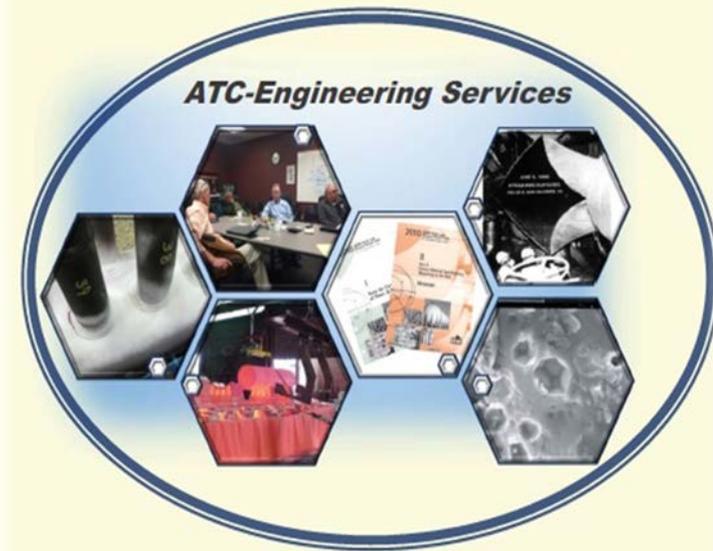


***EXPERIENCE WITH GRADE 91
MATERIAL IN BOILER & HRSG
APPLICATIONS***

Dr. Gang Zhou

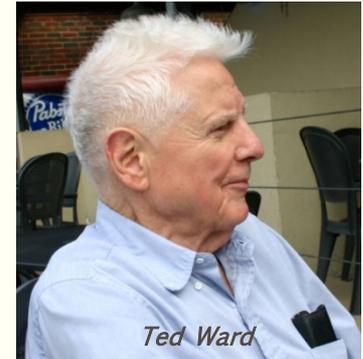


Agenda

- 1st topic Introduction
- 2nd topic Background of Gr. 91 Material
- 3rd topic Failure Analysis of Gr. 91 Components
- 4th topic Current R&D

Development of Gr. 91 Material

- Combustion Engineering (CE) Designed And Developed Grade 91 Material
 - Submitted the first proposal to the US-DOE in 1969 for the development of a Super 9Cr material for the sodium-cooled nuclear reactor application
 - Approval was granted to develop “hardware” at CE by early 1975 under the project administration of ORNL (Oak Ridge National Laboratory)
 - Established the alloy composition & demonstrated favorable properties in 1975-1980
 - Mitsubishi (MHI) & Sumitomo joined in the testing of Grade 91
 - Grade 91 was not optimized for fossil boiler applications
 - Accepted by ASME as CC1943 in 1984
 - We continues research on the effect of manufacture practice on the serviceability of Grade 91 components and weldments, including DMW joints (especially creep properties).



MODIFIED 9 Cr-1 Mo STEEL DEVELOPMENT PROGRAM PROGRESS REPORT
FOR PERIOD ENDING SEPTEMBER 30, 1978

Argonne National Laboratory
Combustion Engineering
Oak Ridge National Laboratory
Westinghouse Advanced Reactor Division

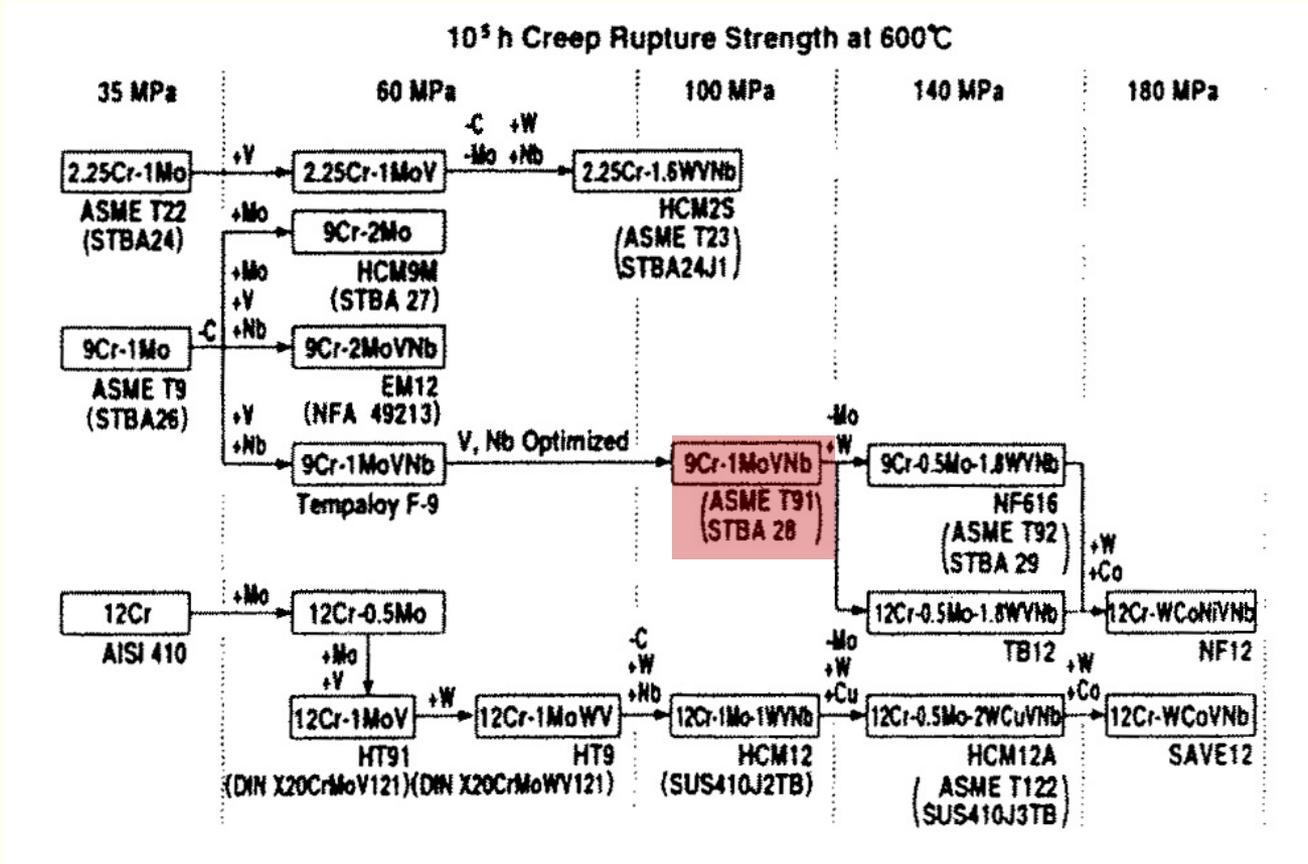
Compiled by: J. R. DiStefano

Date Published: May 1979

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

The initial work on the development of this material was published in a report entitled *A Program for the Development of Advanced Ferritic Alloys for LMFBR Application*, TR-MCD-015, issued in September 1977 by Combustion Engineering.

Cr-Mo Steel Development: Creep Rupture Strength



Grade 91 Material Different from Classic Materials

TABLE 1
CHEMICAL REQUIREMENTS FOR FERRITIC STEEL

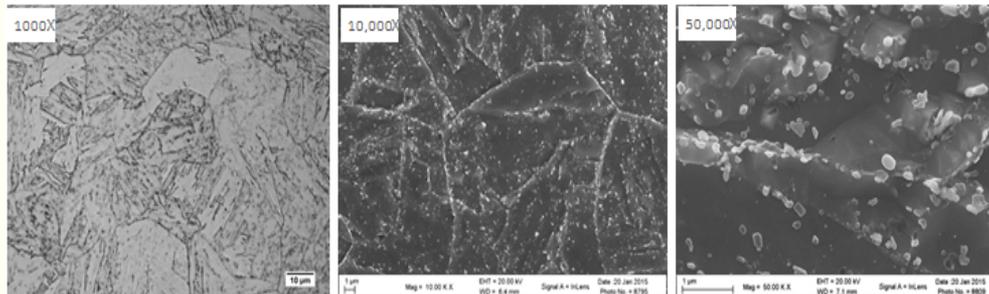
Grade	Composition, %									
	Carbon	Manganese	Phosphorus, max	Sulfur, max	Silicon	Chromium	Molybdenum	Titanium	Vanadium, min	Other Elements
T2 [Note (3)]	0.10–0.20	0.30–0.61	0.025	0.025	0.10–0.30	0.50–0.81	0.44–0.65	
T5	0.15 max	0.30–0.60	0.025	0.025	0.50 max	4.00–6.00	0.45–0.65	
T5b	0.15 max	0.30–0.60	0.025	0.025	1.00–2.00	4.00–6.00	0.45–0.65	
T5c	0.12 max	0.30–0.60	0.025	0.025	0.50 max	4.00–6.00	0.45–0.65	[Note (1)]	...	
T9	0.15 max	0.30–0.60	0.025	0.025	0.25–1.00	8.00–10.00	0.90–1.10	
T11	0.05 min–0.15 max	0.30–0.60	0.025	0.025	0.50–1.00	1.00–1.50	0.44–0.65	
T12 [Note (3)]	0.05 min–0.15 max	0.30–0.61	0.025	0.025	0.50 max	0.80–1.25	0.44–0.65	
T17	0.15–0.25	0.30–0.61	0.025	0.025	0.15–0.35	0.80–1.25	0.15	
T21	0.05 min–0.15 max	0.30–0.60	0.025	0.025	0.50 max	2.65–3.35	0.80–1.06	
T22	0.05 min–0.15 max	0.30–0.60	0.025	0.025	0.50 max	1.90–2.60	0.87–1.13	
T91	0.08–0.12	0.30–0.60	0.020	0.010	0.20–0.50	8.00–9.50	0.85–1.05	...	0.18–0.25	Cb 0.06–0.1 N 0.030–0.070 Ni 0.40 max Al 0.04 max
T92	0.07–0.13	0.30–0.60	0.020	0.010	0.50 max	8.50–9.50	0.30–0.60	...	0.15–0.25	W 1.5–2.00 Cb 0.04–0.09 B 0.001–0.006 N 0.03–0.07 Ni 0.40 max Al 0.04 max
18Cr-2Mo	0.025 max	1.00 max	0.040	0.030	1.00 max	17.5–19.5	1.75–2.50	[Note (2)]	...	N max 0.035 Ni + Cu max 1.00

NOTES:
 (1) Grade T5c shall have a titanium content of not less than four times the carbon content and not more than 0.70%.
 (2) Grade 18Cr-2Mo shall have Ti + Cb = 0.20 + 4 (C + N) min, 0.80 max.
 (3) It is permissible to order T2 and T12 with 0.045 max Sulfur.

Modified by addition V & Nb (MX) and control of N & C

Strengthening Mechanisms: Alloying Effects on Elevated Temperature Properties

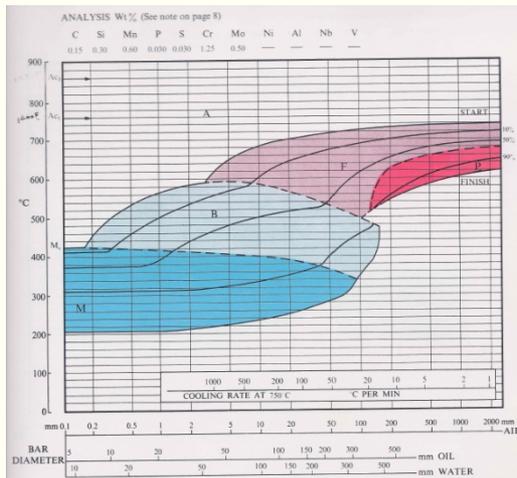
- Strengthening:
 - Solid solution strengthening (lattice strain, clusters, solute drag, etc.)
 - Precipitation strengthening
 - Carbides/Carbo-nitrides: e.g., $M_{23}C_6$, MX [(Cb,V)(N,C)]
 - Nitrides: e.g., Z-phase (CrCbN)
 - Others: e.g., Laves phase [(Fe,Cr) $_2$ (Mo,W)]
- High-Temperature oxidation resistance
 - Stabilization of oxide film (Cr, Si, Al)
 - Limited oxidation resistance above 600°C



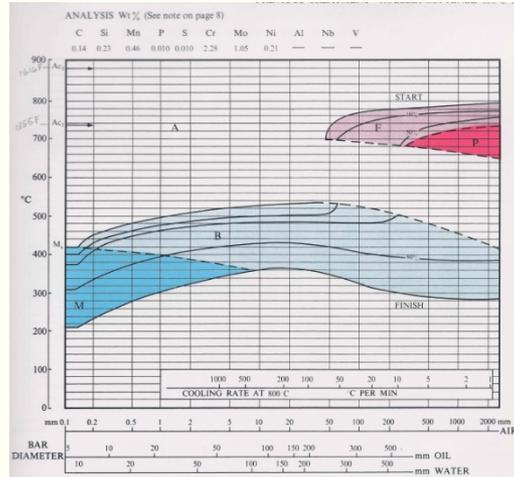
Effect of alloying elements

- As Alloy content (in this case) increases, the nose of the CCT diagram begins to shift to the right allowing martensite to be formed with slower critical cooling rate.

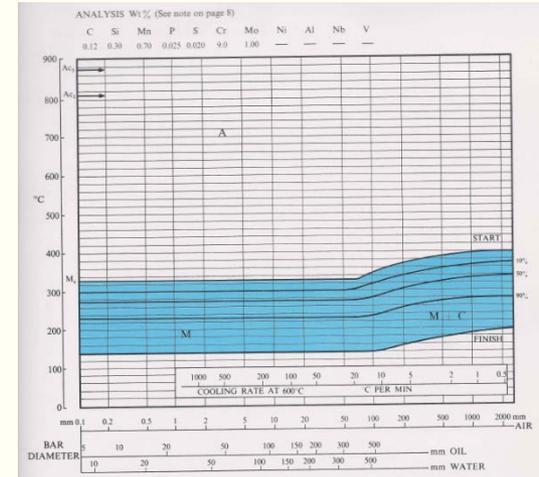
1.25CrMo



2.25CrMo



9CrMo



Increasing Alloy Content

Grade 91 Material “Different “ from Classic Materials

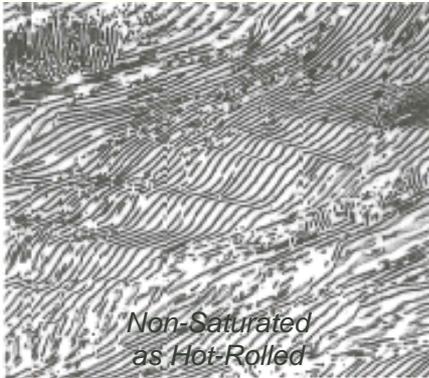
Austenite



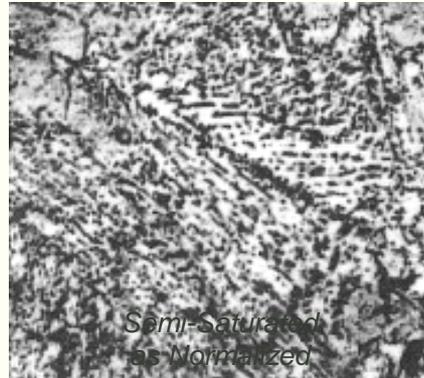
Carbon Steels

T/P11, T/P22

T/P91, T/P92



*Non-Saturated
as Hot-Rolled*



*Semi-Saturated
as Normalized*



*Super-Saturated
as Normalized*

Diffusion: Pearlite

Semi-Diffusion: Bainite

Diffusionless: Martensite

Hot Rolled

Normalized & Tempered

Normalized & Tempered

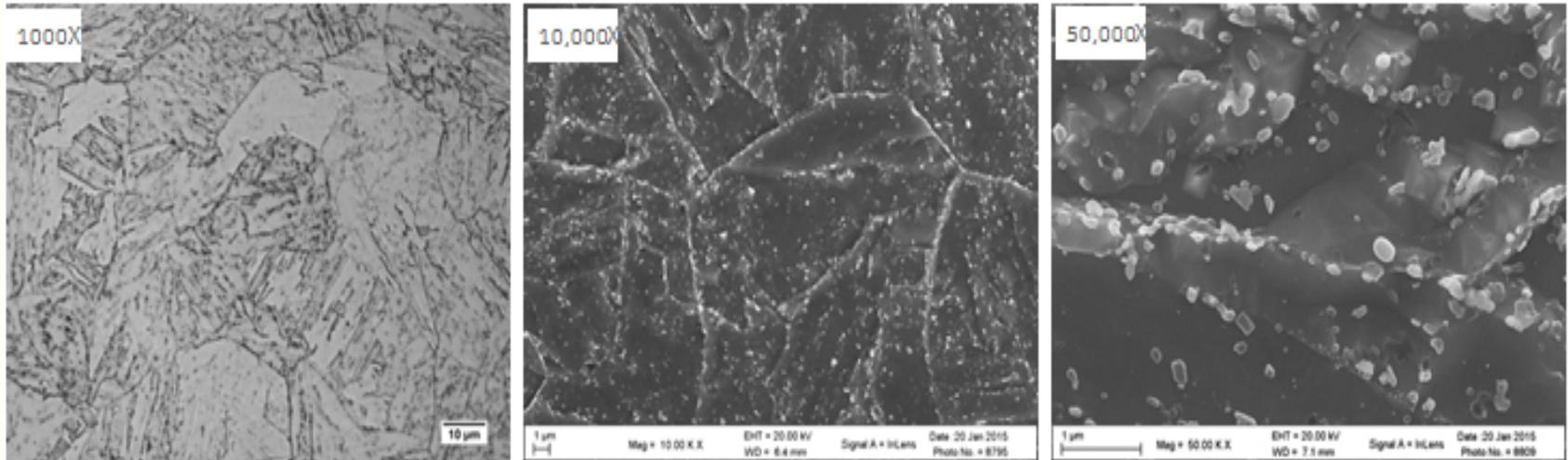
Ferrite + lamellar Carbides

Ferrite + Mixed-size Carbides

*Ferrite + Fine & Dispersive
Carbides*

Diffusion → Fe₃C/MX

Grade 91 Material – Tempered Martensite



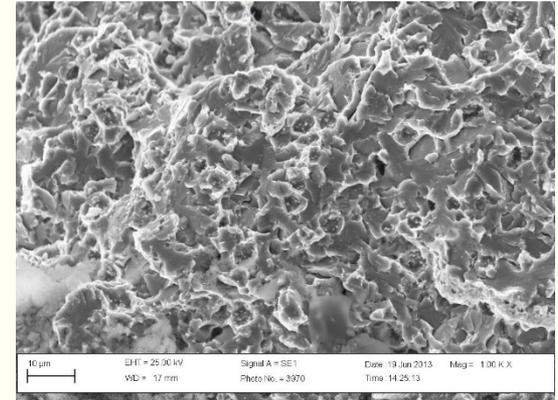
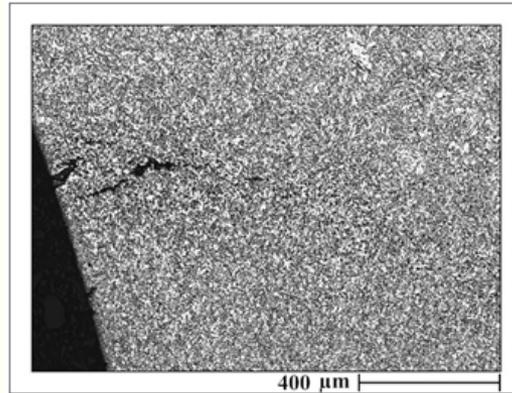
Grade 91 Base Metal in N&T condition

Ferrite + Fine & Dispersive Carbides

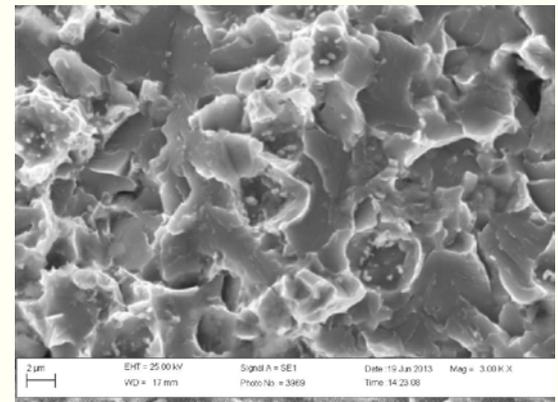
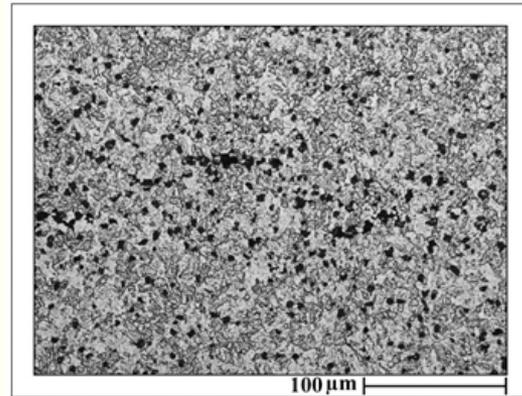
Issues of Gr. 91 Material & Components

- *Pre-mature Failure of Grade 91 Components*
- *Improper microstructure of original Grade 91 material ---- Tube, Pipe or Plates)*
- *Improper microstructure of Grade 91 components ---- Superheater, Reheater or header)*
 - *Slow cooling from normalizing (low hardness)*
 - *PWHT temperature over A_{C1} (Can be normal hardness)*
 - *Over-tempering (accumulated effect - normally low hardness)*
- *Early creep damage after short period of service (20-40k hrs)*
 - *Abnormal microstructure with ultra-fine grains (ASTM No. 10 or finer) mixed with coarse grains (ASTM No. 1 or coarser)*
 - *Abnormal inclusions – elementary features consistent with refractory*
 - *Type IV damage*
 - *DNW joints failures*

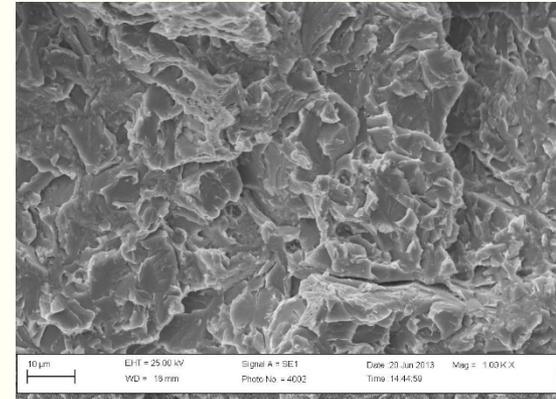
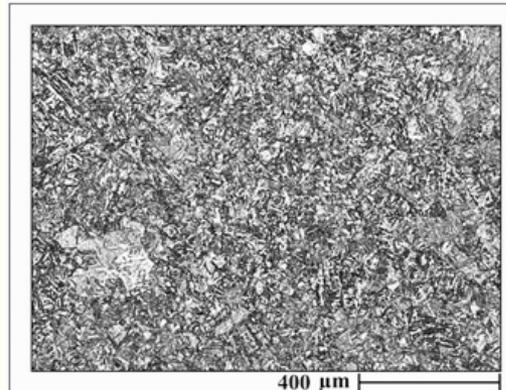
Case Study 1: Cracking in Type IV and Creep Damage in Base Metal



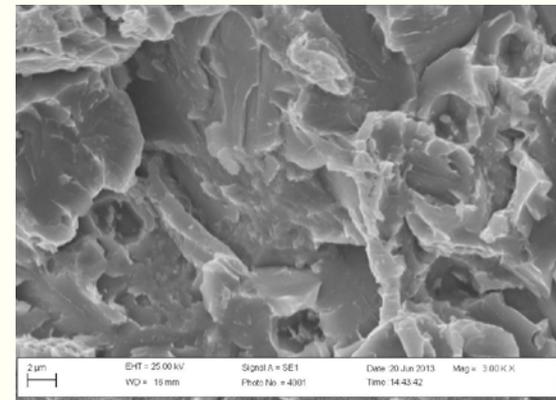
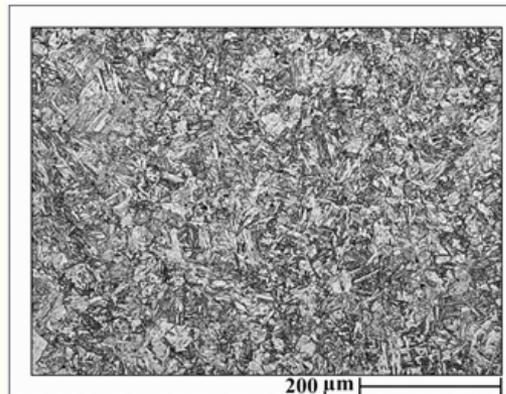
- P91 main steam manifold saddle joint.
- ASME SA-335, P91, 4" NPS x Sch.120.
- 27,000 hrs in service.
- Cracking found in FGHAZ of joint at saddle point



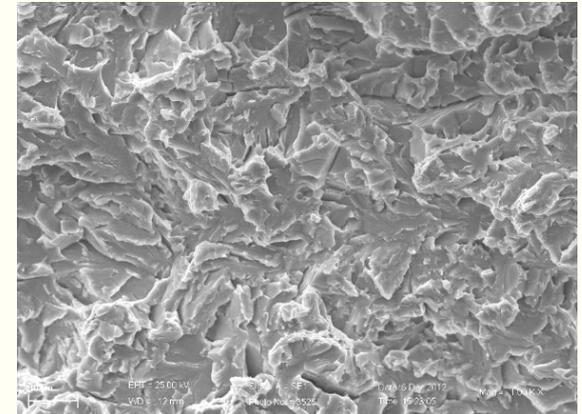
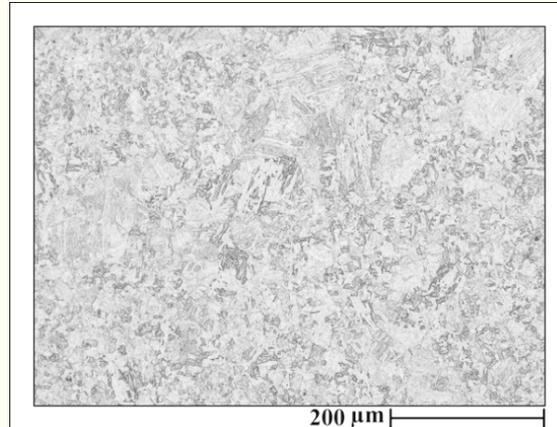
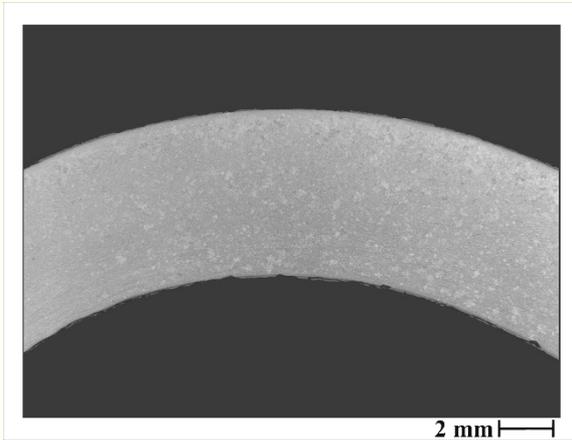
Case Study 1: Cracking in Type IV and Creep Damage in Base Metal



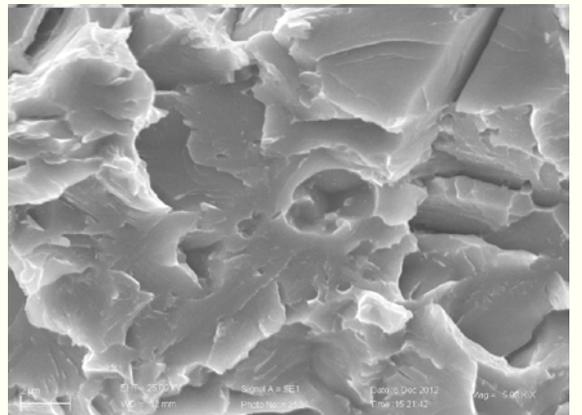
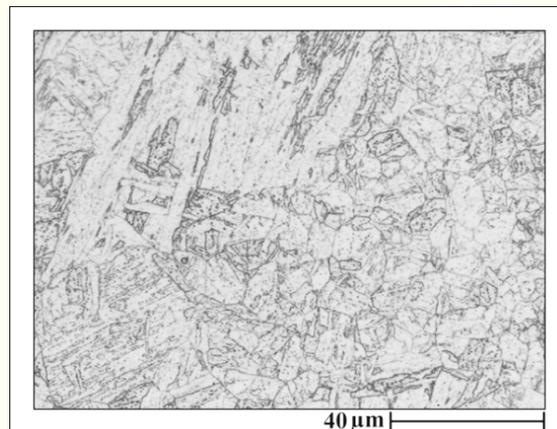
- P91 main steam manifold saddle joint.
- ASME SA-335, P91, 4" NPS x Sch.120.
- 27,000 hrs in service.
- Creep Damage in BM with uncharacteristic microstructure – ultra-fine mixed with ultra-coarse grains



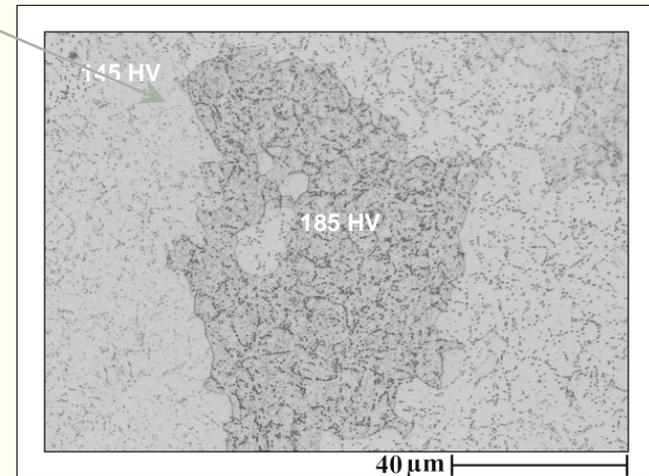
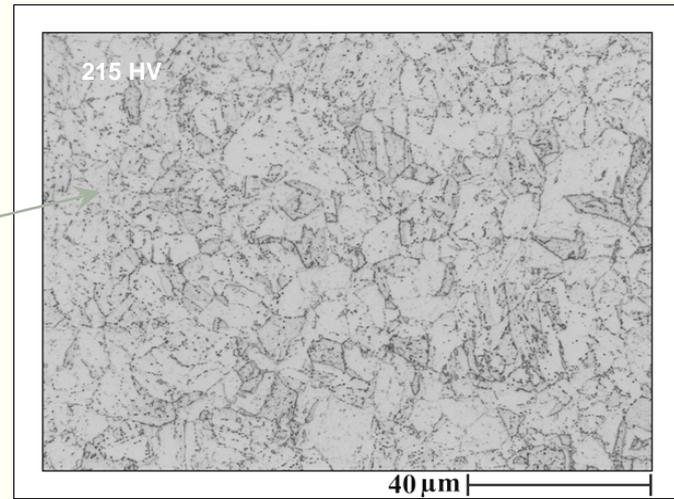
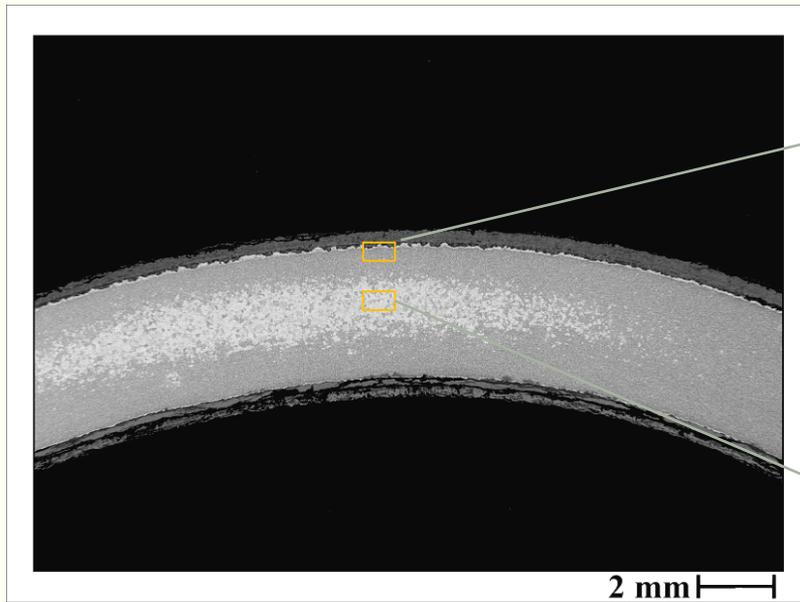
Case Study 2: Abnormal Microstructure and creep damage in T91 Final Superheater Tube



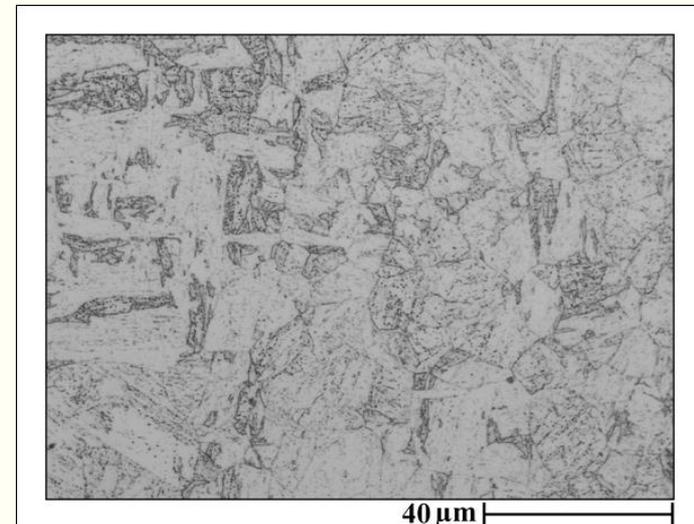
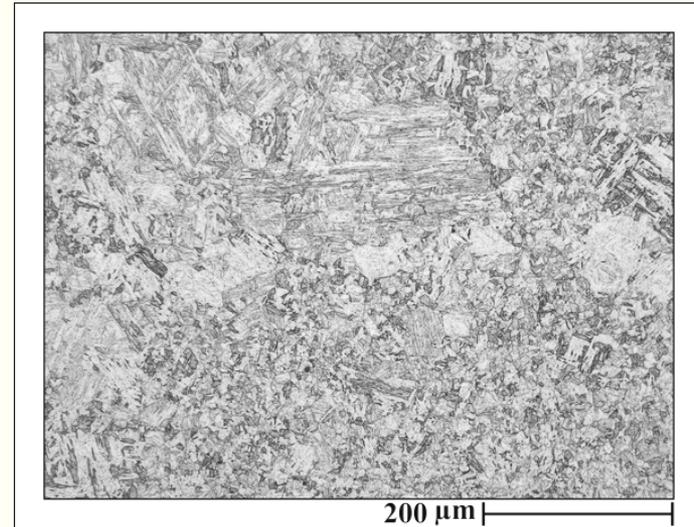
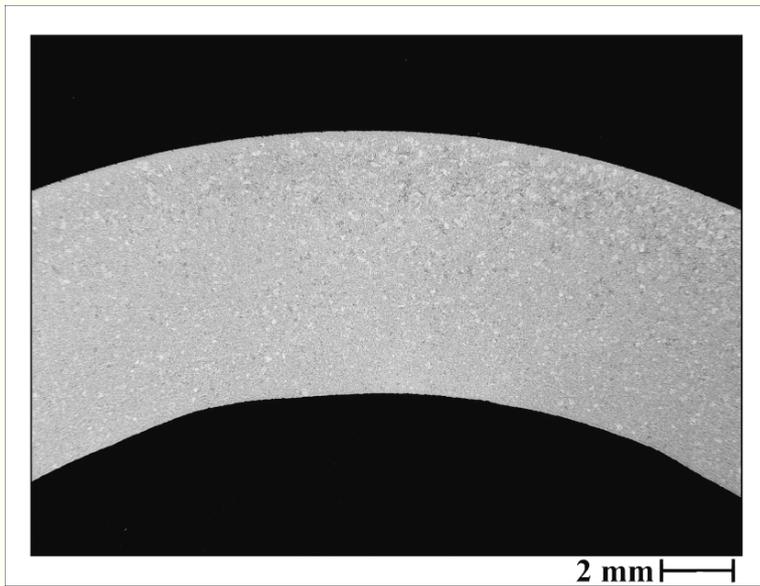
- T91 final SH tubing.
- ASME SA-213, T91, 1.75" OD x 0.225" MWT.
- 23,000 hrs in service.
- SH assemblies suffered multiple failure. This is a unfailed tube.



Case Study 3: Abnormal Microstructure in T91 Final Reheater Tube



Case Study 4: Abnormal Microstructure in New T91 tubing

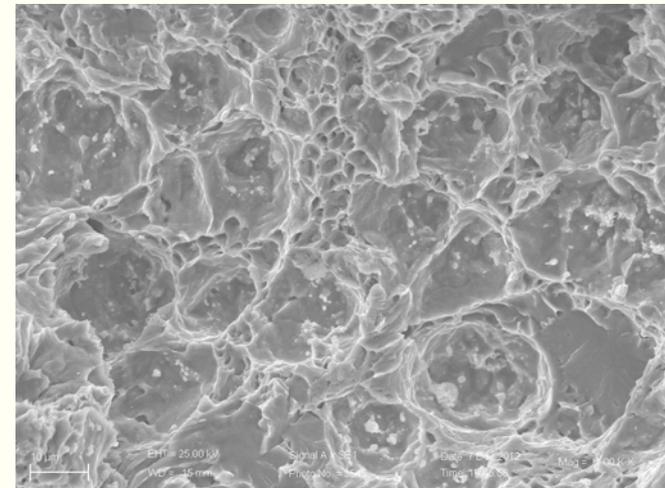
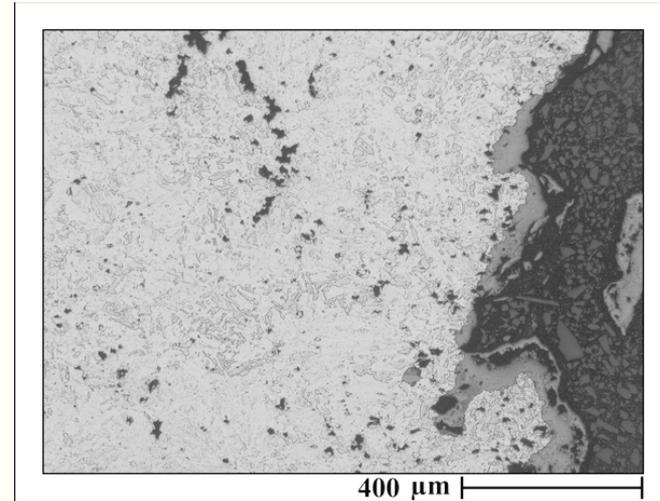
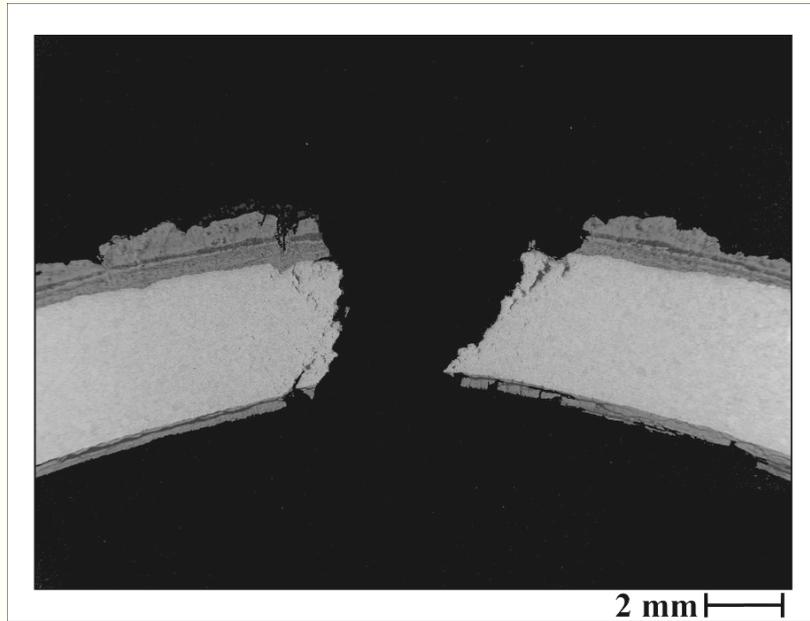


Case Study 5: T91 Reheater Tube

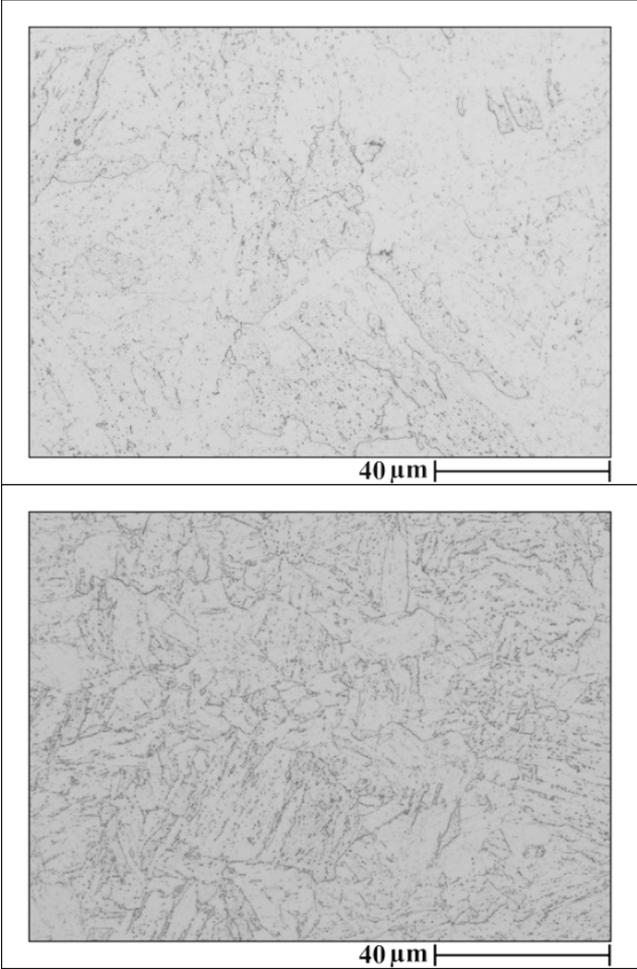
- Multiple Failures on the intrados of the front bend after ~17,000 hrs in service.
- ASME SA-213, T91, 2.75" OD x 0.150" MWT.



Case Study 5: T91 Reheater Tube



Case Study 5: T91 Reheater Tube



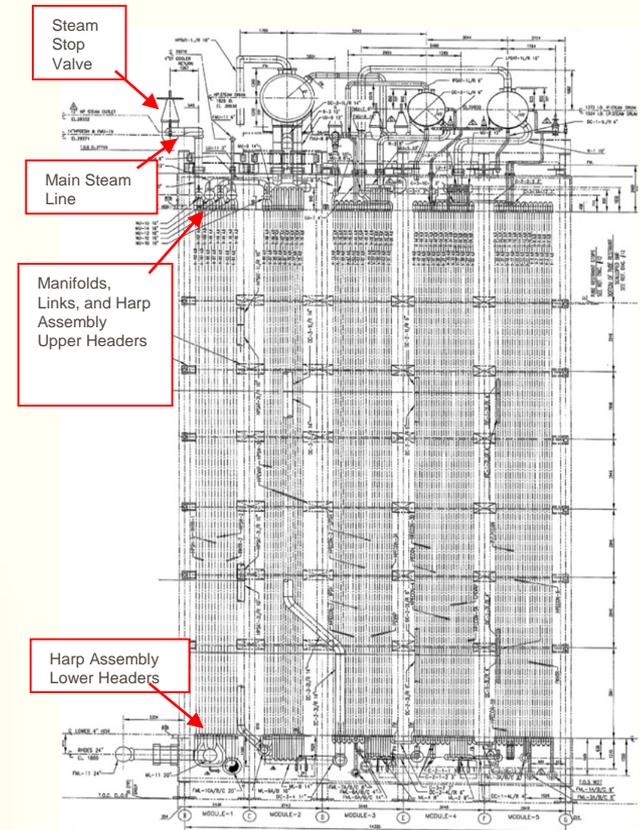
VICKERS HARDNESS VALUES-HV (HRB)*
Vickers hardness tester with a 20-kg test load

Sample	Location		Average	Range	
				Min.	Max.
RH-7	Bend (Micros A & B)	Crack Center (intrados)	149 (78)	135	164
		Crack End (Intrados)	172 (85)	155	184
		Extrados	218 (95)	216	219
	Straight (Micro C)	Front Side	217 (95)	216	217
		Back Side	203 (92)	201	206
RH-8	Bend (Micro D)	Intrados	176 (86)	158	192
		Extrados	216 (94)	209	223
	Straight (Micro E)	Front Side	214 (94)	209	217
		Back Side	208 (93)	203	211

Conclusion: Torch-Heating Intrados of Bend in Manufacture

Case Study 6: Uncharacteristic P91 with Low Hardness Values

- Issue was started with a crack at the toe of a connection weld between the main steam line and the superheater.
- Extensive NDE inspection be made from Main steam, manifolds and harp assembly upper and lower headers.
- BM: ASME SA-335, P91 & ~27,000 hrs in service.
- Low hardness values (as low as 158 HB) were found in HTSH upper and lower headers.
- Replica examination revealed 1) a fine-grained uncharacteristic microstructure in HTSH upper & lower headers & 2) possible creep damage in Type IV zone of many welds in HTSH.
- Suspected overheating during low-load operation with GT exhaust-gas temperature up to 650°C.
- Question about over-tempering during manufacture & installation.



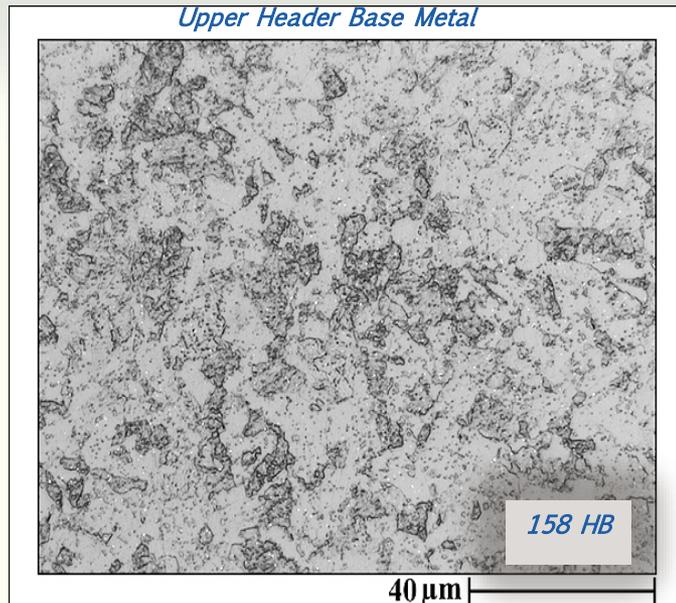
430 MW HRSG

Case Study 6: P91 with Low Hardness

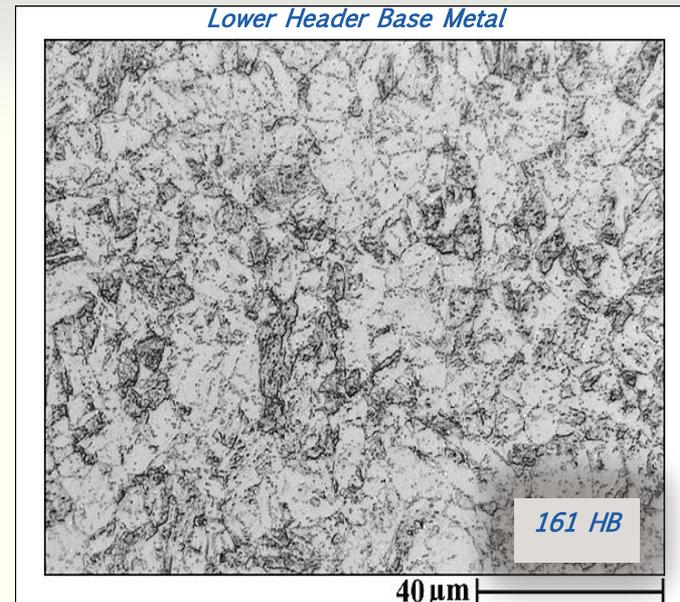
Questions:

- Was the low hardness in upper & lower headers of harp assemblies the result of overheating?
- Did accumulated-temper effect in manufacture & installation play any role?
- The MTR data of the original pipe appears to be normal. Could it be possible that this was the original piping condition? If so, how did the original piping have this condition?

Upper Header Base Metal



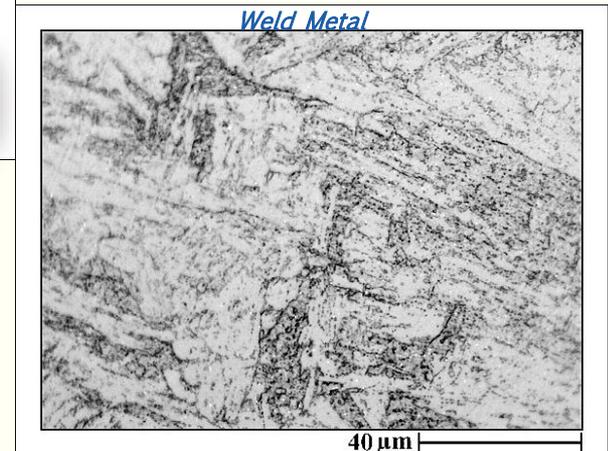
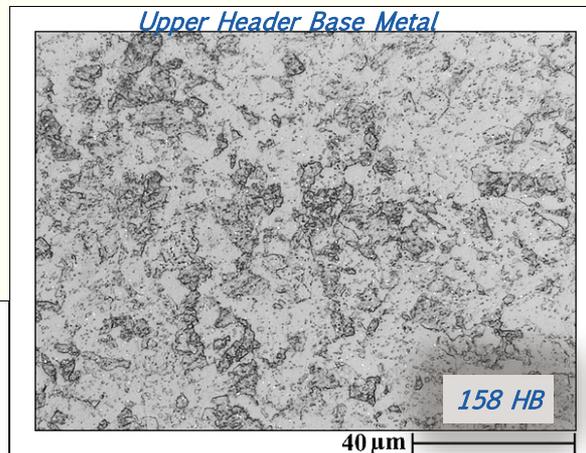
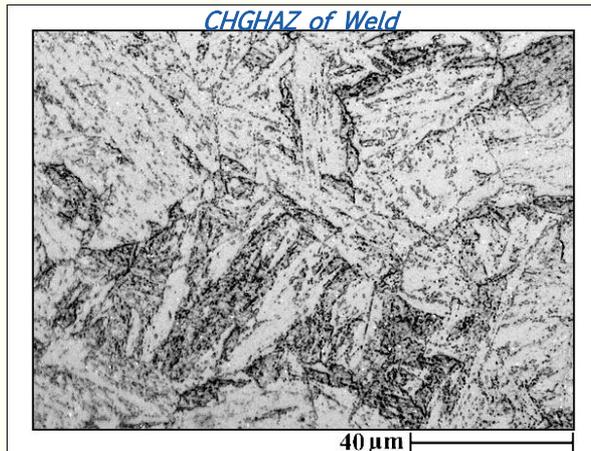
Lower Header Base Metal



Case Study 6: P91 with Low Hardness

More Questions:

- Where are the metallurgical evidence for the answer?
- What does it mean that over 50 replicas from upper & lower headers revealed identical metallurgical condition?



Case Study 6: P91 with Low Hardness

Result of Replica Examination & Recommendation:

- The condition of the CGHAZ and weld metal appears to be normal with no sign of any overheating and consistent with a normal Gr. 91 weld.
- The fine-grained ferrite structure with moderately spheroidized precipitates are likely consistent with improper-normalizing practice and a slow-cooling rate.
- It is recommended:
 - Investigate the details of the heat-treatment in the pipe mill.
 - Remove the sample(s) for destructive examination.
 - Determine the creep properties of the low-hardness pipe.
 - Design-review to determine whether Gr. 22 fits the design criteria for lower header.
 - Discuss the recommendations above with customer.

Metallurgical Condition of BM is The Key for Creep Properties

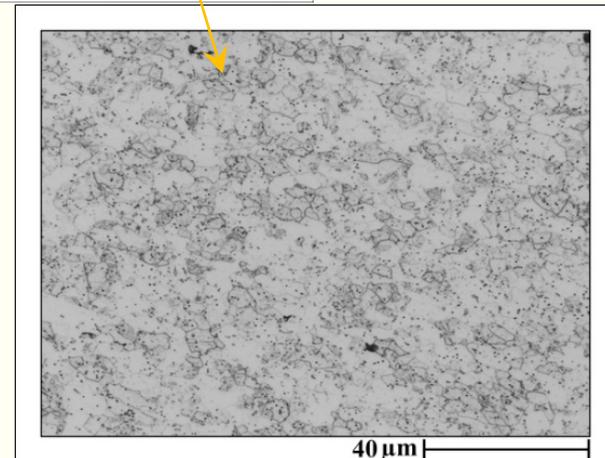
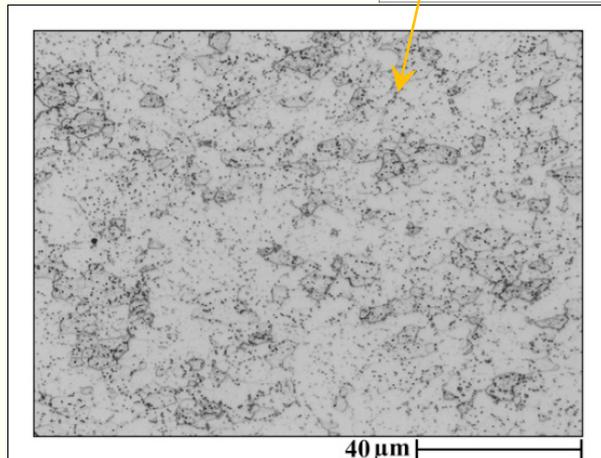
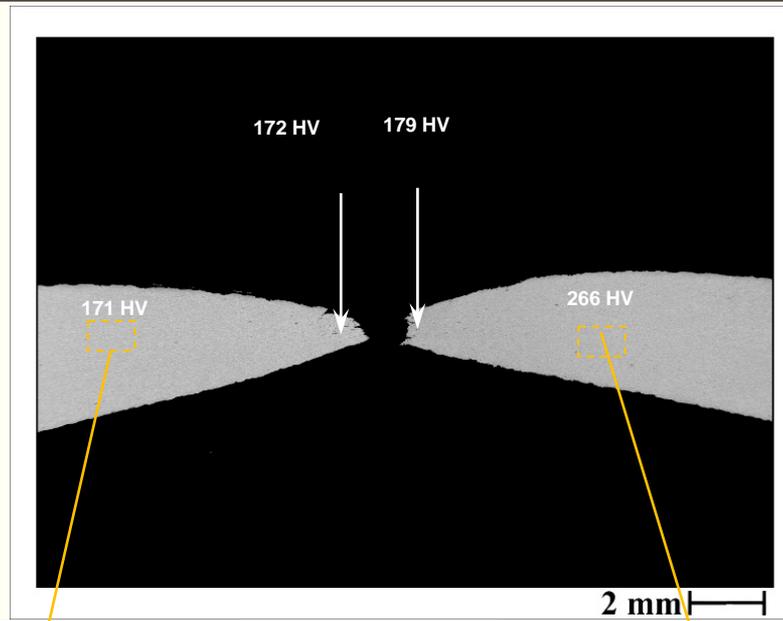
Case Study 7: T91 Superheater Tube Failure

- A front bend in finishing superheater assemblies failed after over 20,000 hrs service.
- ASME SA-213, T91, 2.25” OD x 0.240” MWT.
- Failure caused severe damage to the entire loop.

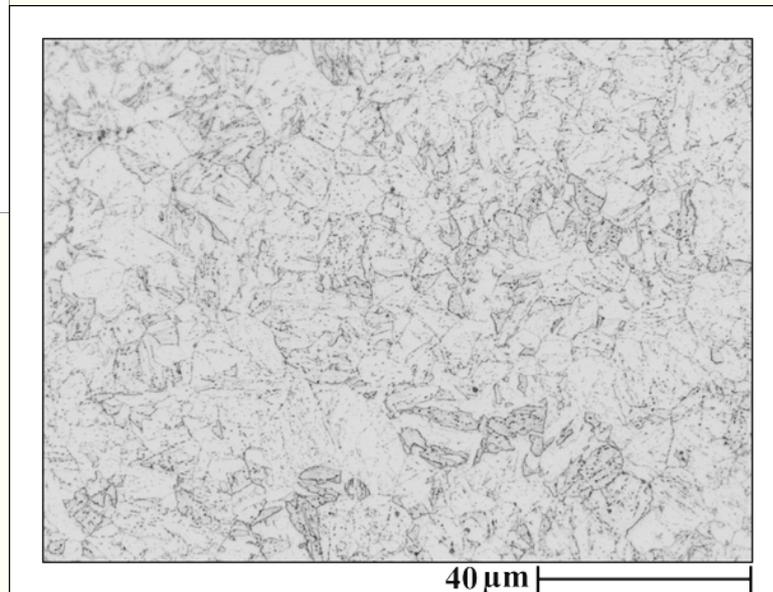
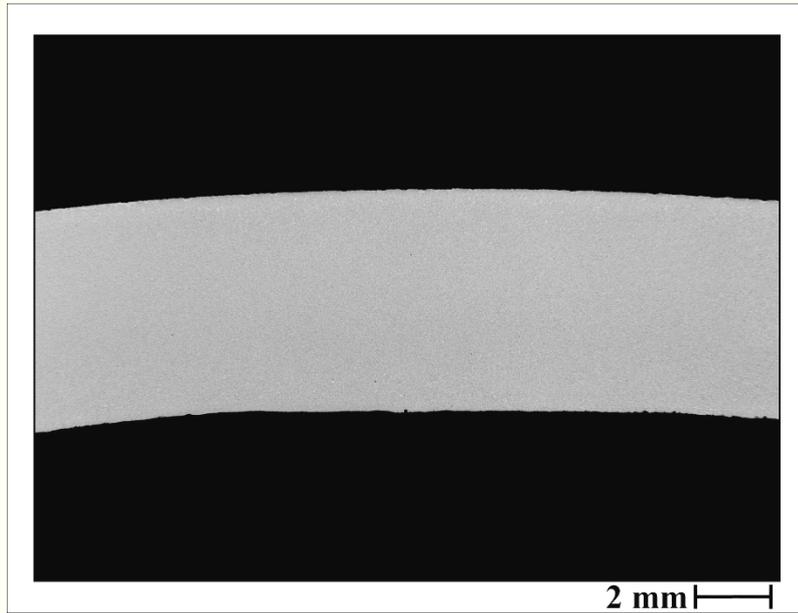


Chemical Composition (Weight Percent)		
ELEMENT	FSH-P15T4	ASME Specification SA-213, T91*
CARBON	0.100	0.07 - 0.14
MANGANESE	0.46	0.30 - 0.60
PHOSPHORUS	0.017	0.020 (max)
SULFUR	0.007	0.010 (max)
SILICON	0.30	0.20 - 0.50
NICKEL	0.22	0.40 (max)
CHROMIUM	8.66	8.00 - 9.50
MOLYBDENUM	0.886	0.85 - 1.05
VANADIUM	0.200	0.18 - 0.25
COLUMBIUM	0.071	0.06 - 0.10
TITANIUM	0.003	0.01 (max.)
COBALT	0.016	***
COPPER	0.10	***
ALUMINUM	0.019	0.02 (max)
BORON	0.0002	***
TUNGSTEN	0.02	***
ANTIMONY	0.001	***
ARSENIC	0.004	***
TIN	0.007	***
ZIRCONIUM	0.002	0.01 (max.)
LEAD	<0.001	***
NITROGEN	0.048	0.030 - 0.070
OXYGEN	0.015	***
ZINC	0.004	***
TANTALUM	<0.01	***
CALCIUM	0.0004	***
*2010 Section II, Part A		

Case Study 7: T91 Superheater Tube Failure



Case Study 7: T91 Superheater Tube Failure



Case Study 7: T91 Superheater Tube Failure

VICKERS HARDNESS VALUES-HV (HRB/HRC)* Vickers hardness tester with a 20-kg test load					
Sample	Location		Average	Range	
				Min.	Max.
Micro A (Vertical Section in FSH-P15T4-FB)	Front Side		210 (93 HRB)	209	211
	Back Side		211 (94 HRB)	209	212
Micro B (Front Bend in FSH-P15T4-FB)	Extrados Side		192 (90 HRB)	185	204
	Intrados Side		200 (92 HRB)	198	202
Micro C (Failure Site in Front Bend in FSH-P15T4-FB)	Extrados Side	Right Side of Rupture	266 (25 HRC)	248	276
		Left Side of Rupture	171 (85 HRB)	171	172
	Intrados Side		192 (90 HRB)	191	193
Micro D (Rear Bend in FSH-P15T4-RB)	Extrados Side		218 (95 HRB)	216	221
	Intrados Side		210 (93 HRB)	209	210
Micro E (Vertical Section in FSH-P15T4-RB)	Front Side		214 (94 HRB)	214	215
	Back Side		212 (94 HRB)	211	215

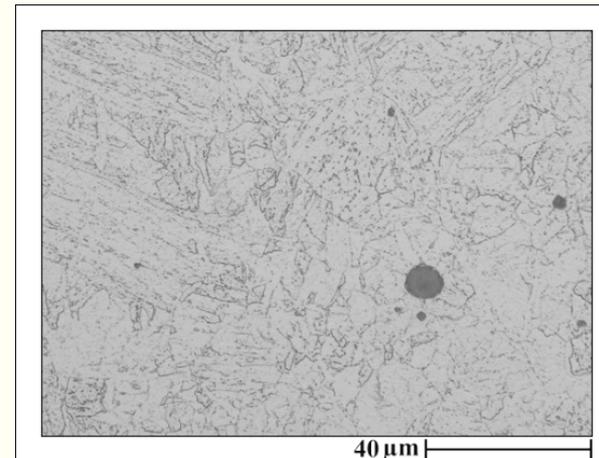
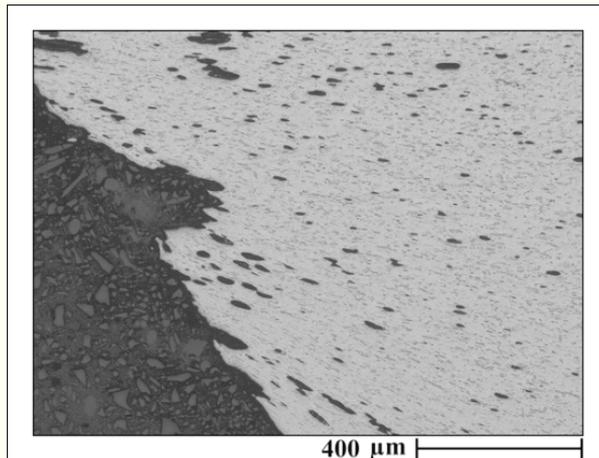
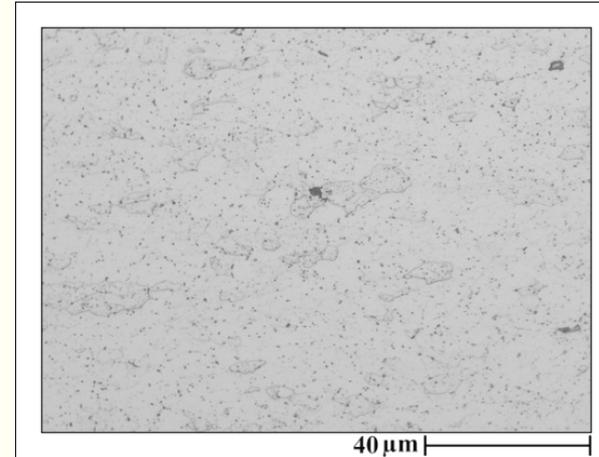
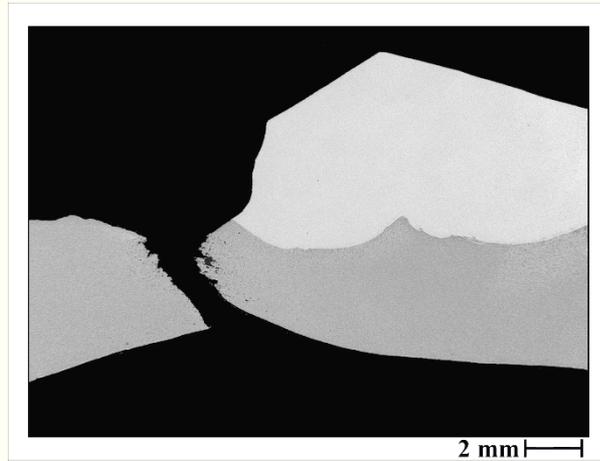
Conclusions: The bends had been improperly heated during manufacture.

Case Study 8: T91 Superheater Tube Failure

- Over 800 lugs failed after 23,000 hrs service and weld repaired
- A T91 FSH tube failed when the unit was back on-line.
- ASME SA-213, T91, 2.25" OD x 0.240" MWT.
- Repair Procedure: B9 build-up and ENiCrFe-2 (Inco-Weld® A)



Case Study 8: T91 Superheater Tube Failure



Conclusion: The failure along the toe of the repair weld was the result of stress rupture that occurred in the low-temperature region (slight over A_{C1}) of the base metal heat-affected zone (HAZ) associated with the weld repair

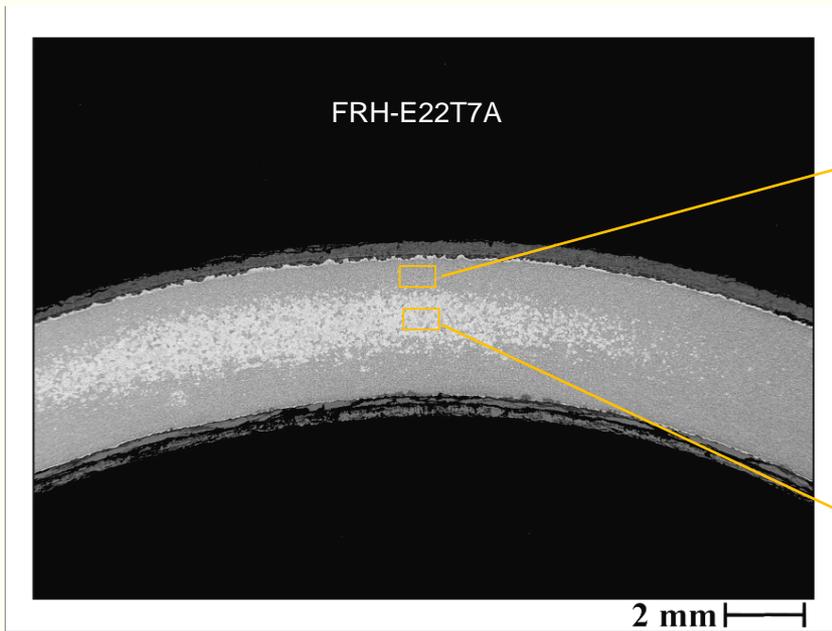
Case Study 9: T91 Final Reheater Tubes

- Five failures in final reheater bends
- ASME SA-213, T91, 2.0" OD x 0.150" MWT.
- Suspect that T91 bends were not improperly manufactured.

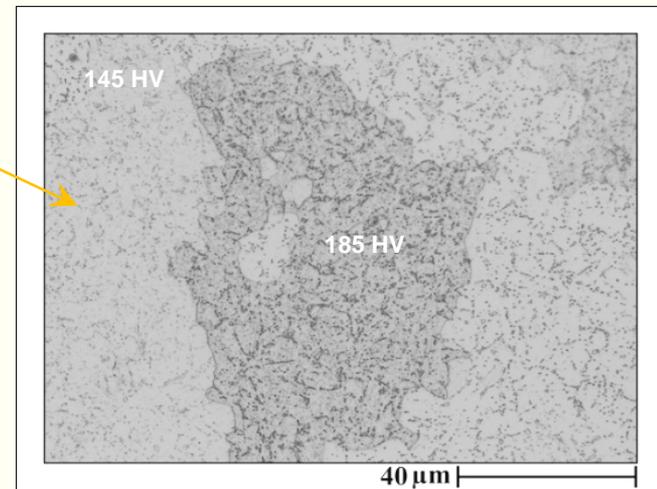
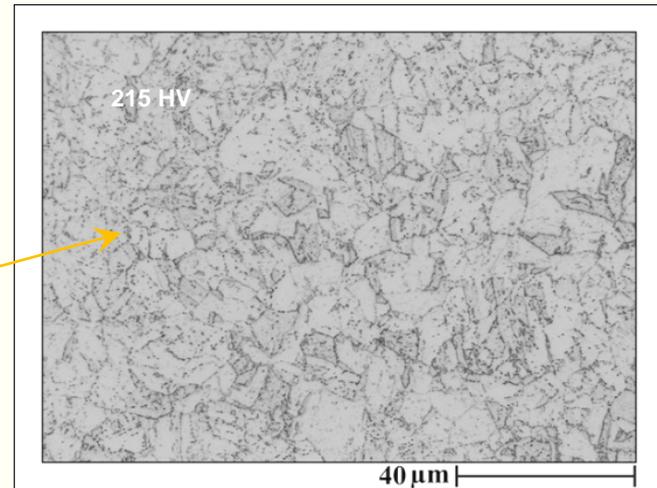


Chemical Composition (Weight Percent)						
ELEMENT	FRH- E22T7A	FRH- E37T11	FRH- E52T8A	FRH- E52T9A - Original	FRH- E52T9A - Replace	ASME Spec. SA-213, T91
CARBON	0.12	0.10	0.11	0.11	0.11	0.07 - 0.14
MANGANESE	0.43	0.44	0.42	0.43	0.44	0.30 - 0.60
PHOSPHORUS	0.017	0.016	0.013	0.016	0.012	0.020 (max)
SULFUR	0.001	0.001	0.001	0.001	0.007	0.010 (max)
SILICON	0.27	0.30	0.26	0.29	0.50	0.20 - 0.50
NICKEL	0.05	0.05	0.06	0.05	0.10	0.40 (max)
CHROMIUM	8.63	8.68	8.71	8.63	8.69	8.00 - 9.50
MOLYBDENUM	0.88	0.86	0.86	0.86	0.85	0.85 - 1.05
VANADIUM	0.194	0.196	0.195	0.194	0.201	0.18 - 0.25
COLUMBIUM	0.072	0.084	0.074	0.082	0.079	0.06 - 0.10
TITANIUM	0.005	0.006	0.008	0.006	0.002	0.01 (max.)
COBALT	0.016	0.009	0.016	0.009	0.012	***
COPPER	0.020	0.020	0.020	0.020	0.110	***
ALUMINUM	0.00	0.02	0.02	0.02	0.00	0.02 (max)
BORON	0.0002	0.0002	0.0002	0.0002	0.0003	***
TUNGSTEN	0.010	0.010	0.010	0.010	0.010	***
ANTIMONY	0.002	0.001	0.001	0.001	<0.001	***
ARSENIC	0.002	0.002	0.002	0.002	0.003	***
TIN	0.002	0.003	0.002	0.003	0.007	***
ZIRCONIUM	0.001	0.001	0.001	0.001	0.001	0.01 (max.)
LEAD	<0.001	<0.001	<0.001	0.001	0.001	***
NITROGEN	0.047	0.052	0.051	0.048	0.043	0.030 - 0.070
OXYGEN	0.007	0.006	0.004	0.003	0.003	***
ZINC	0.003	0.003	0.003	0.003	0.004	***
TANTALUM	<0.01	<0.01	<0.01	<0.01	<0.01	***
CALCIUM	0.0008	0.0011	0.0011	0.0010	0.0004	***

Case Study 9: T91 Final Reheater Tubes



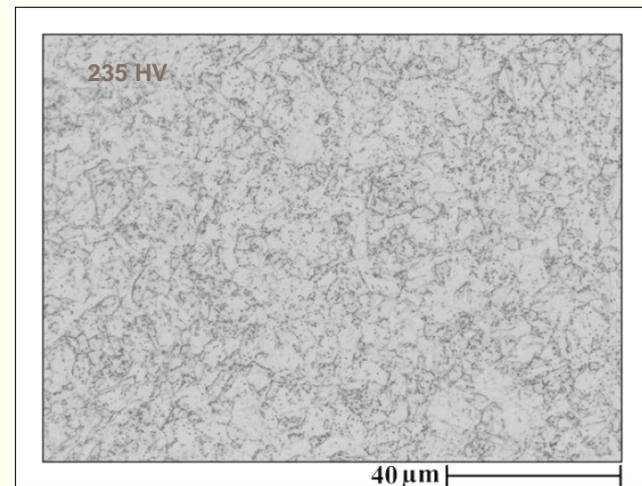
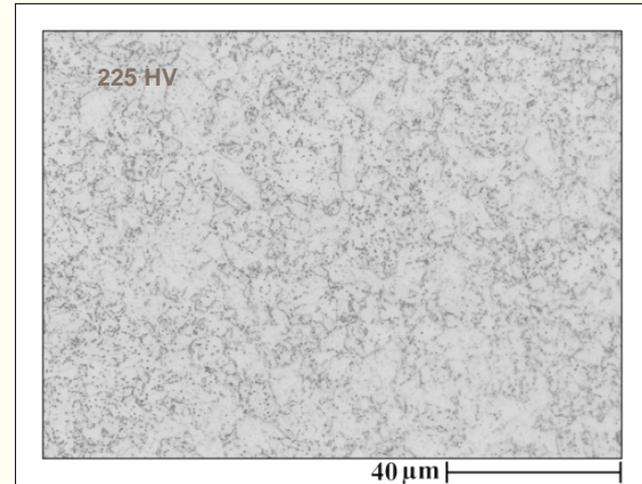
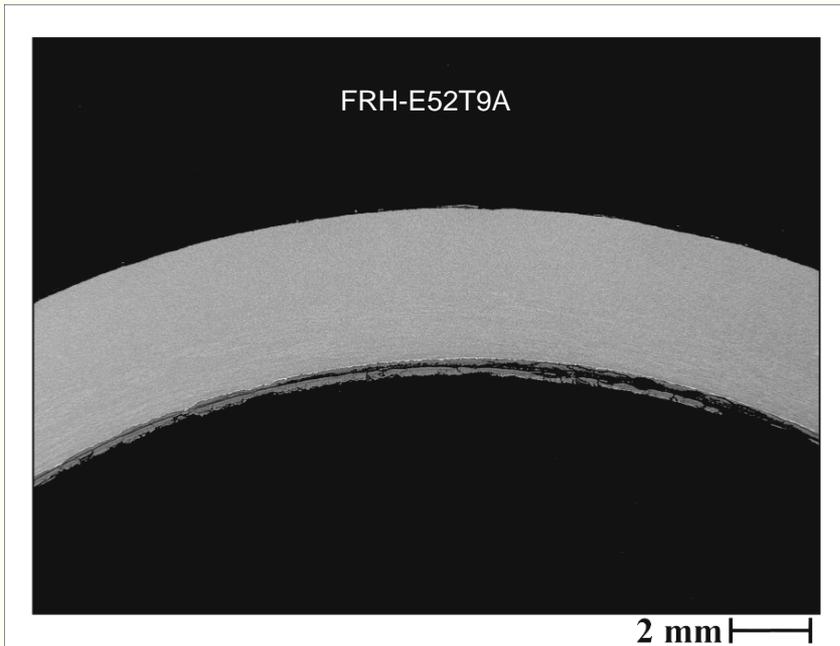
Bend was improperly heated during manufacture



Case Study 9: T91 Final Reheater Tubes

Element	Distance from OD surface on extrados of front bend					ASME Specification SA-213, T91
	0.039"	0.059"	0.079"	0.099"	0.119"	
CARBON	0.11	0.11	0.11	0.12	0.12	0.07 - 0.14
MANGANESE	0.45	0.45	0.44	0.43	0.43	0.30 - 0.60
PHOSPHORUS	0.017	0.017	0.017	0.017	0.016	0.020 (max)
SULFUR	0.001	0.001	0.001	0.001	0.001	0.010 (max)
SILICON	0.30	0.29	0.28	0.28	0.27	0.20 - 0.50
NICKEL	0.05	0.05	0.05	0.05	0.05	0.40 (max)
CHROMIUM	8.68	8.68	8.66	8.61	8.62	8.00 - 9.50
MOLYBDENUM	0.89	0.89	0.87	0.88	0.88	0.85 - 1.05
VANADIUM	0.2	0.2	0.2	0.2	0.2	0.18 - 0.25
COLUMBIUM	0.08	0.08	0.07	0.07	0.07	0.06 - 0.10
TITANIUM	0.01	0.01	0.01	0.01	0.01	0.01 (max.)
COBALT	0.016	0.016	0.016	0.016	0.016	***
COPPER	0.02	0.02	0.02	0.02	0.02	***
ALUMINUM	0.01	0.01	0.01	0.00	0.01	0.02 (max)
BORON	0.0003	0.0004	0.0003	0.0002	0.0002	***
TUNGSTEN	0.01	0.01	0.01	0.01	0.01	***
ANTIMONY	<0.001	0.001	0.001	0.001	0.002	***
ARSENIC	0.002	0.002	0.002	0.002	0.002	***
TIN	0.003	0.003	0.002	0.002	0.002	***
ZIRCONIUM	0.00	0.00	0.00	0.00	0.00	0.01 (max.)
LEAD	<0.001	<0.001	<0.001	<0.001	<0.001	***
IRON	0.000	0.000	0.000	0.000	0.000	***
NITROGEN	0.060	0.059	0.056	0.058	0.057	0.030 - 0.070
OXYGEN	0.001	0.003	0.002	0.001	0.001	***

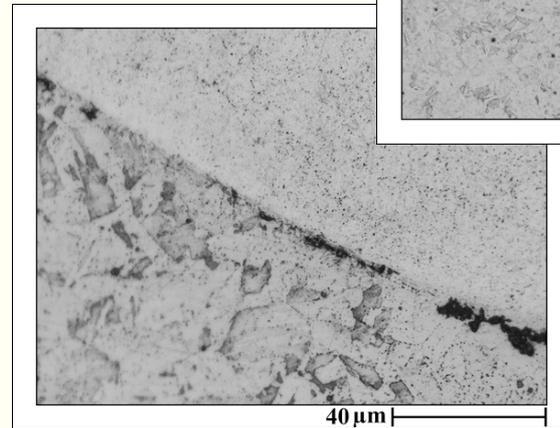
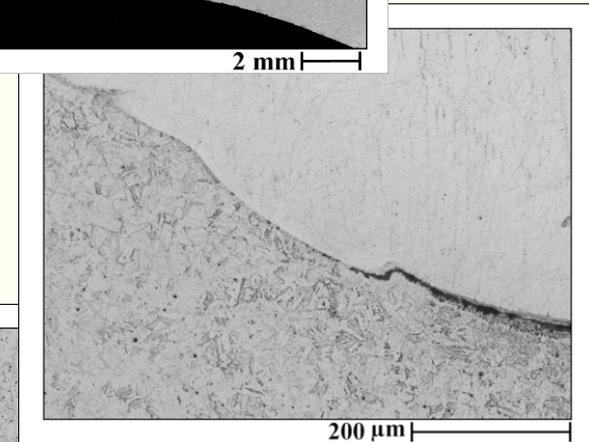
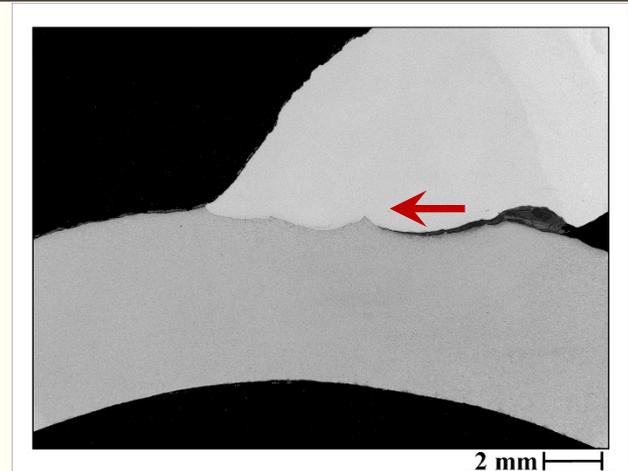
Case Study 9: T91 Final Reheater Tubes



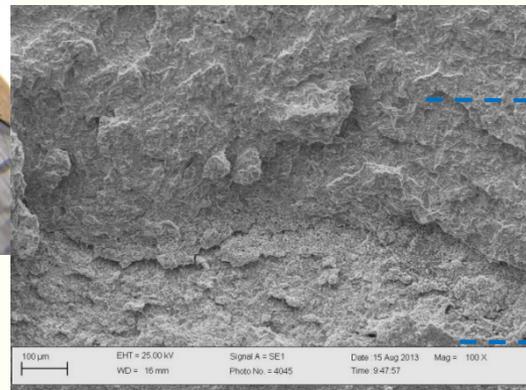
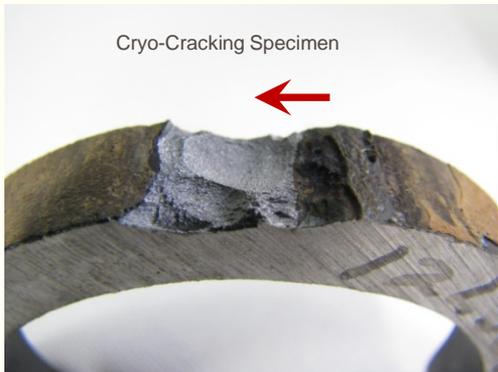
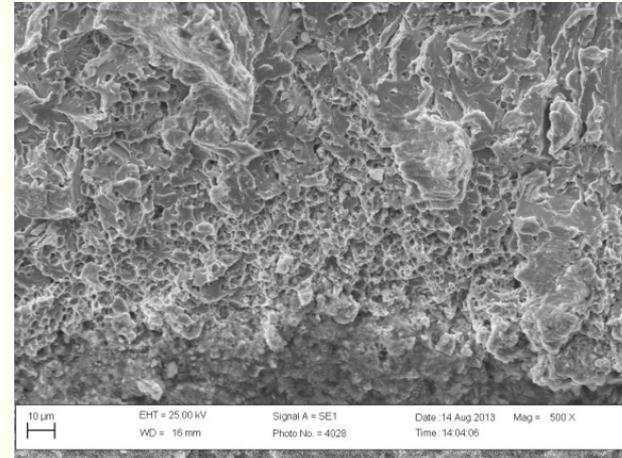
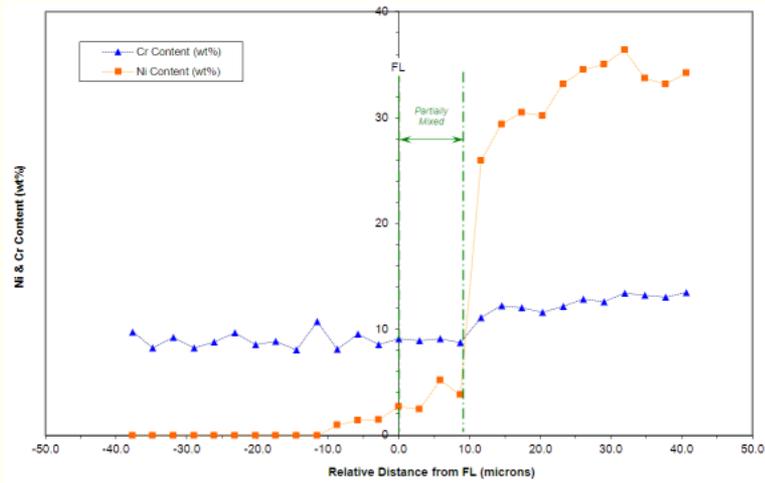
Conclusion: Bend was improperly tempered during manufacture with tempering temperature > A_{C1}

Case Study 10: T91 Attachment

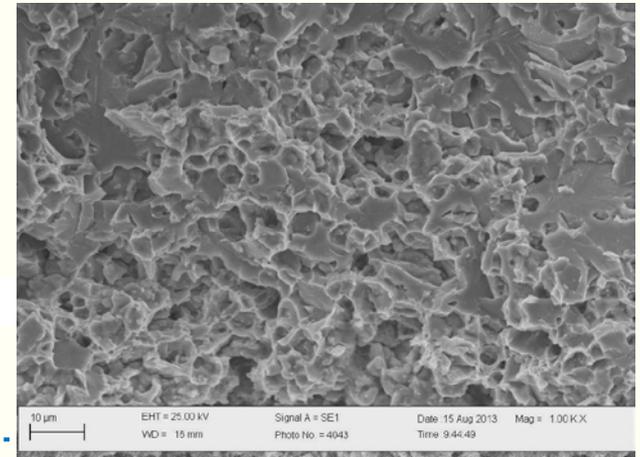
- More than 800 attachment welds failed after 23,000 hrs in service
- BM: SA-213, T91
- Lug: ASTM A297, Grade HH
- Filler Metal: ENiCrFe-2 (Inco-Weld® A)
- Cracking was an intergranular fracture along the partially mixed zone on the weld metal side
- 100-150 microns deep creep cavitated zone in front of the crack tip
- Up to 5%Ni in the partially mixed zone
 - Significantly lower Ac1
 - PWHT temperature over Ac1 of the partially mixed zone
 - A creep weak zone after PWHT
- Notch at weld root and bending load



Case Study 10: Cree-Fatigue Crack



~400 μ m
Crack Tip



Case Study 11: Low Hardness in Grade 91 Header

Effect of Over-Tempering Accumulative

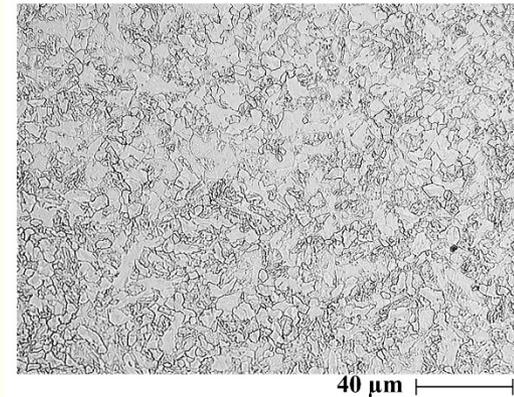
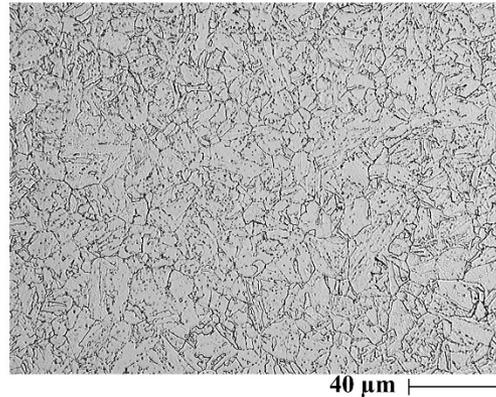
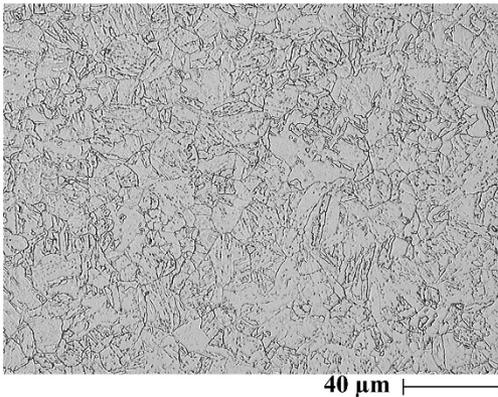


Hardness Measurements after PWHT revealed ~150 HV.

Case Study 11: Uneven Hardness in Grade 91 Header

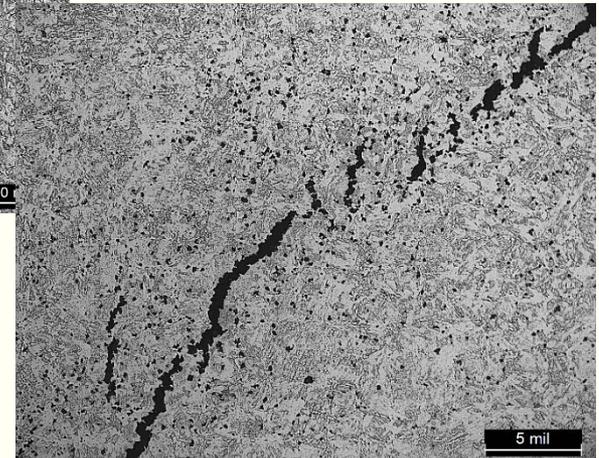
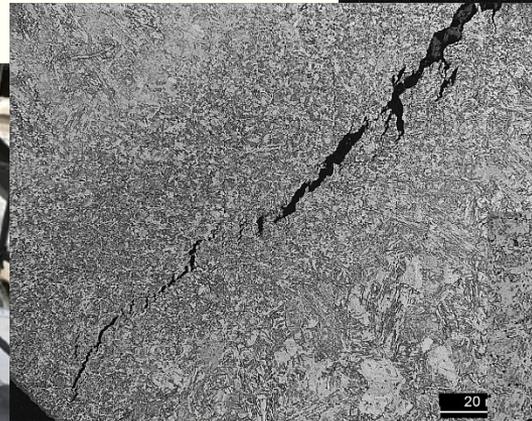
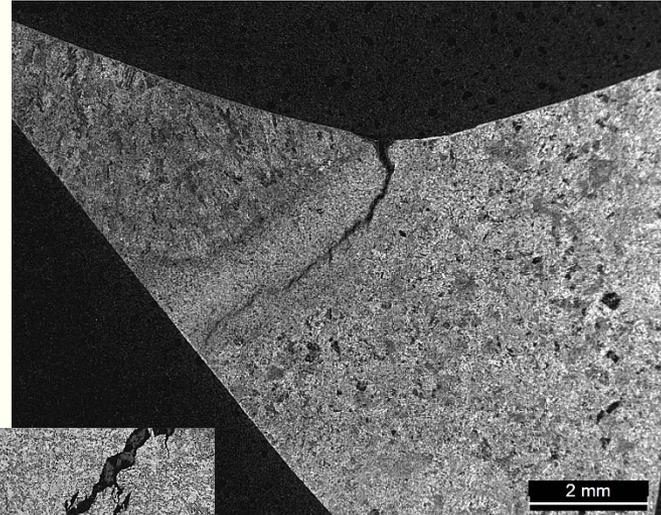
Effect of PWHT Temperature > A_{C1}

HARDNESS VALUES-HV* (Equotip)					
Sample	Location	0°	90°	180°	270°
Header Body	North**	214	216	218	224
	South**	213	213	210	208
Girth Weld	North	258	267	280	274
	South	227	241	229	230
Hemi-Head	North	135	137	160	141
	South	168	176	175	172



Case Study 12: Type IV Damage in P91 Girth Weld

- 20" OD Sch. 40 ASME SA335 P91
- Design temperature: 1067°F
 - Design pressure: 450 psig
- ~70,000 hrs in service
- Primary cracks were located from about 9:00 to 12:00 on the crotch side of the wye block



Fundamental Questions

- *What is creep properties of these Grade 91 components?*
- *Can these components safely operate as designed?*

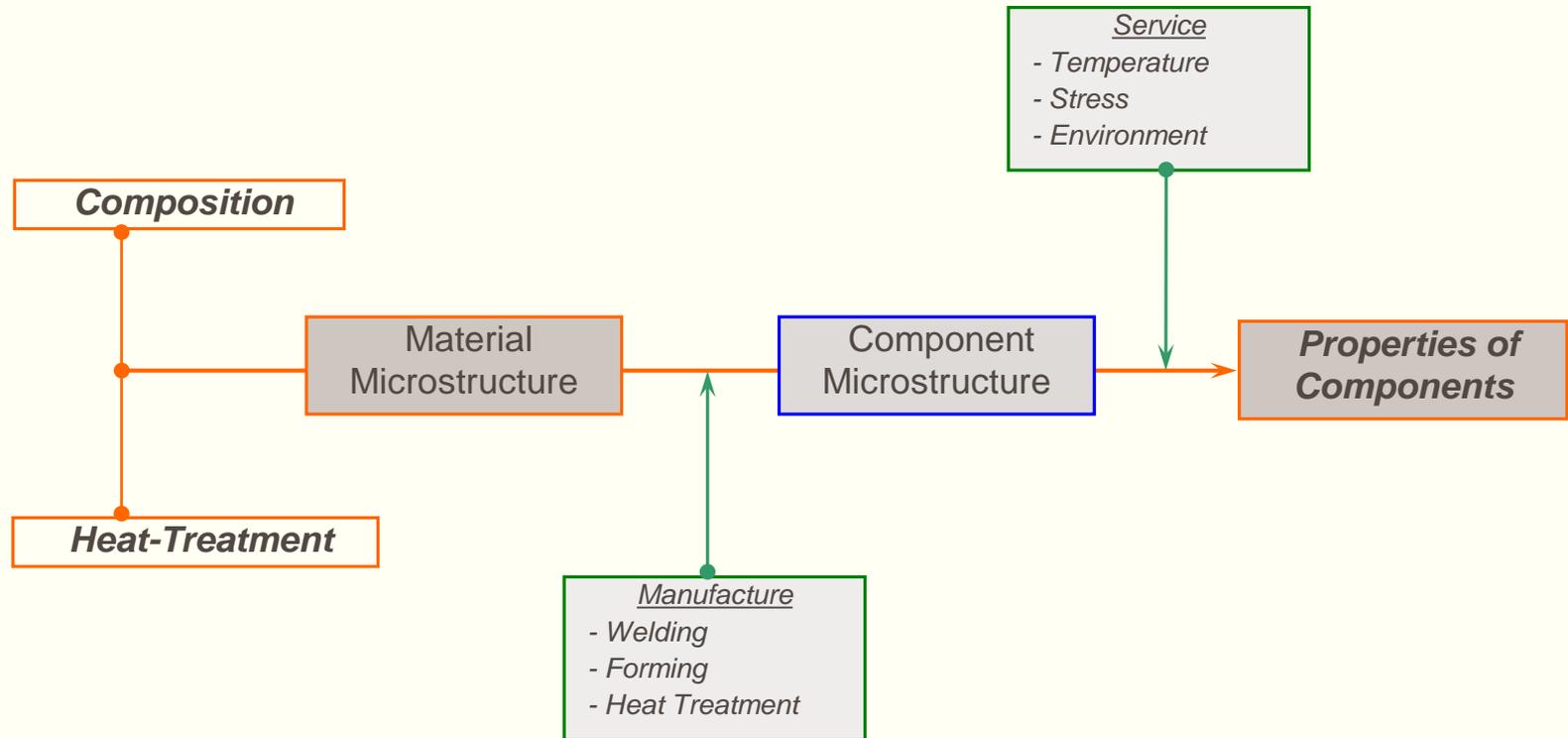


Creep Properties of Grade 91 material?

- No creep data provided in any purchasing MTR
- Gr. 91 was specified in AMSE or ASTM by composition and tension properties /hardness
- >50% of boiler component – SH & RH tubing, header and piping designed based on creep properties – maximum allowable stress
- Serviceability of these components controls by creep properties
- Any alternation of Gr. 91 microstructure will change creep properties & serviceability of Gr. 91 and can lead to premature failure

Fundamental Metallurgy:

Microstructure, Properties & Serviceability



Microstructure → Properties

Problems encountered in the use of of Grade 91 material

Problems encountered in the use of the CSEF materials can be categorized as originating from one or more of the following areas:

– Design

- *Failing to consider inherent limitations of material, such as oxidation*
- *Failing to consider potential impact of manufacture, such as weld design & DMW*
- *Design margins related to specific operating conditions*

– Material Production (Tube, Pipe and Plate)

- *Chemical composition, Cr content, Ni+Mn, tramp elements (Sn, Sb, As...)*
- *Casting and forging to produce uniform composition & microstructure*
- *Heat treatment, uniform heating & cooling during normalizing and tempering treatments, adequate time at temperature*

– Manufacturing (Fabrication)

- *Effective experience with Grade 91*
- *Receipt Inspect of “raw” material*
- *Control of bending and other forming operations*
- *Control of welding operations*
- *Close control of all thermal processing operations*

– Installation

– Operation

