

# Nickel-Base Superalloys for Advanced Power Systems



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Special Metals Corporation**



**The 4<sup>th</sup> International Symposium –Supercritical CO<sub>2</sub> Power Cycles  
September 9-10, 2014, Pittsburgh PA**

# Presentation Outline

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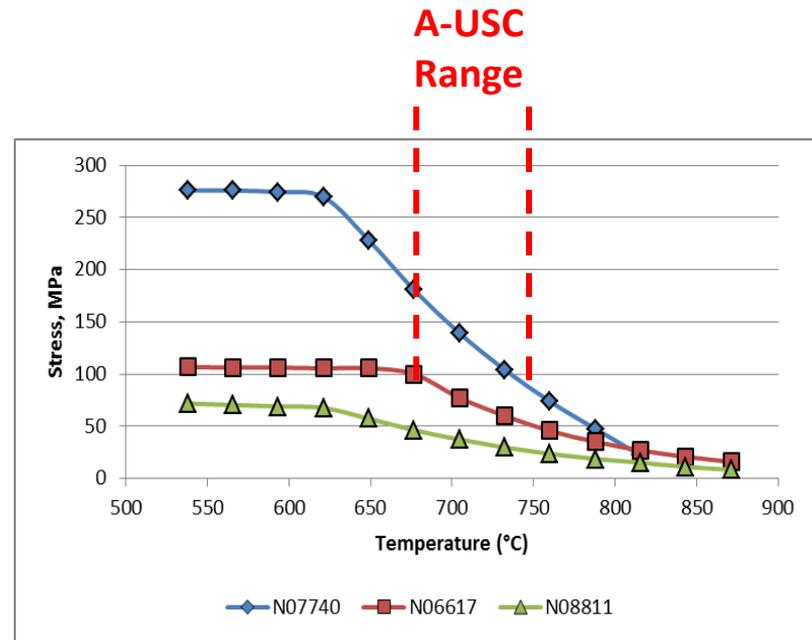
- **Superalloys – from Aerospace to Energy**
- **Mechanical Properties**
- **Microstructure Stability**
- **Corrosion Properties**
- **Manufacturing Mill Forms**
- **Fabrication**
- **What remains to be done?**



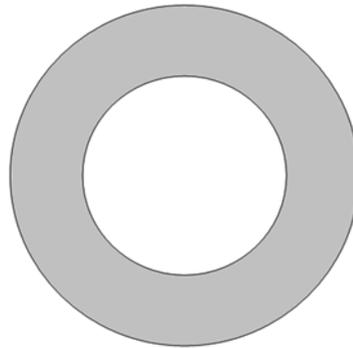
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# Why Superalloys?

- USC to A-USC
  - 100/150°C temp Increase
  - Oxidation/corrosion rate increases significantly
- Materials
  - Ferritic Stainless Steel
  - Austenitic SS/Nickel-Base
  - Superalloys
- Cost
- Availability

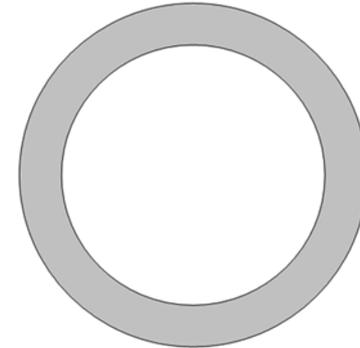


ASME Design Stress Max



**617**

**368 mm OD**  
**82.5 mm W**  
**324 cm<sup>2</sup> A**  
**626 kg/m**



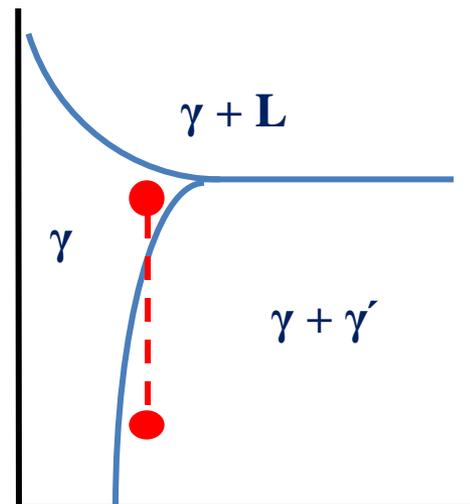
**740H**

**368 mm OD**  
**46.6 mm W**  
**594 cm<sup>2</sup> A**  
**380 kg/m**

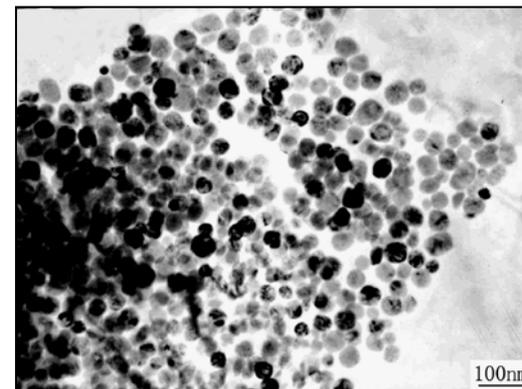


# Superalloys = Age-Hardened Nickel Base Alloys

- Gamma prime ( $\gamma'$ ) Strengthened Alloys
  - Soft and ductile in annealed condition
  - Age-harden to increase strength
  - $\text{Ni}_3(\text{Al}, \text{Ti}, \text{Nb})$  precipitate
  - Cubic, coherent, sub-micron size
  - Stable at high temperature
- Phase diagram
- Adjust other elements for specific properties (Cr, Mo, Co)



Pseudo-binary phase diagram



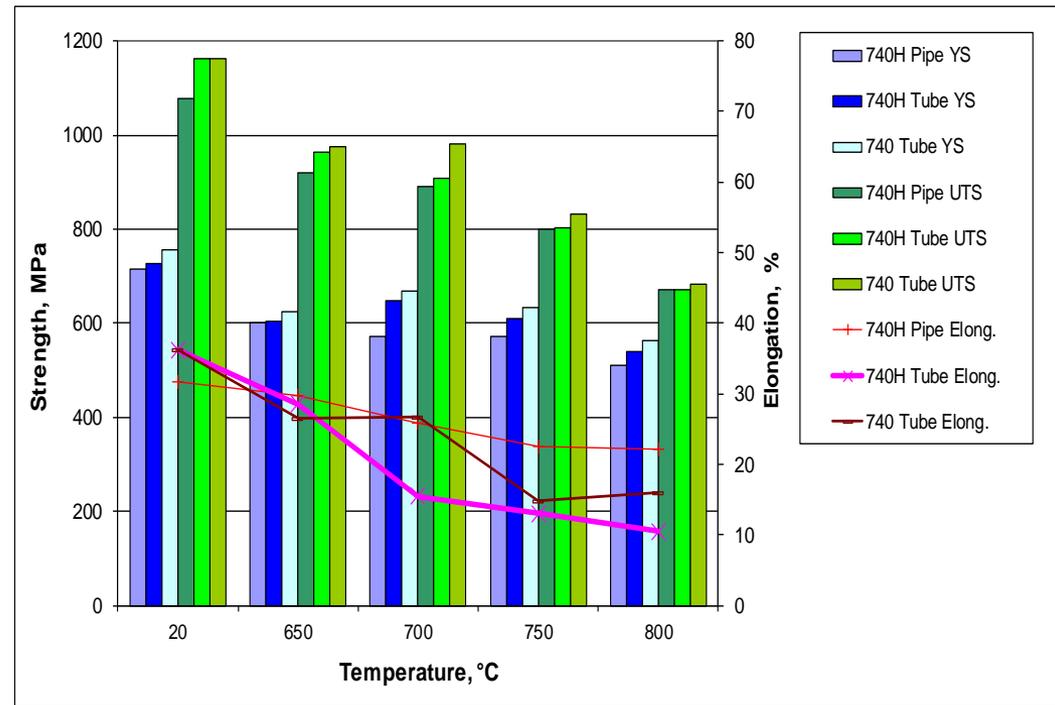
TEM Showing fine  $\gamma'$  particles (Xie)

Alloy	C	Cr	Mo	Co	Al	Ti	Nb	Si
263	0.06	20	6	20	0.4	2.2	0	0.15
740	0.03	25	0.5	20	0.9	1.8	2	0.5
740H	0.03	25	0.5	20	1.35	1.35	1.5	0.15



# Tensile Properties

- ASME code requirement based on room temperature tensile test
- Impact and creep properties for information
- ASME minima
  - YS: 90 ksi (620 MPa)
  - TS: 150 ksi (1035MPa)
  - El: 20%



Ambient and elevated temperature tensile properties of tube and pipe

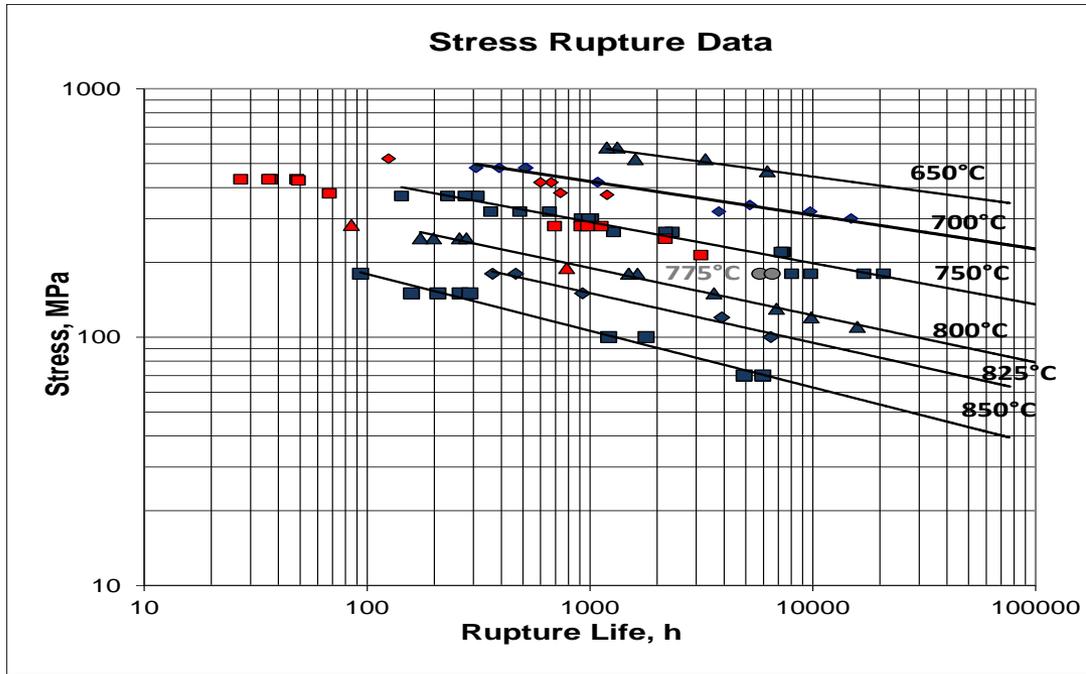
## Standard Heat Treatment for 740H

- SA: 1100°C (min), 1 h/it, WQ
- AH: 800°C, 4 h (min) +, AC

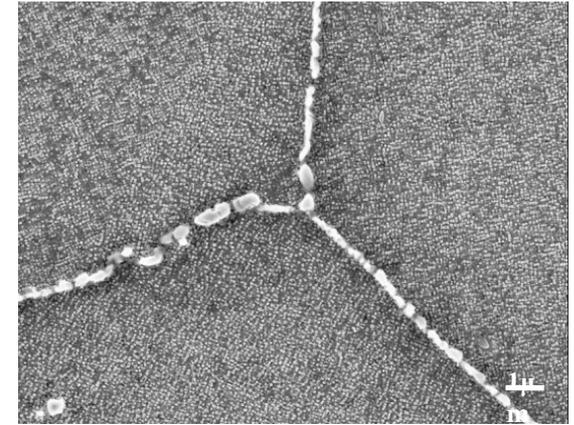


# Creep Properties

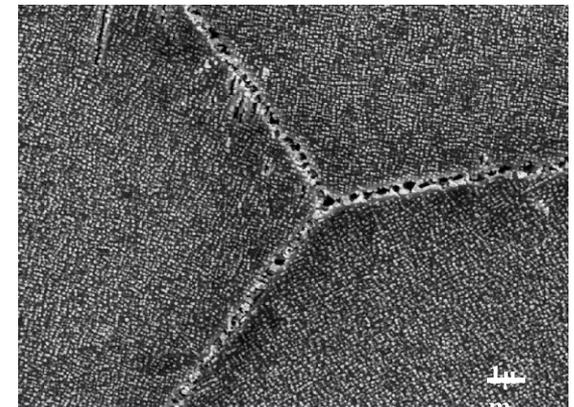
- US Consortium data generated at ORNL
- Recent data to 45,000 h
- Tests now running will exceed 100,000 h



Composite data from US Consortium and SMC Tests



Sample from shoulder, rupture in 1087.4 h at 750°C and 280 MPa

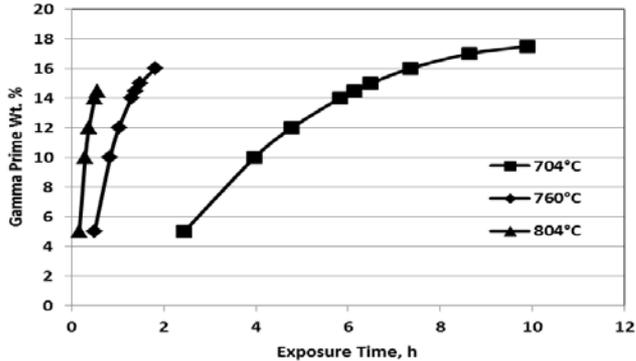


Sample from reduced section

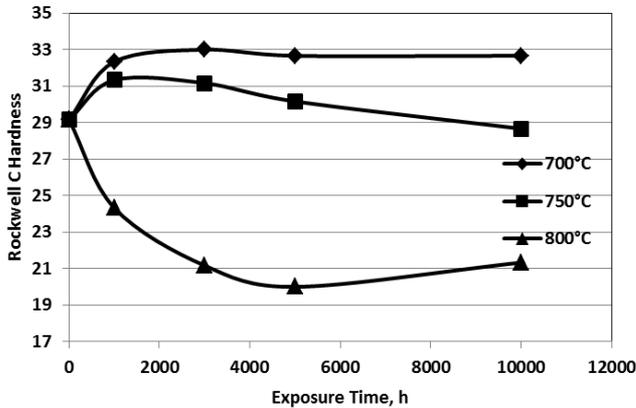


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# Microstructure

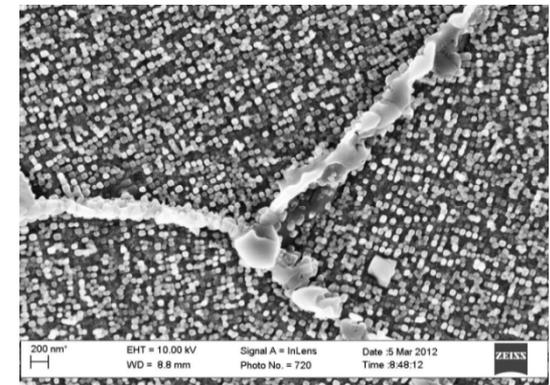


## JMatPro prediction of $\gamma'$ volume

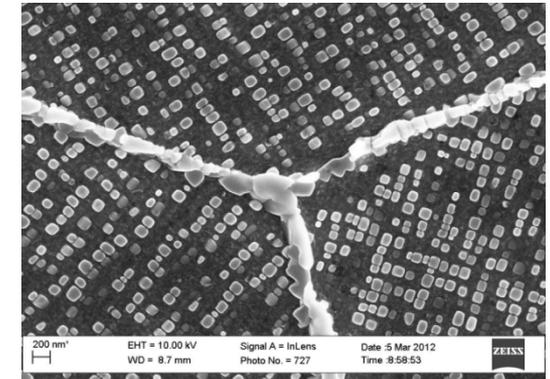


## Rockwell C Hardness

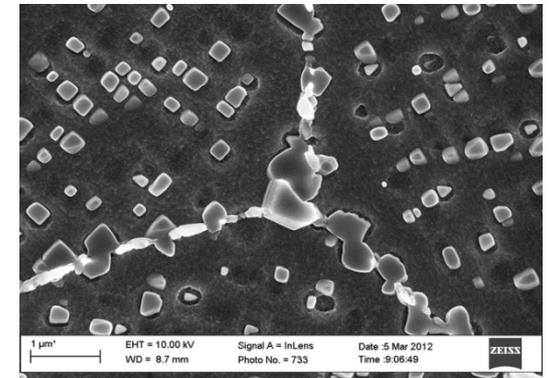
- Amount of  $\gamma'$  decreases with increasing temp.
- Size of  $\gamma'$  increases with time and Temp.
- Particles remain cubic
- Volume fraction and size affect strength



700°C



750°C

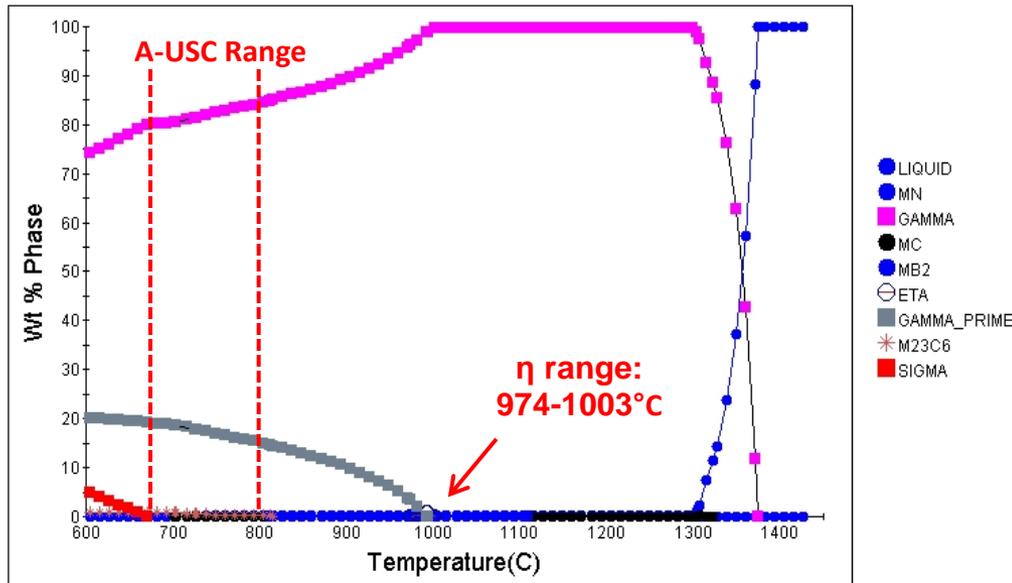


800°C

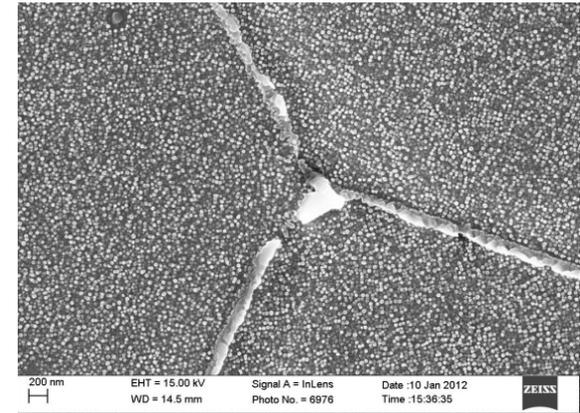
# Microstructure Stability

- Isothermal stress-free aging studies conducted for 10,000 h
- No  $\eta$ -phase or G-phase detected

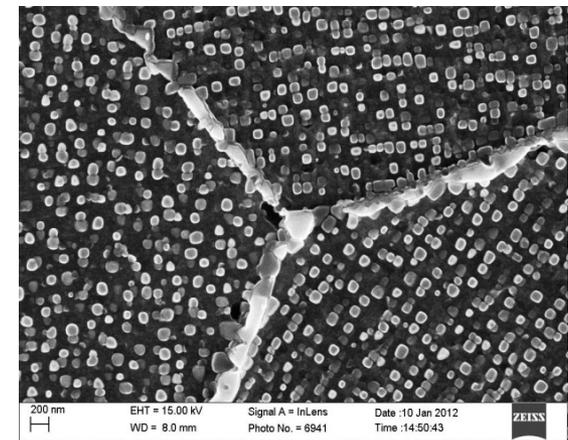
Ni-24.75Cr-0.04W-0.006Mo-0.234Mn-0.136Si-1.32Al-0.045C-20.17Co-0.2387Fe-0.031C



Thermo-Calc predicted equilibrium diagram for alloy 740H showing restricted stability for  $\eta$ -phase



Microstructure after aging



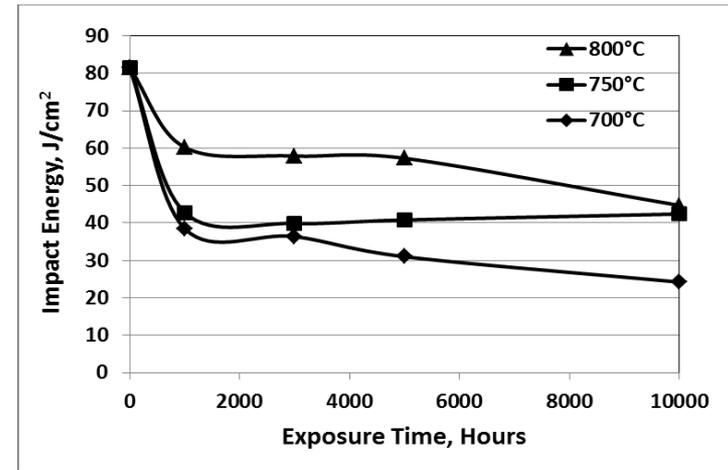
Microstructure after exposure at 750°C for 3000 h



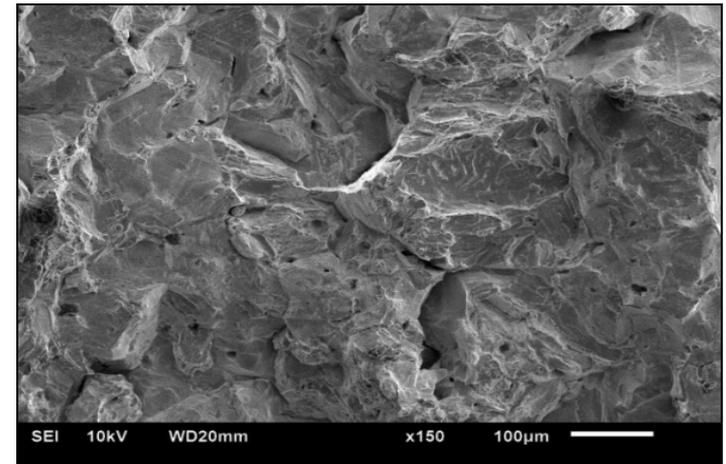
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# Impact Toughness

- As-aged, CVN ambient temp impact toughness high
- Initial drop possibly due to increased carbide coverage at grain boundary
- Toughness stabilizes after 1000 h
- Fracture path largely inter-granular after exposure



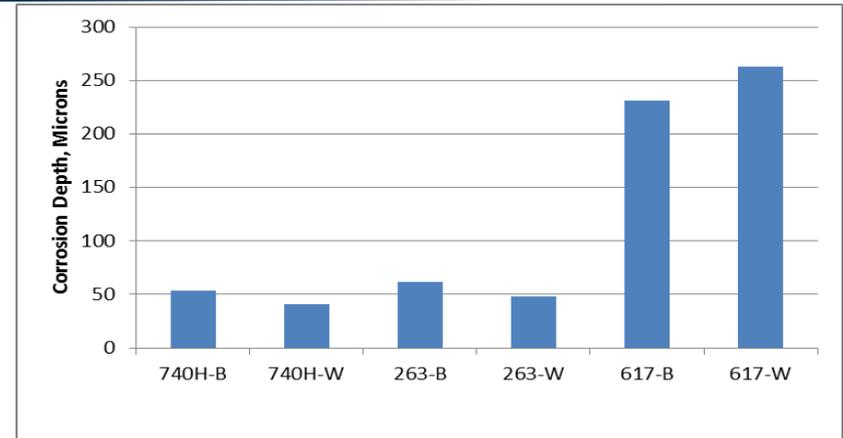
Extruded and heat-treated pipe samples



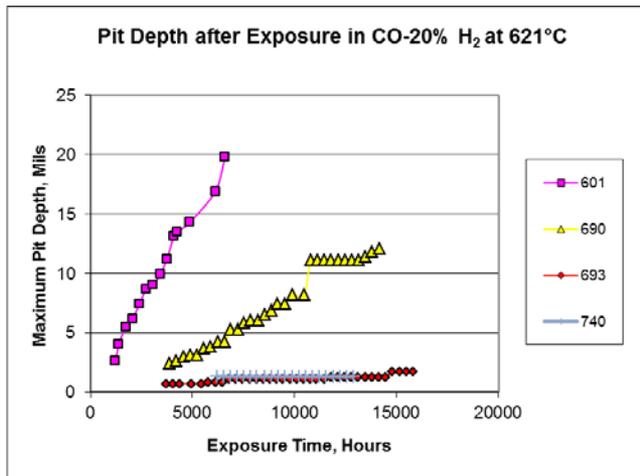
SEM Fractograph of pipe sample exposed for 3042 h at 700°C

# Oxidation and Corrosion

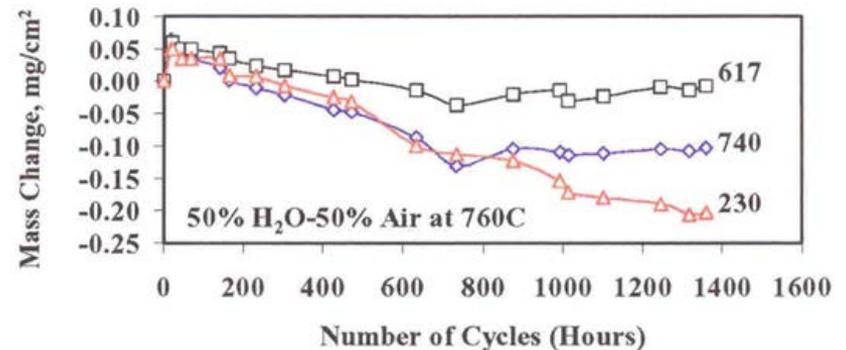
- Air Oxidation
- Steam Oxidation
- Coal Ash Corrosion
- Supercritical CO<sub>2</sub>
- Metal Dusting
- Stress-Corrosion



Pit depth, base metal and matching weld metal. 1000 h at 750°C in simulated Chinese coal ash



Pit depth after exposure in H<sub>2</sub>O-20% CO<sub>2</sub> at 621°C



Mass change in 50% H<sub>2</sub>O-50% Air at 760°C



# Manufacturing – Ingot Production

- Vacuum Induction Melting
  - Cleanliness, Composition Control
- Vacuum Arc Remelt
  - Cast Structure Control
- Large Ingots (27,000 lb/ 12,250 kg) have been produced



VAR ingot in shop after cooling



Head macro-etch slice of homogenized 750 mm diameter VAR ingot

Element	Edge	Mid-Radius	Center
C	0.044	0.044	0.043
Cr	24.61	24.63	24.64
Al	1.36	1.36	1.36
Ti	1.34	1.33	1.33
Co	20.12	20.12	20.14
Nb	1.46	1.45	1.44



# Manufacturing Tube

- Forge bar, machine and trepan billet, extrude shell
- Pilger, draw or roll form tube
- Heat treat (SA vs SA + A)
- Sizes made:
  - 21.3 mm (0.83 in) OD x 2.7 mm (0.10 in) W to
  - 50.8 mm (2 in) OD x 8 mm (0.31 in W)
- Possible size range:
  - 12.7 mm (0.5 in) OD to
  - 280 mm (11 in) OD



Tube shell emerging from extrusion press



Finished, bundled tube



# Manufacturing Pipe

- Forge rod, cut mult, block & pierce, machine billet, vertical extrude
- Condition
- Heat-treat
- Sizes made:
  - 323 mm (12.7 in) OD x 22.5 mm (0.88 in) W and
  - 378 mm (14.8 in) OD x 88 mm (3.46 in) W
- Sizes possible:
  - 254 mm (10 in) OD x 25.4 mm (1.0 in) W to
  - 790 mm (31 in) OD x 63.5 mm (2.5 in) W
  - Many other OD/W combinations



Wyman-Gordon 15 kT blocking press and  
35 kT extrusion press



378 mm (14.8 in) OD x 88 mm (3.5 in)  
W x 10 m (33 ft) L extruded 740H pipe

# Tube and Pipe Bends

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- **Tube bending**
  - Cold or hot
  - Cold workability similar to 625
  - If strain  $> 5\%$ , assembly must be re-annealed
  - Bending in the aged condition is not recommended
- **Pipe bending**
  - Must be done hot ( $>1950^{\circ}\text{F}$ ) due to the high strength of the alloy
  - Induction bend to be demonstrated later this year



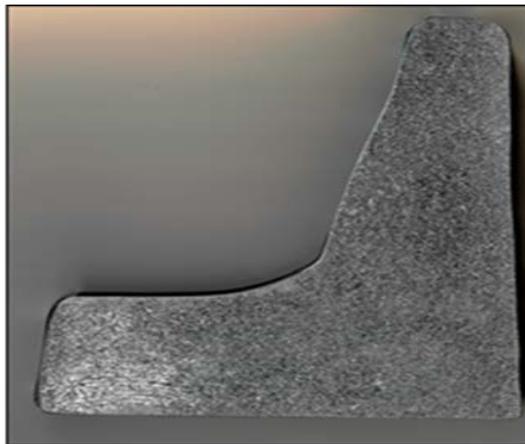
Tube bends and welds  
produced by Babcock &  
Wilcox for US  
Consortium

# Small Forged Fittings

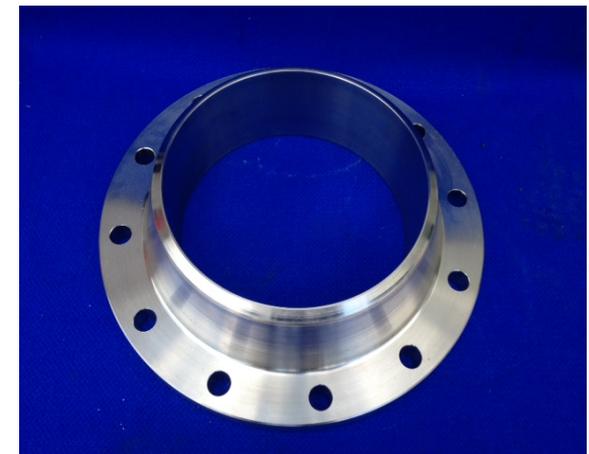
- Flanges, nipples, saddles, weldolets, reducers, tees and wyes
- Hammer or press forge
- Example weld-neck flange made at Maass Flange (Houston TX)
- Properties of heat-treated forging met ASME Code requirements
- More difficult shapes will be demonstrated in future



As-forged weld neck flange



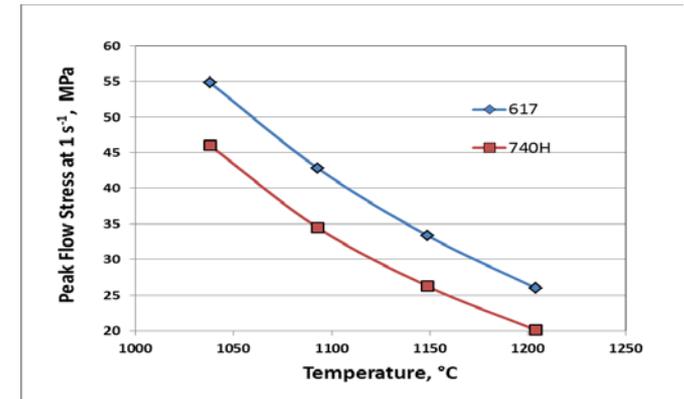
Etched cross-section



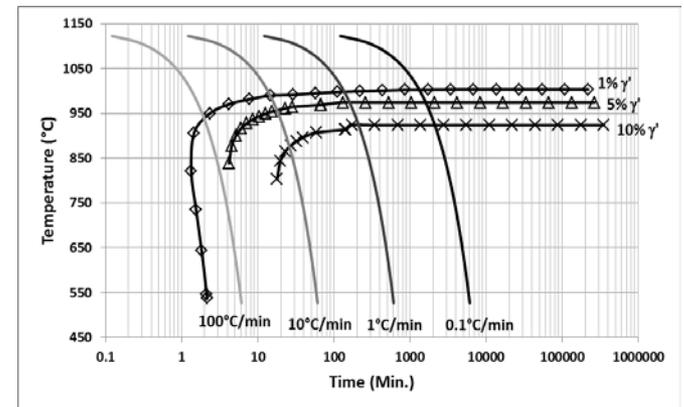
Machined flange

# Large Forged Shapes

- Valve bodies, large wyes and tees, turbine casings and nozzle guide vanes
- Press forged or ring rolled
- Flow stress of 740H less than most superalloys
- Due to auto-aging, large forgings must be given spheroidizing treatment before machining
- Properties of heavy forged bar being determined



Peak compressive flow stress at strain rate of 1 sec<sup>-1</sup>



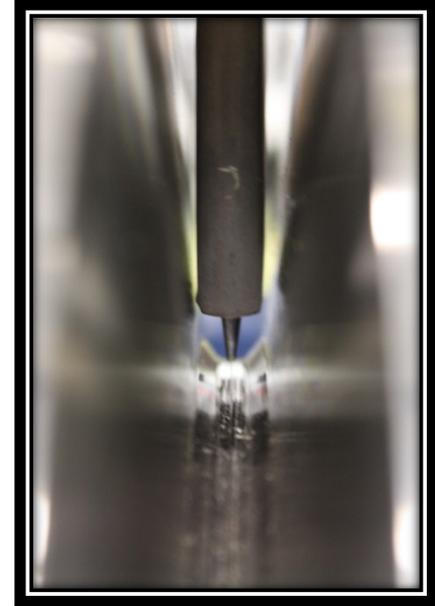
CCT diagram simulated using JMatPro



# Welding

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- Welding has been a major focus for 740H development
- Procedures have been developed for GTAW and GMAW welding processes
- SMAW and SAW processes are not recommended due to low recovery of reactive (strengthening) elements
- ASME requires tube and pipe to be joined in aged condition. Welding in annealed condition is possible but not now code approved.
- Qualified welds have been made in material with wide range of thickness: 6.4 mm (0.25 in) to 88 mm (3.5 in)
- Best welding practices include control of shielding gas, close thermal management, control of bead geometry and interpass surface grinding
- ASME applies a WJSRF of 0.70 for longitudinal welds in creep limited applications.

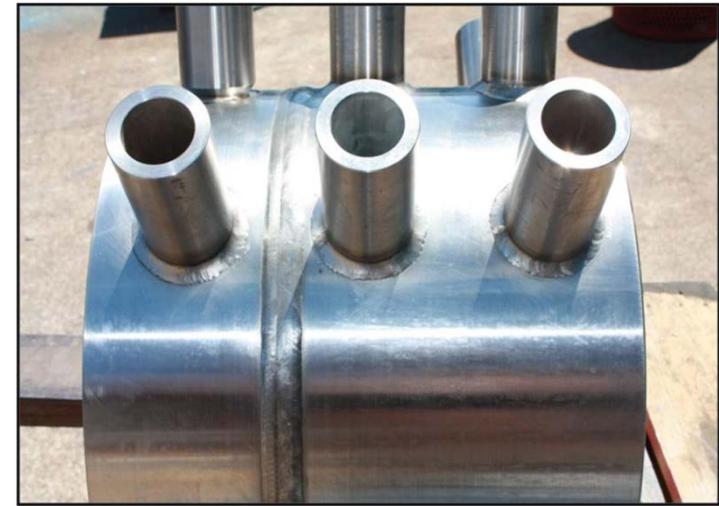


**HW/NG GTAW  
welding of 740H pipe**



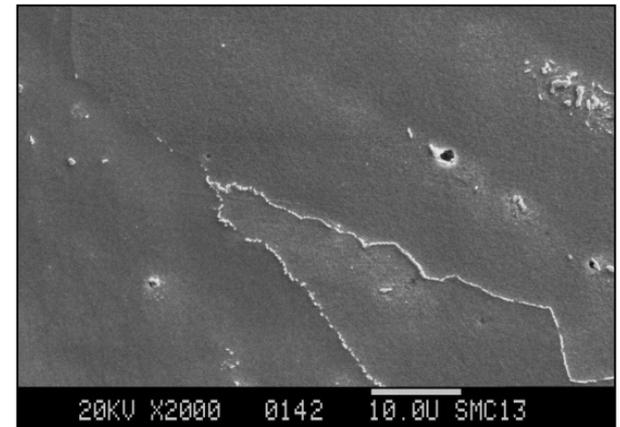
# A-USC Header Pipe

- Simulated header made from 355 mm OD x 76 mm W pipe
- Hot-Wire Narrow-groove GTAW process for girth weld (at B&W)
- Nipples welded internally with rotary GTAW torch, externally with manual GTAW
- Stress relieved (aged) at 800°C using external ceramic heating blanket



Appearance of finished header pipe segment

Cross-section of pipe weld with 1 degree bevel



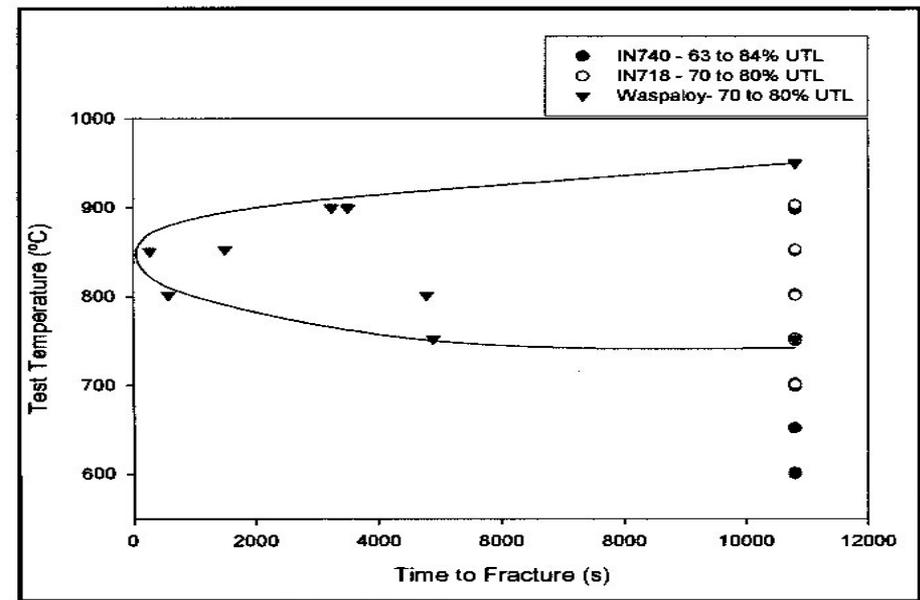
Weld metal after 10,000 h exposure at 700°C



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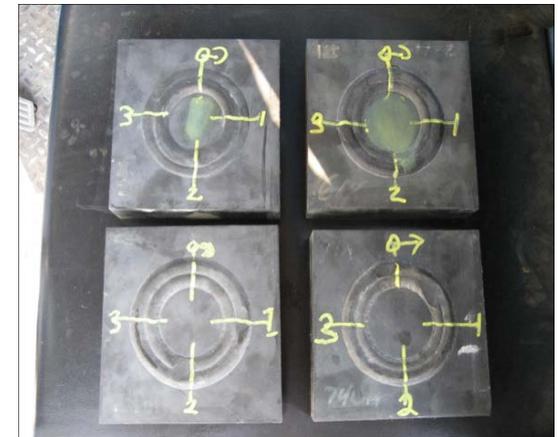
# Stress Relaxation Cracking

- Delayed cracking is seen in many creep-resistant alloy welds
- Strain aging mechanism
- Partial mitigation via stress relief treatments
- Ramirez showed 740H is similar to 718 in gleeble simulations
- No stress relief cracking reported in any 740H restrained weldment
- SMC Borland Test studies
  - No Cracking in 5000 h at 700°C



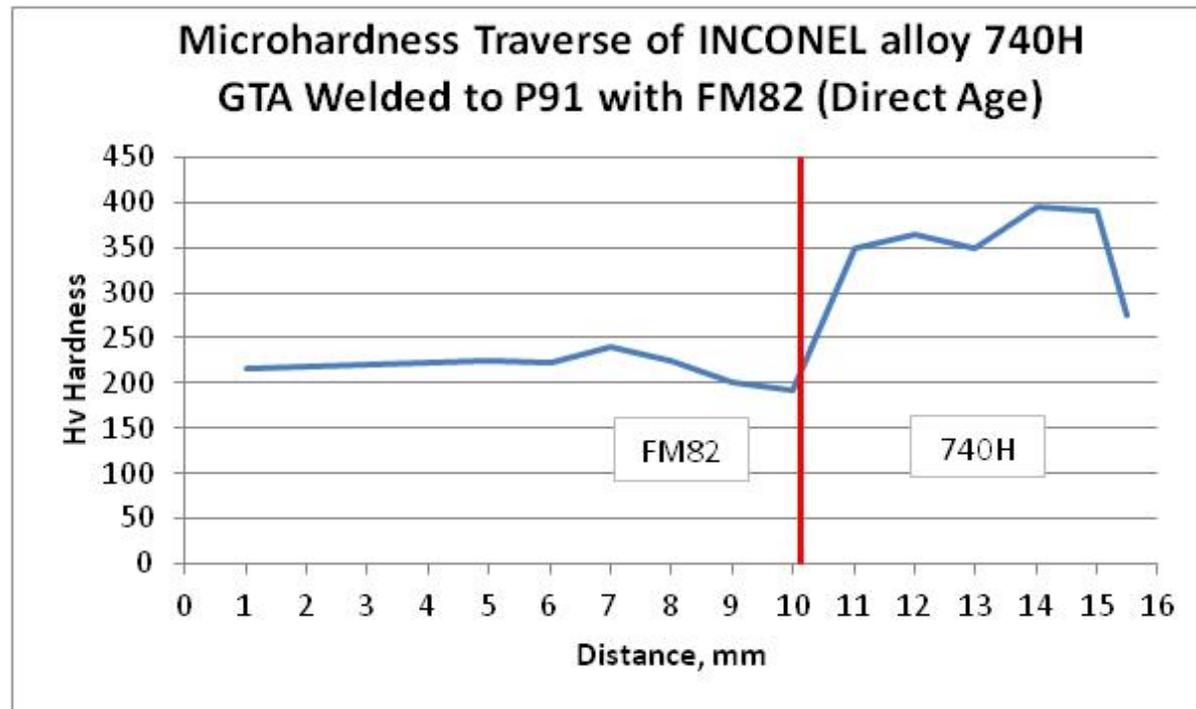
Gleeble tests. Specimens preheated to 1250C, cooled to RT, heated at 50C/s to test temp. and static loaded to % UTS (Ramirez/EWI)

Appearance of Borland test soecimens of 617 and 740H after 5,000 h.



# Dissimilar Metal Welds

- 740H will only be used in the hottest section of the A-USC plant
- Welded to ferritic or austenitic steel
- Experimental welds made to P92 and 316SS with FM82 and EPRI P87 fillers
- Qualification testing completed (bends and tensile tests) with tensile failure in steel



# What Remains to be Done?

- **Wide range of tube and pipe made to code requirements**
  - Refine manufacturing processes to reduce variability
  - Demonstrate 0.78 m OD pipe capability
- **Excellent corrosion resistance in many environments**
  - Generate data for more specific environments (Salt, CO<sub>2</sub>, Bio-mass)
- **Fittings and forged components**
  - Develop process and property data for representative components
- **Fabrication**
  - Improve weld creep-strength
  - Fully characterize stress relaxation cracking resistance
  - Develop repair welding capability
- **Characterize damage tolerance of base metal and welds**

