWHT at 1200°F or above
- Room temperature impact strength is very poor - you cannot bend it easily
- Creep strength roughly equivalent to low alloy materials above 1050°F - poor cost benefit

Evolution of Ferritic / Martensitic Steels



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Austenitic Stainless Steels

- Good oxidation resistance to 1100°F
- Good creep resistance to 1200°F
- Strength set by cold or warm working - no transformation hardening
- Very weldable no PWHT
- Easy to bend and form
- Lots of experience in SH/RH applications in conventional boilers both sub and supercritical

Austenitic Stainless Steels

- Mostly based upon the AISI 304 alloy (18% Cr - 8% Ni)
- Variations in carbide stabilizer additives (321, 347)
- Variations in carbon weight % (L-grades)

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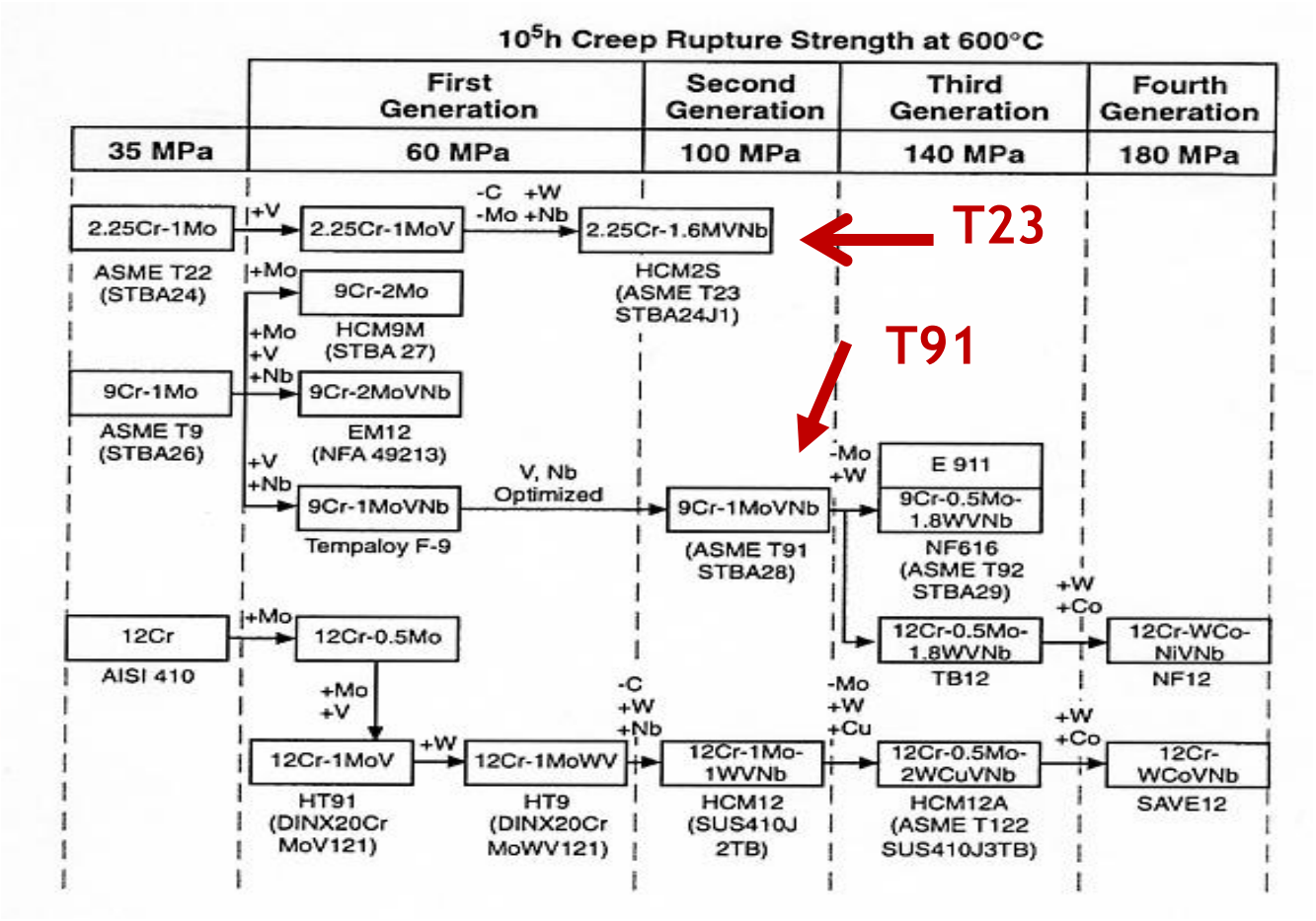
CSEF / Super Ferritic Steels

- Based upon low alloy steels
- Chromium is primary alloying element, oxidation resistance approaching the austenitic alloys
- Strength at all temperatures depends on Martensitic or Banitic transformation caused by heat treatment plus precipitation of secondary carbides
  - Martensite/Bainite can temper and lose strength with age
  - Carbides precipitate with age - restoring some strength
- Includes P/T91/P/T92/, and T23/T24, and a family of derivatives

Evolution of Super Ferritics (CSEF)



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Benefits of Higher Alloy Content

- More Carbon
  - Better creep strength
  - More hardness capability, tensile strength can be developed by heat treatment
  - Can form multiple crystal structures with increasing content and thermal treatment
- More alloy - Chromium (<5%)
  - Better oxidation resistance
  - Better resistance to in-service degradation, graphitization / spheroidization of pearlite
  - RESISTANCE TO Flow Accelerated Corrosion (FAC) less than 0.10wt/% required

Benefits of Higher Alloy Content (Cont'd)

- More alloy - Chromium (>5%)
  - Better oxidation resistance
  - Will form Martensite on air cooling- very high strength
- More alloy - Molybdenum
  - Better creep resistance
  - Better resistance to in-service degradation, stabilization of Bainite
- More Nickel >5%
  - Steel will remain austenitic on cooling (non-magnetic)
  - Good toughness at low temperatures

Pitfalls of Higher Alloy Content

- More Carbon
  - Susceptible to hydrogen embrittlement in service and in welding
  - More carbon - poorer weldability weld HAZ can be embrittled by welding heat (generally 0.25% Carbon equivalent is critical point)
- More alloy - Chromium (<5%)
  - Poor weldability
  - Poor cold formability for tubing
  - Will form carbides in service - grain boundary weakened

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Pitfalls of Higher Alloy Content (Cont'd)

- More alloy - Chromium (>5%)
  - Will magnetize on storage and during MT inspection
  - Will form Martensite on air cooling from welding – poor toughness
- More alloy - Molybdenum
  - Will form Carbides in service - grain boundary weakened
  - Better resistance to in-service degradation, stabilization of Bainite
- More Nickel >5%
  - Susceptible to stress corrosion cracking
  - Not possible to strengthen by heat treatment only mechanical working

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Other Alloy Additions

- Nitrogen - added at very low percentages as an interstitial hardening agent - can react with other alloying elements to form detrimental phases
- Boron - added at very low percentages as an interstitial hardening
- Aluminum / silicon - strong oxide formers - determines adherence of oxide deposits - affects greatly by steel making practice
- Tungsten - european substitute for Molybdenum
- Titanium – carbide former good or bad
- Niobium- carbide former

Nickel Based Alloys

- Inconel 740 tubing has been used in one prototype plant
  - Expensive
  - B&PV Code Recognition
  - Joining tubes to headers: tube to tube welds - dissimilar metal welds
  - Lack of History on performance - especially long-term

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Issues with 12% Chromium Steels- Martensitic / Ferritic Stainless Steels

- Fabrication requires extensive post weld heat treatment of all welds (greater than 1200°F)- impractical for field erection
- Very little operational experience in boiler applications - used extensively in refinery and chemical plants

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Issues with Austenitic Stainless Steels

- Microstructures produced at manufacturing/fabrication are meta-stable; they will alter over time to detrimental constituents
- These steels will "sensitize" during service leading to the occurrence of stress corrosion cracking (SCC) during layup periods
- At high operating temperature (>1125°F) these alloys will form a steam-side scale that will exfoliate causing fouling / plugging of the system
  - Tube ruptures caused by starvation
  - Solid particle erosion of valves and turbine blades
- Microbiological Influenced Corrosion (MIC)

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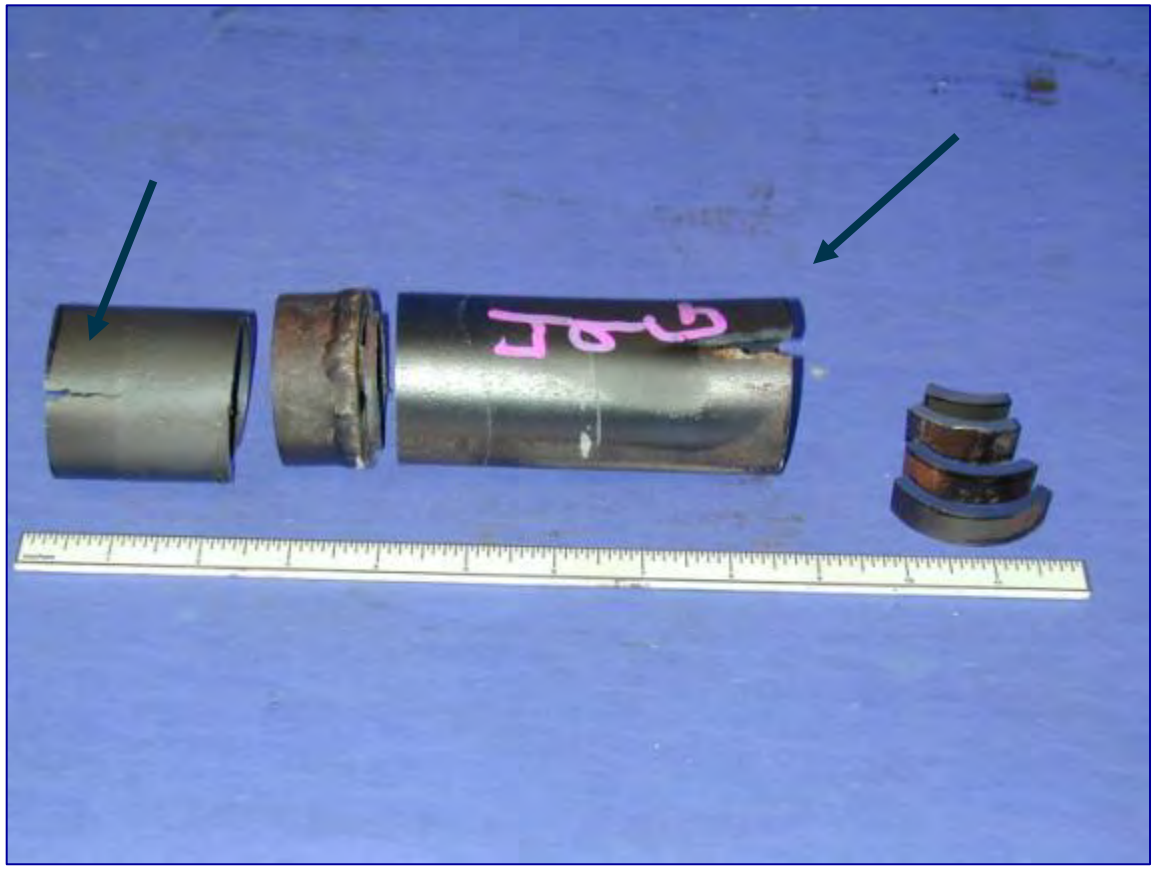
Case Study - Metallurgical Alteration in Service

- Philadelphia Electric Eddystone - designed to operate at 1300°F and 4500 psi - had 316 SS for main steam piping
  - Piping cracked due to formation of SIGMA phase (TCP) after 40,000 hours of operation
  - SIGMA evolved from long term operation at high temperatures

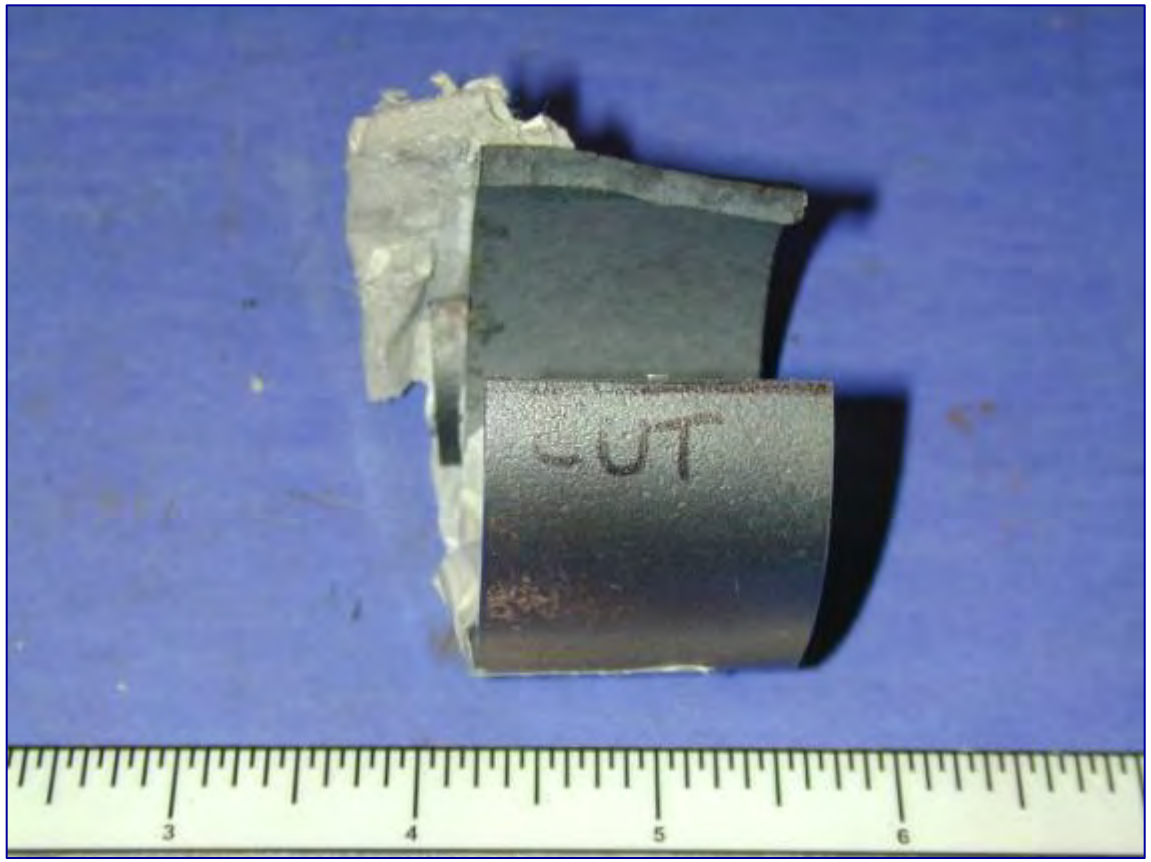
Case Study - SCC of Superheater Tubing

- Southwestern Utility - had extensive cracking of 347 stainless steel U-Bends in high temperature superheater caused by SCC
  - Tubing was sensitized as it operated with a metal temperature of 1050°F (sensitization range of 800°F to 1200°F)
  - Chloride in western coal fly ash led to cracking

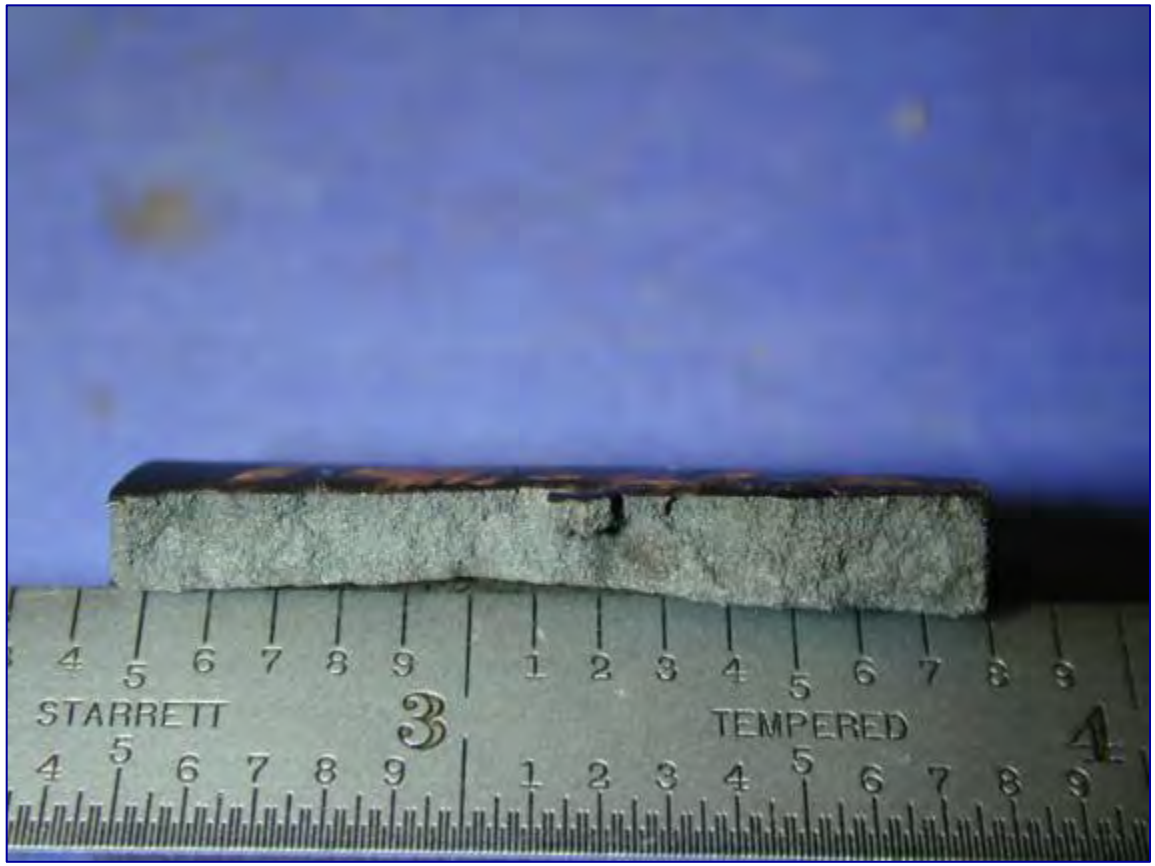
Tube Samples as Received for Analysis



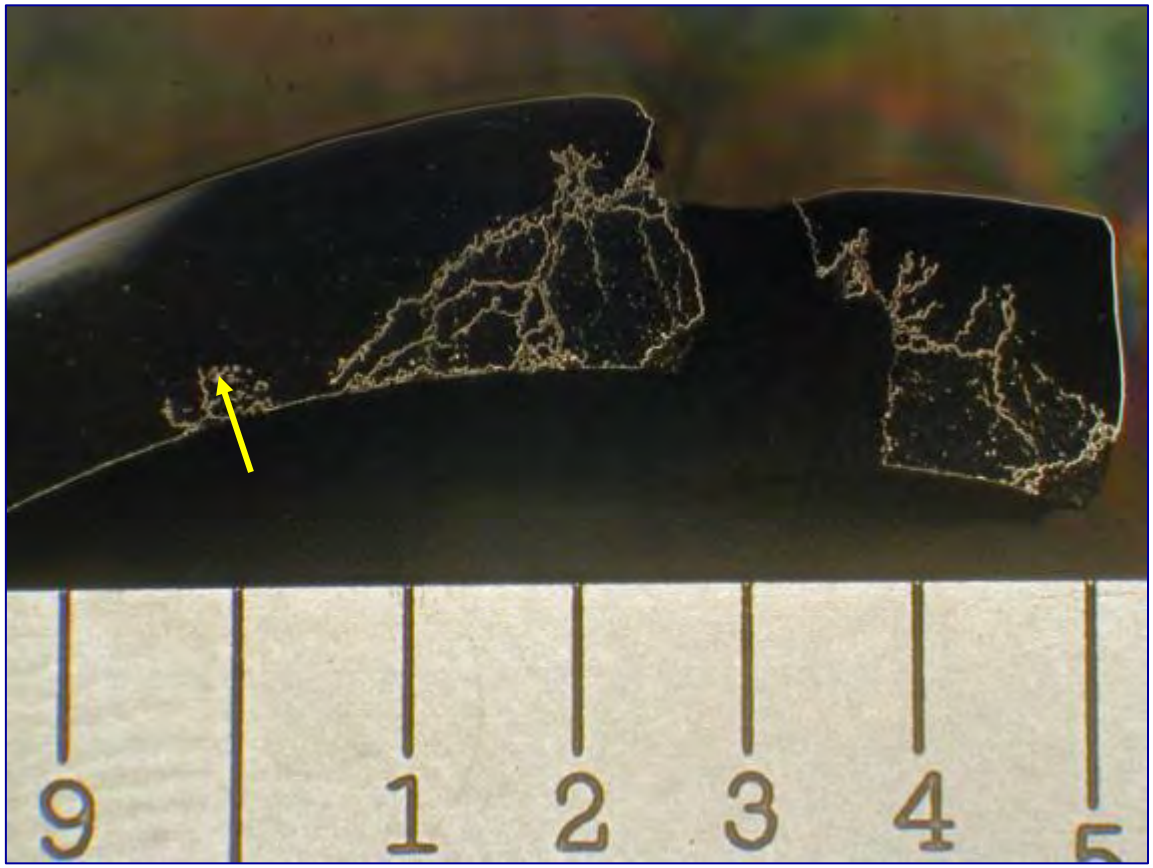
Close-Up of Tube Rupture



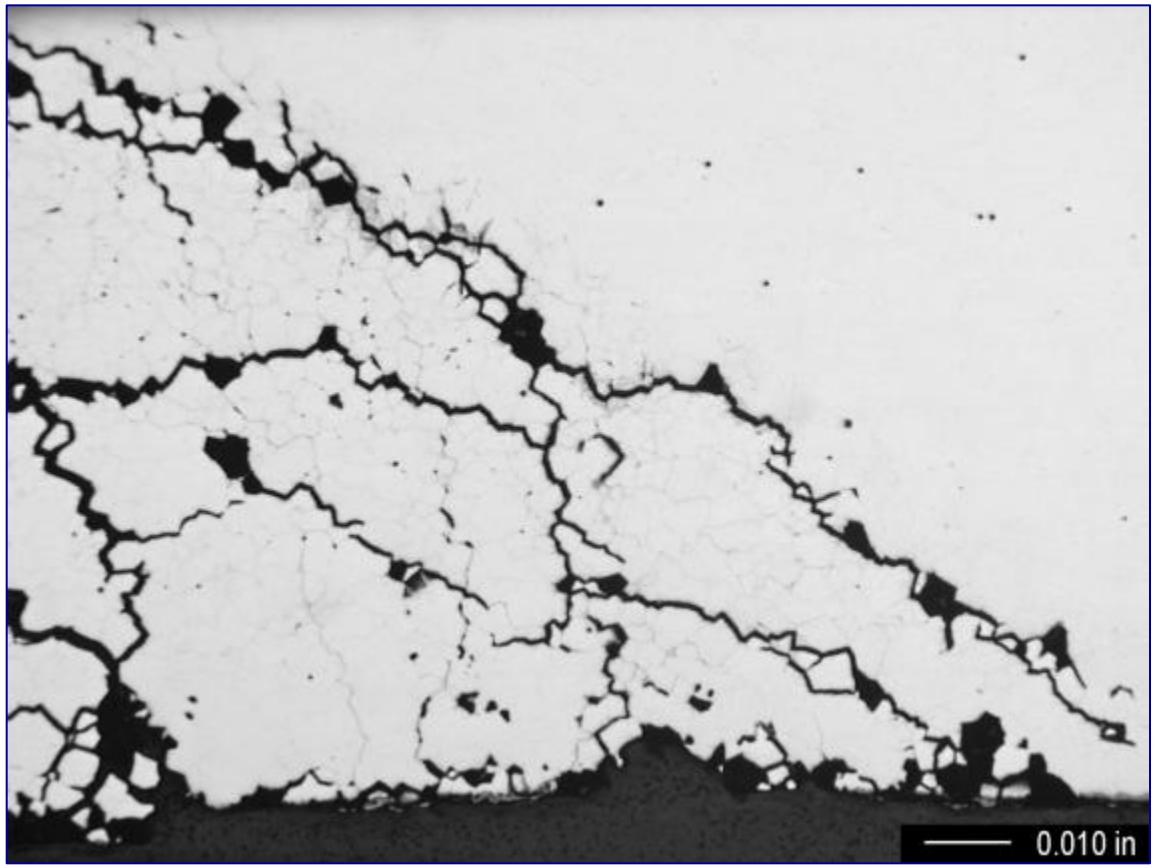
Close-Up of Fracture



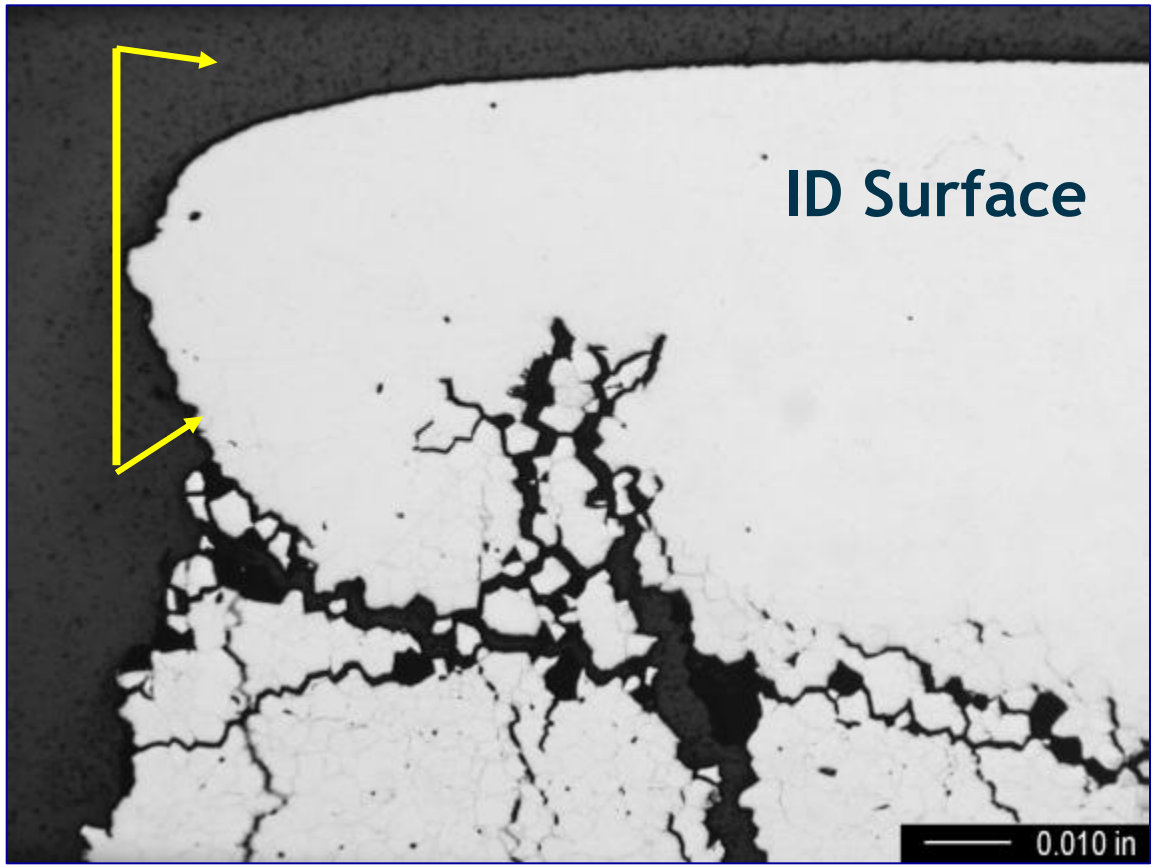
Metallographic Section



Intergranular Cracking with Grains Falling Out



Tensile Rupture Tip of Fracture



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Case Study-Duplex Stainless Steels In an FGD Absorber

- Units fabricated from a duplex stainless steel (austenitic and ferritic) -$$$$
- Suspected Microbiological Influenced Corrosion (MIC)
- Several units have had unexpected corrosion pitting to perforation after less than one year of service

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Case Study- Severe Exfoliation of High Temperature SH/RH Tubing

- Several new USC plants have had tube pluggage caused by the accumulation of steam-side scale deposits
  - Global issue (Australia, Taiwan, US)
  - Exfoliated deposit plugs U-bends leading to steam flow disruption and starvation of upstream tubing
  - Exfoliated deposits lead to solid particle erosion of main steam valve seats and HP/IP turbine blades/nozzles
  - Frequent outages to section tubes and remove deposits

Stress Rupture Failure

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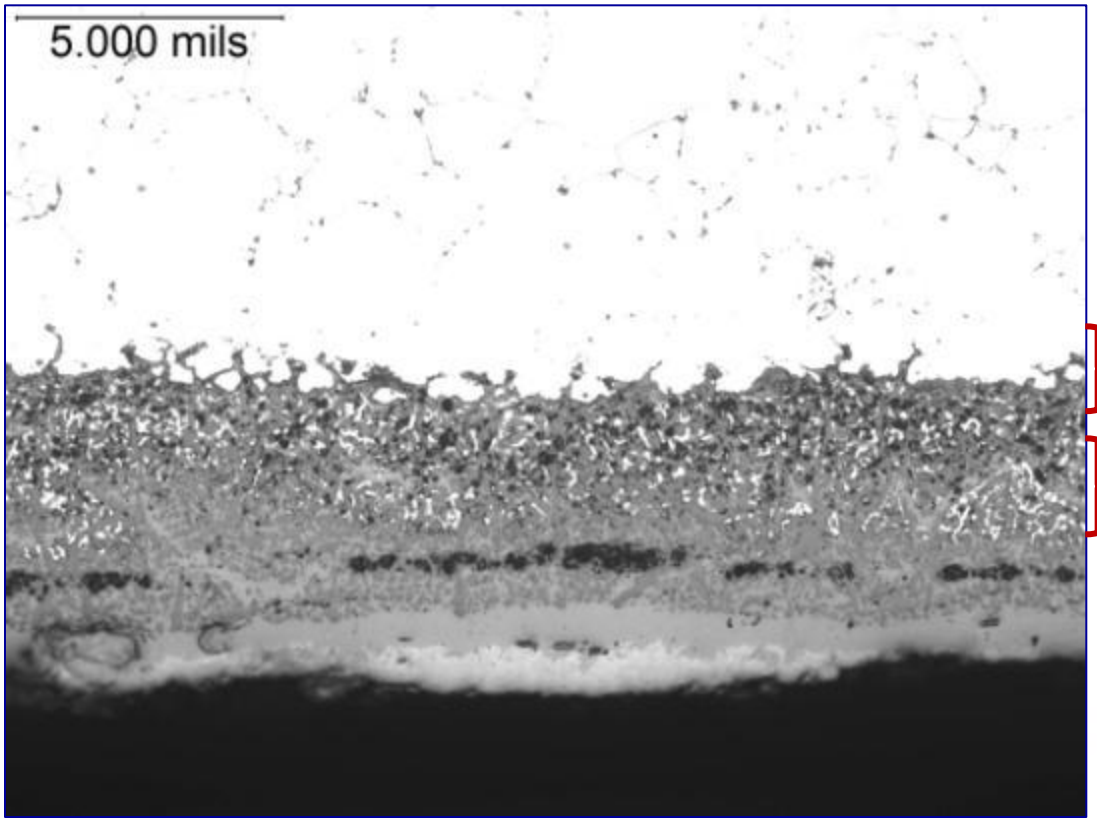
Typical Internal Scale on SS SH Tube



Cr Rich “bond”

Spinel “barrier layer”

Loose Magneite “exfoliation”

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“Solutions” to Exfoliation Issue

- Using fine grained stainless steels
- Shot-peening steam-side surfaces
- Speculated issue will decrease with tubing age as tubes “season”

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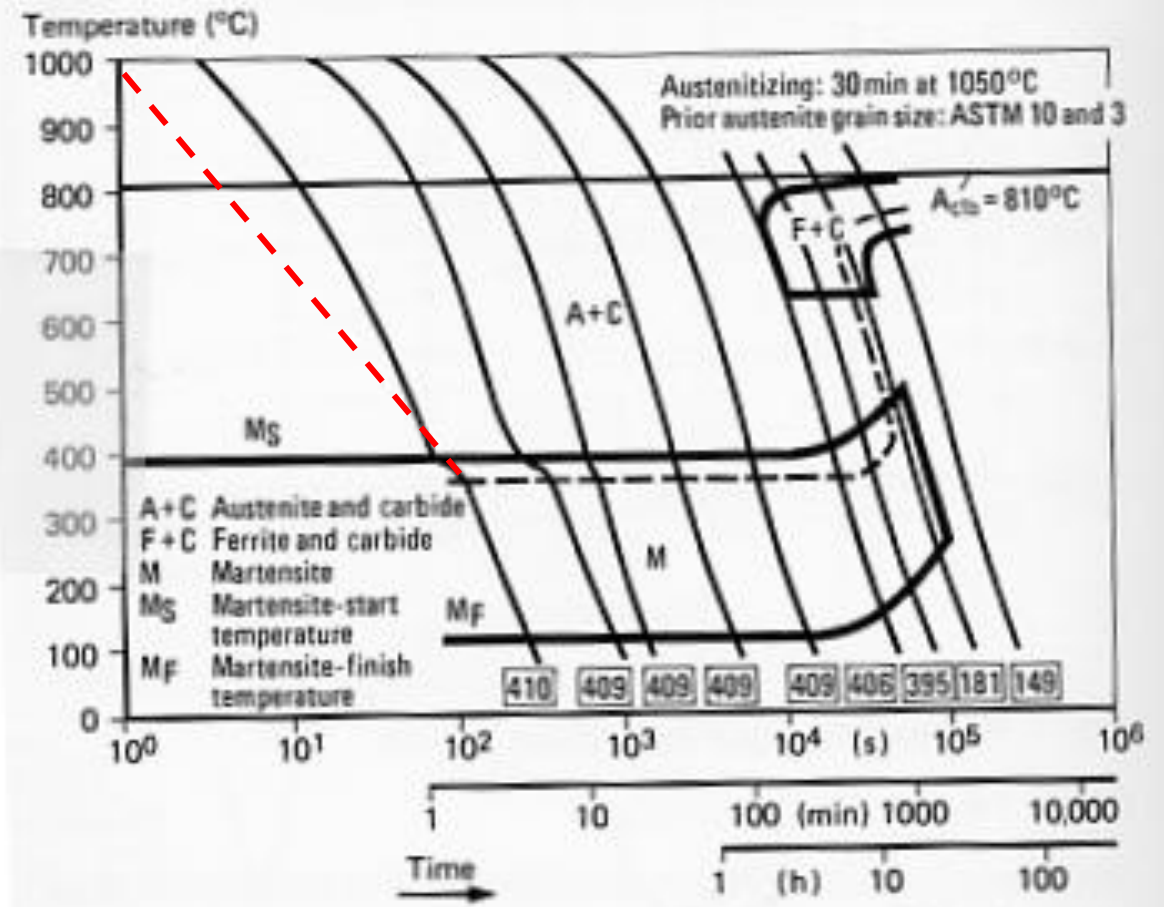
Issues with the CSEF Materials

- Boiler erection issues
- Uncontrolled heating (abuse) of assemblies leading to brittle fracture (T23)
- Lack of welding pre-heat at field erection leading to hard weld HAZ's and SCC (T23 and T24)
- Errors in processing in the vendor supply chain leading to creep failures (P91)
- PWHT errors in T91
- Unusual fireside corrosion

Metallurgical Pitfalls in T/P 91

- Strength (martensite formation) depends upon heat treatment (any action which alters the as-heat treated structure degrades the strength)
  - Hot Forming
  - Forging
  - Welding
  - Post Weld Heat Treatment

Continuous Cooling Transformation Curve for T/P 91 Alloy



Continuous cooling transformation diagram of T/P91 steel

Case Study T23 Fabrication

- Erector used torch to enlarge lifting holes
  - Torch heat altered microstructure and caused brittle fracture of waterwall panels

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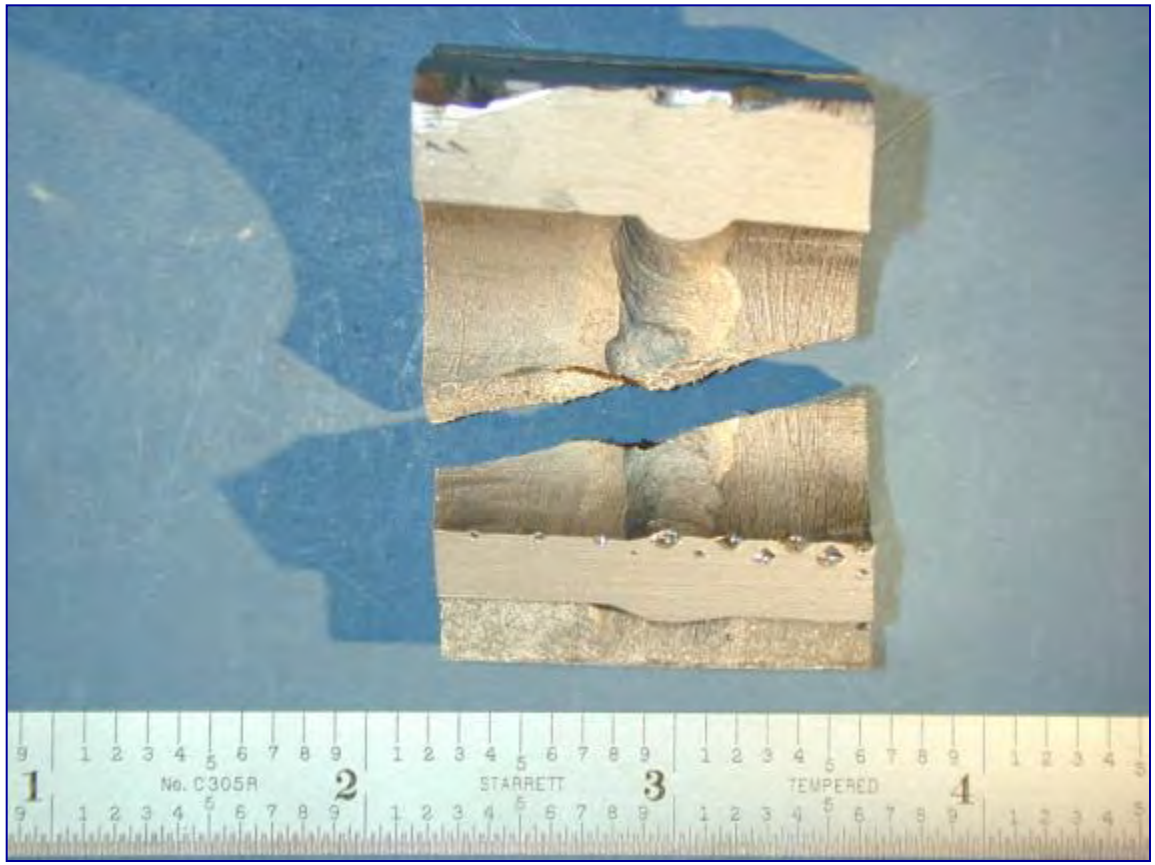
Case Study - Weld Design issue

- Tube joint also lacked PWHT leading to high hardness in HAZ
- Butt weld T12 to T23 near roof of boiler caused weld joint with high degree of restraint
- Hundreds of these welds failed by Stress Corrosion Cracking during first year of service

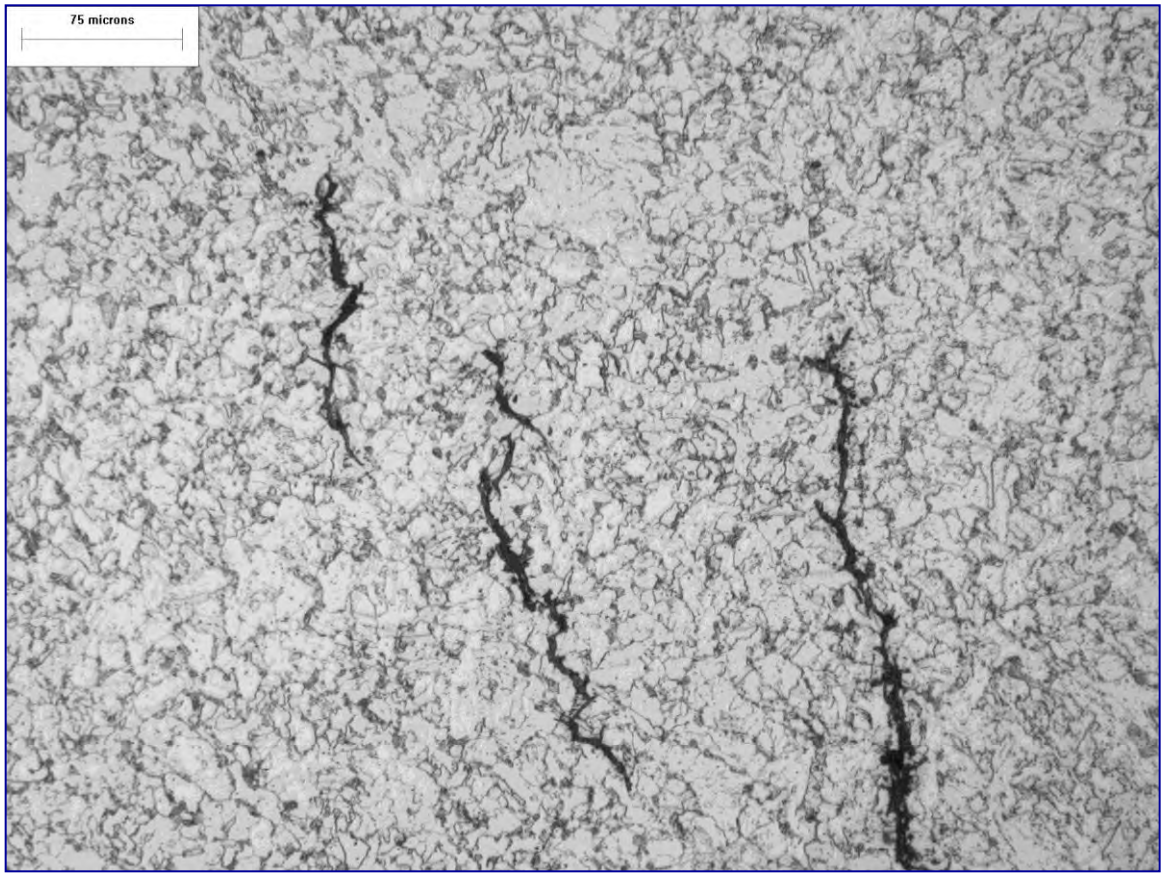
SCC of CSEF Steel

T23 Opened crack



T23 Tube Crack Opened

Micrograph of SCC



SCC of T23 and T24 Alloys

- Problem is widespread in Europe - attributed to high hardness in weld HAZ aggravated by high restraint (membranes and tube clips)
- Problem experienced in US - high HAZ hardness likely created by welding without adequate preheat
- Does NOT require an “aggressive “corrodent- hydrogen is the culprit - Cathodic SCC

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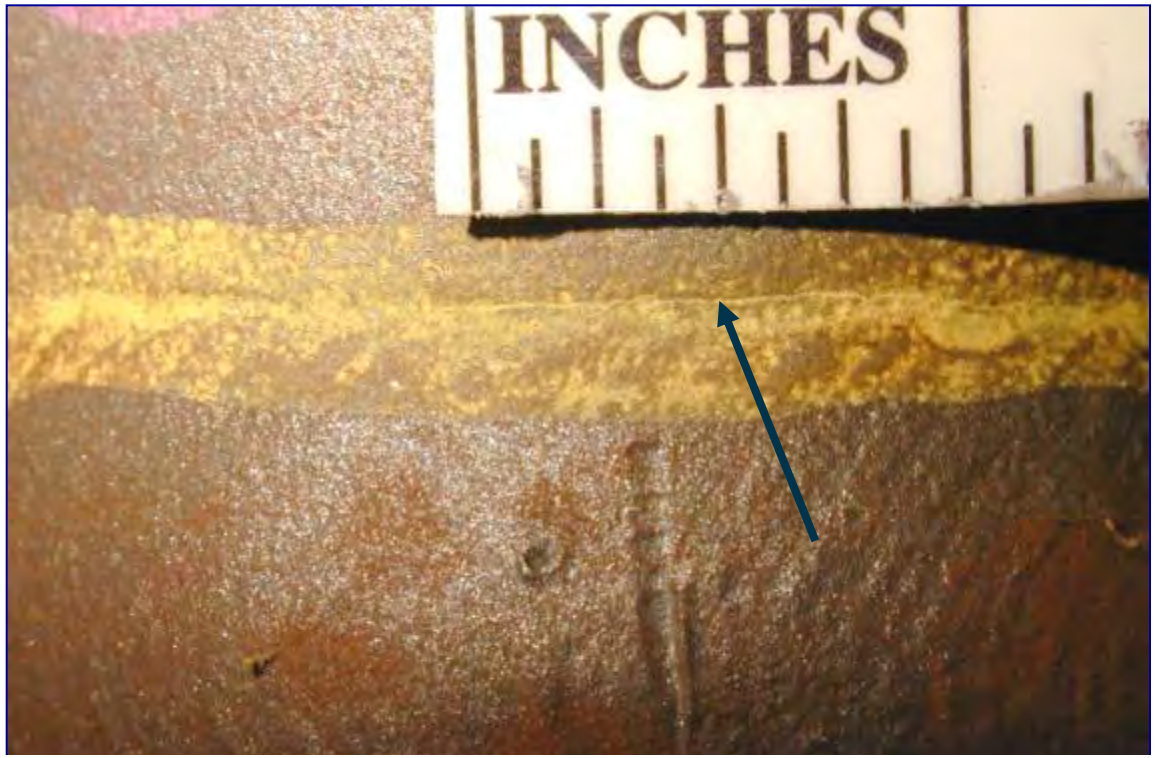
Case Study - Cracking of T91 Header Stub Tubes

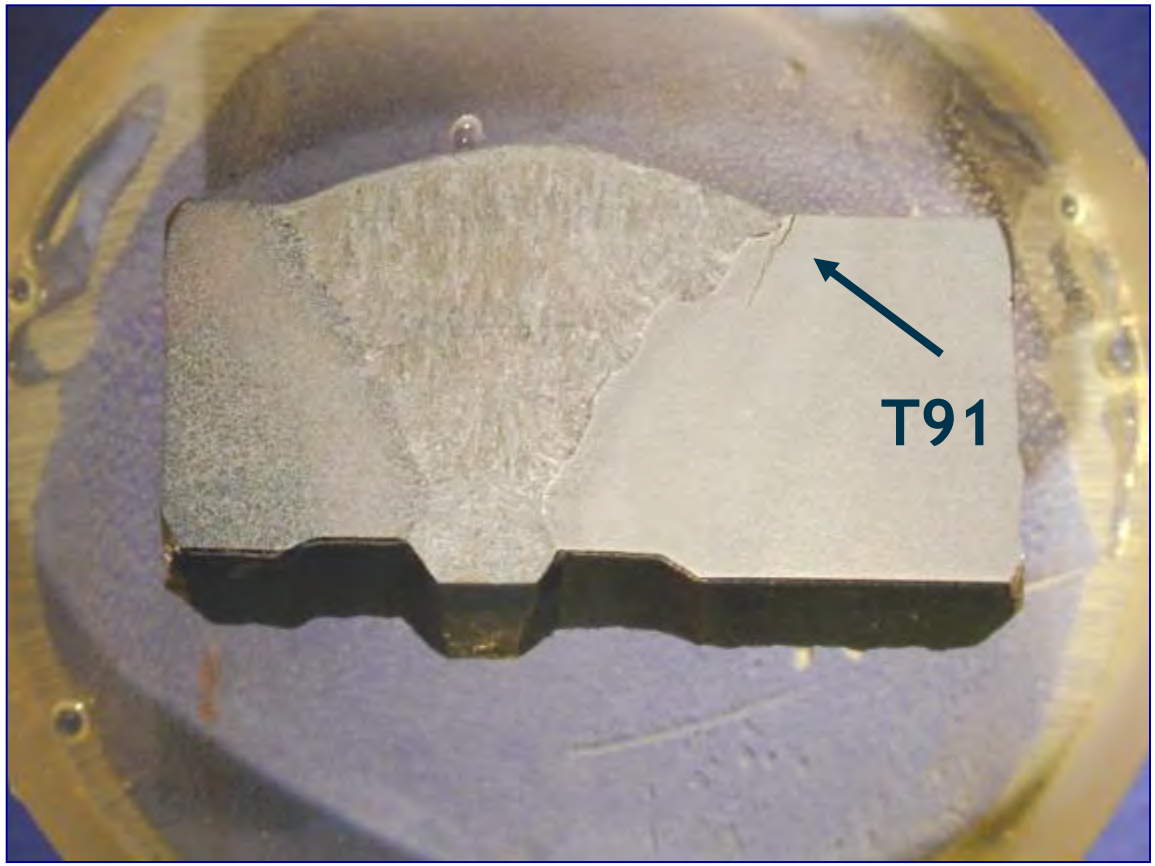
- P22 header was replaced with P91 header because of long-term creep damage
- T91 stubs welded into P91 header sockets at header supplier shop to make field erection easier
- P22 tubes 9 pups) welded onto T91 stubs at supplier shop to avoid field welds of T91 and T22
- After several years of service, cracks were found on T91 side of T22/T91 shop weld

Safe-End Stubs As Received for Analysis

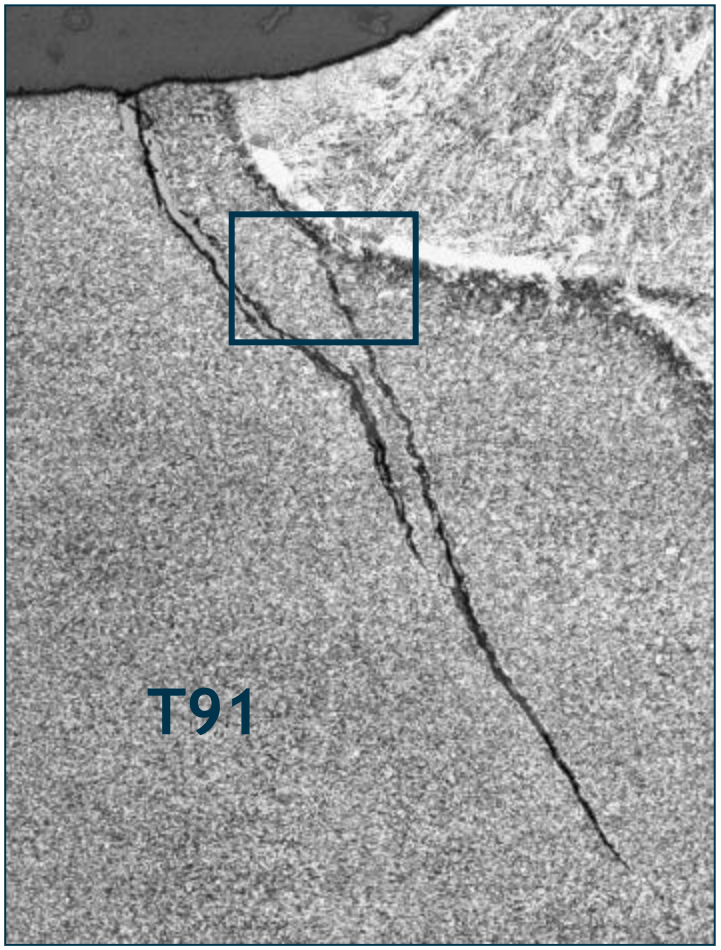
Close-Up of Crack T91 Side of Weld



Cracking on Safe-End, F91CN



Cracking Under the Weld Cap and at the Toe, F91CN



AEGIS

Cracking of T91 Header Stub Tubes (Cont'd)

- Cracking was Corrosion Assisted (SCC or Hydrogen) that Transitioned to HCF
- Cause was Delay in PWHT on T22/T91 Shop Weld
- Hydrogen generated by superficial "rusting" of assembly in high humidity

AEGIS

Case Study - Arc Blow in Fabrication of P91/P22 Pipe Joint

- During plant construction, welders reported that the P91 piping “would not melt”
- Extensive metallurgical workup could find nothing wrong with the P91 material weld procedure or consumables
- Finally discovered the P91 was highly magnetized- pipe degaussed and welds easily made
- Guilt by association

AEGIS

Case Study - Regression to Austenitic SH Elements Due to High Maintenance Cost

- Midwest Utility had replaced their T22 SH elements with T91
- Operated 8 years, but fly ash erosion dictated the need for weld overlay repairs
- PWHT restriction led utility to replace T91 with Austenitic alloy to eliminate high PWHT costs

Questions / Comments??

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