

Materials for Advanced Ultra-Supercritical (A-USC) Steam Boilers

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Advanced Materials Program*

Pat Rawls

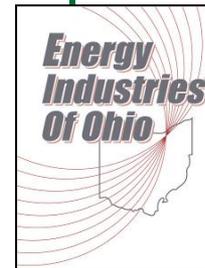
Vito Cedro, III



*Federal – State –
National Laboratory
Non Profit – For Profit
Cost Sharing Consortium*



**MAKING OHIO COAL
THE CLEAN CHOICE**



imagination at work



RILEYPower
A Babcock Power Inc. Company

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

This Project Plays a Key Role in the U.S. A-USC Boiler Effort

- Mechanical Properties of Advanced (Ni-based) Alloys
 - Creep-Rupture
 - Tensile
 - Wrought forms, welded components
 - Microstructural factors

- Steam-Side Oxidation Resistance

I.G. Wright and R.B. Dooley, “A review of the oxidation behaviour of structural alloys in steam,” *International Materials Reviews* 55 (2010) 129-67



Including the Successful ASME Code Case for Inconel 740

EPRI | ELECTRIC POWER RESEARCH INSTITUTE



U.S. DEPARTMENT OF ENERGY

Energy Industries of Ohio

Ohio Coal Development Office

Inconel® Alloy 740 Code Case Approval is Major Step for Advanced Ultrasupercritical Power Plants

A consortium funded by the U.S. Department of Energy (DOE) Office of Fossil Energy and the Ohio Coal Development Office (OCDO) has successfully gained American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code (B&PVC) approval for use of Inconel® Alloy 740 in Fossil Steam Boilers. This is a major step by the U.S. Department of Energy in the development of high-temperature materials needed for Advanced Ultrasupercritical (A-USC) steam cycles. These materials enable steam temperatures up to 760° C (1400° F), which can dramatically improve efficiency and reduce emission of all effluents (including carbon dioxide [CO₂]) by about 30% over the current U.S. coal-fired power generating fleet.

The long-term research necessary to gain approval was conducted by the U.S. DOE/OCDO A-USC Steam Boiler Consortium made up of the U.S. Boiler Manufacturers (ALSTOM Power, Babcock & Wilcox, Babcock Power, and Foster Wheeler) led by the Energy Industries of Ohio (EIO), the Electric Power Research Institute (EPRI), and the National Energy Technology Laboratory (NETL), with support from Oak Ridge National Laboratory (ORNL). The program has recorded a number of major accomplishments, and ASME B&PV Code approval of Inconel® Alloy 740 is one of the most critical steps needed before an A-USC demonstration power plant can be constructed.

The U.S. DOE/OCDO A-USC Consortium



Hot extrusion of an Inconel® Alloy 740 (ASME Code Case 2702) pipe at Wyman-Gordon (PCC Energy), Houston, Texas. The 10,000-plus-pound ingot was cast by Special Metals Corporation, Huntington, West Virginia. Inconel® Alloy 740 is the prime candidate alloy for advanced ultrasupercritical steam boilers. (Photo courtesy of Wyman-Gordon)

“The approval of Code Case 2702 will help enable future power steam boilers to operate with very high efficiencies, beyond today’s technology, significantly reducing CO₂ emissions from coal-fired power plants.”

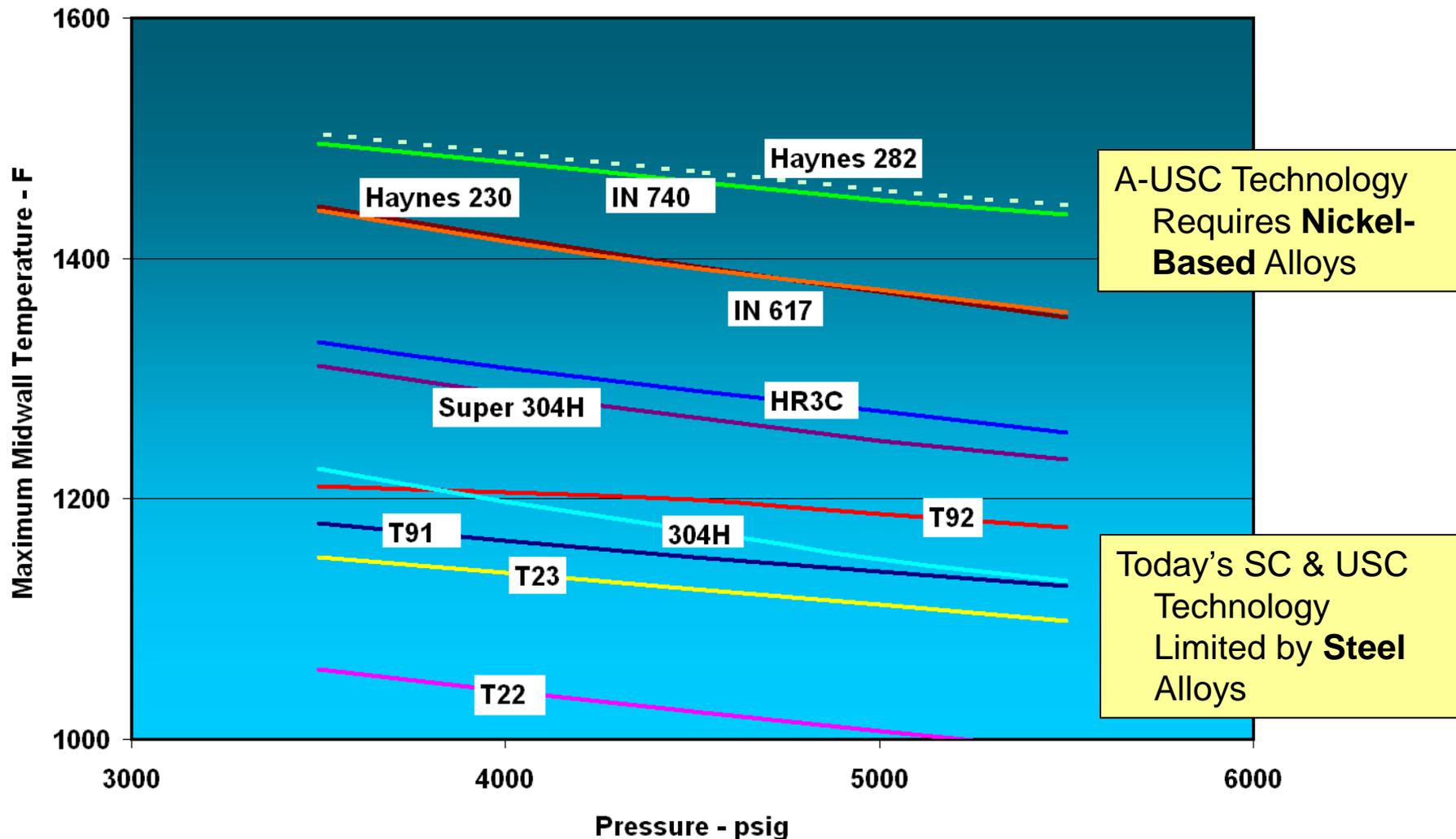
~ John Shingledecker,
EPRI Senior Project
Manager and A-USC Steam
Boiler and Turbine
Consortia Technical Lead

“World has taken notice.....precedent-setting case for age-hardening material”

Jack deBarbadillo
Special Metals, PCC
April 11, 2012

turbine suppliers to develop a
ency coal-fired power plants
materials technologies neces-
sures up to 760°C (1400°F).
tional supercritical to A-USC
ge systems. Higher-efficiency
nvironmental control systems,
ls which could withstand the
veloped a comprehensive pro-
gram with research primarily focused on a group of nickel-based alloys, including research into

Materials Selection for A-USC Alloys (Boiler Superheater/Reheater Tubing Strength)



A-USC Technology Requires **Nickel-Based** Alloys

Today's SC & USC Technology Limited by **Steel** Alloys

Courtesy EPRI



Creep-Rupture Testing, Data Interpretation, and Characterization are Highest Priority

- Generate data using accepted test methods, understand creep behavior & mechanisms, predict life
 - ASME Code Cases: Inconel 740 & Haynes 282
 - Supplement minimum required data for code-approved alloys: e.g., alloys 230 & 617
 - Identify and understand fabrication & welding issues: e.g., effects of cold-work on creep, weld strength factors
- Provide creep (and other) data for boiler design activities
- For creep tests, multiple stresses and temperatures

Minimum Creep Rate and t_f Measurements

- Minimum creep rates at constant stress tend to obey Arrhenius' law:

$$\dot{\epsilon}_m = A_0 \exp\left[-\frac{Q_c}{RT}\right]$$

$$A_0 = f(\sigma)$$

- Monkman and Grant observed that for a wide range of materials and test conditions:

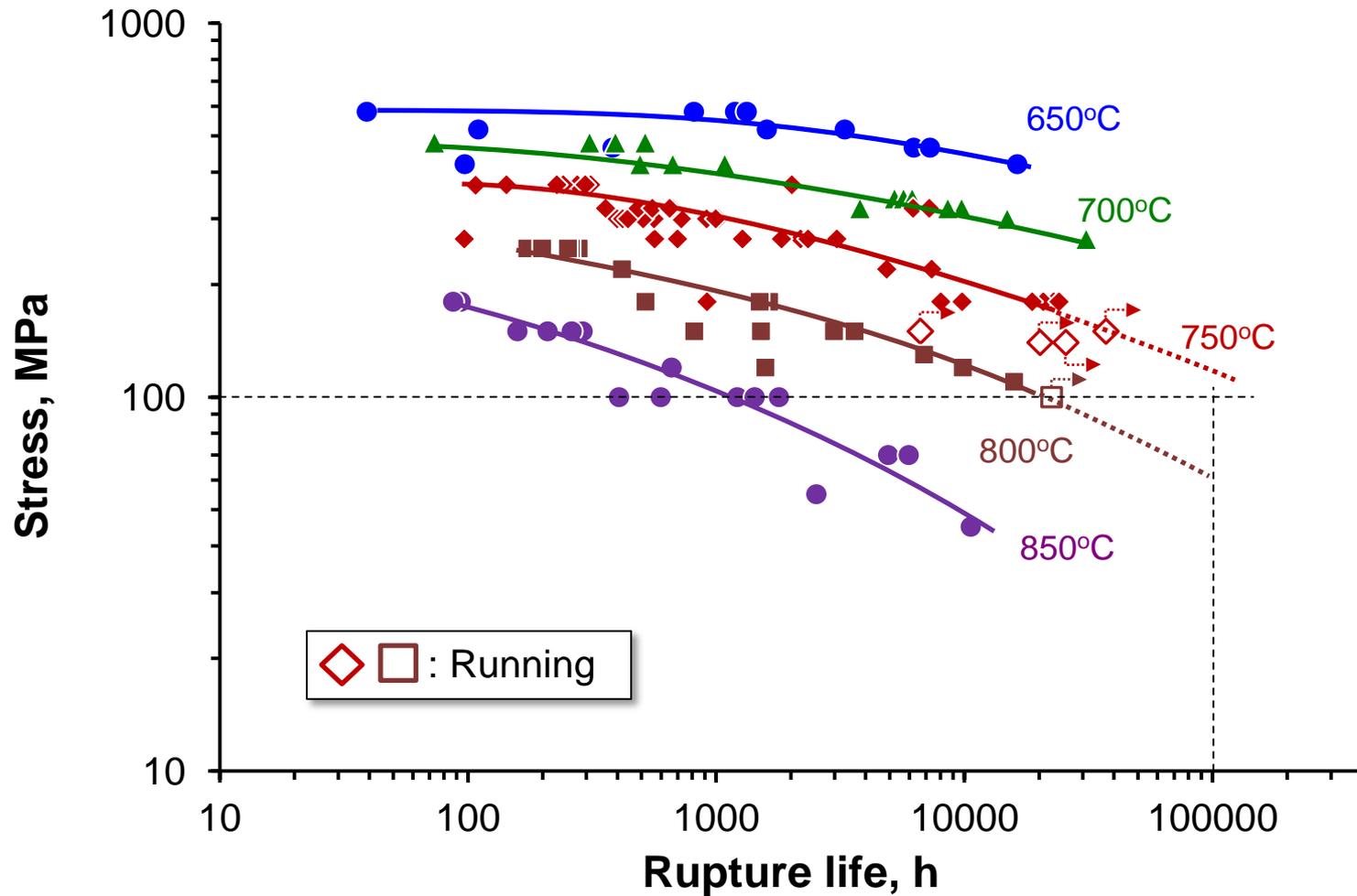
$$\dot{\epsilon}_m t_f = M$$

- Combining results in power law description of creep:

$$M / t_f = \dot{\epsilon}_m = A \sigma^n \exp(-Q_c / RT)$$

$$M / t_f = \dot{\epsilon}_m = A^* (\sigma / \sigma_Y)^n \exp(-Q_c^* / RT)$$

Longer-Time Tests of Inconel 740 Confirm Strength Retention Up to ~30,000h



Generating Similar Data for Haynes 282

Creep Data Analysis Should Permit Reasonable Life Predictions

- Power law often fails to permit reliable long term estimates based on short term data and does not capture some of the physical mechanisms known to be at play
- Based on accepted power law description, Wilshire et al. proposed:

$$\left(\sigma / \sigma_{TS} \right) = \exp \left\{ -k_1 \left[t_f \exp(-Q_c^* / RT) \right]^u \right\}$$

easy to manipulate, i.e., a linear relation exists between a log transformation of time and a transformation of stress and temperature

References

- Burt and Wilshire, Metallurgical and Materials Transactions 37A (2006) 1005-1015
Wilshire and Battenbough, Materials Science and Engineering A 443 (2007) 156-166
Wilshire and Scharning, International Materials Review 53 (2008) 91-103
Wilshire and Scharning, Materials Science and Technology 25 (2009) 242-248
Williams, Bache, and Wilshire, Materials Science and Technology 26 (2010) 1332-1337

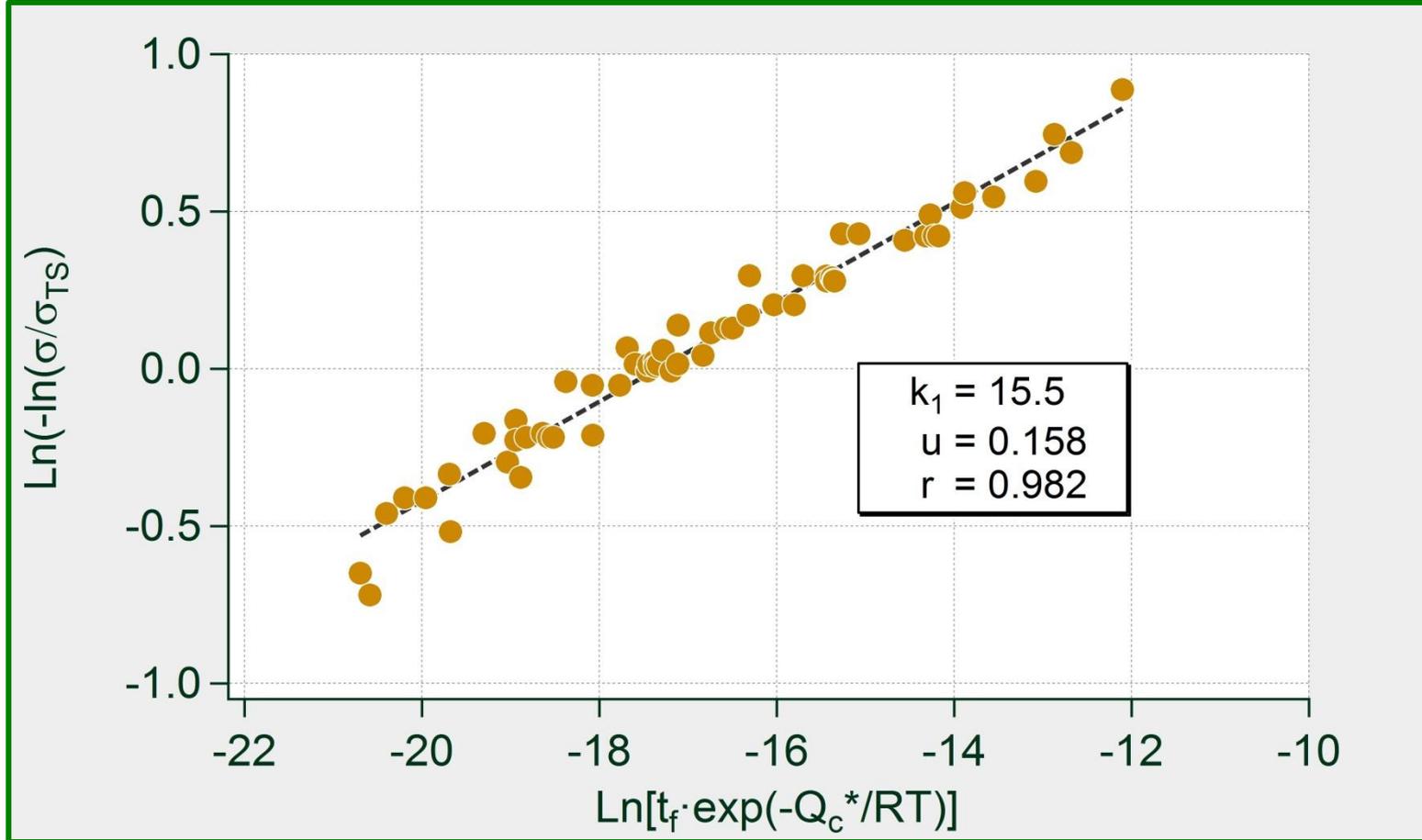
Wilshire-Scharning (W-S) Analysis Does Capture Some of the Materials Behaviors

$$\left(\sigma / \sigma_{TS} \right) = \exp \left\{ -k_1 \left[t_f \exp(-Q_c^* / RT) \right]^u \right\}$$

- $t_f \rightarrow 0$, as $\sigma \rightarrow \sigma_{TS}$
- $t_f \rightarrow \infty$, as $\sigma \rightarrow 0$
- Has the form of a Weibull distribution function, special case of more a general cumulative probability distribution function
- Need to measure σ_{TS}
- Need to determine k_1 & u
- Aim is reliable prediction of 100,000 h life using data limited to 5,000 h or less

Analysis Based on our Inconel 740 Database

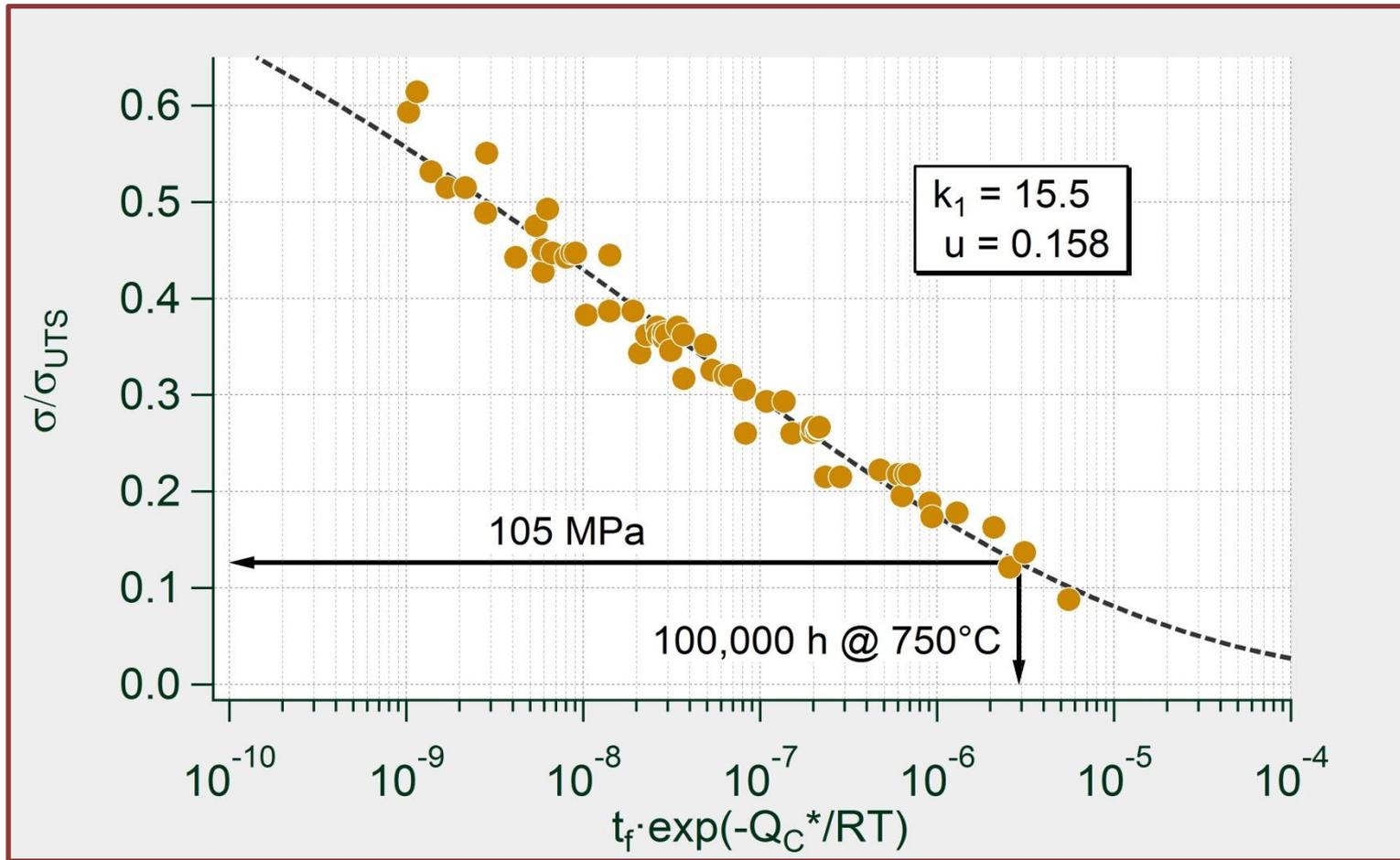
$$\ln[-\ln(\sigma / \sigma_{TS})] = \ln k_1 + u[\ln\{t_f \exp(-Q_C^* / RT)\}]$$



Linear regression yields the Wilshire constants, k_1 & u

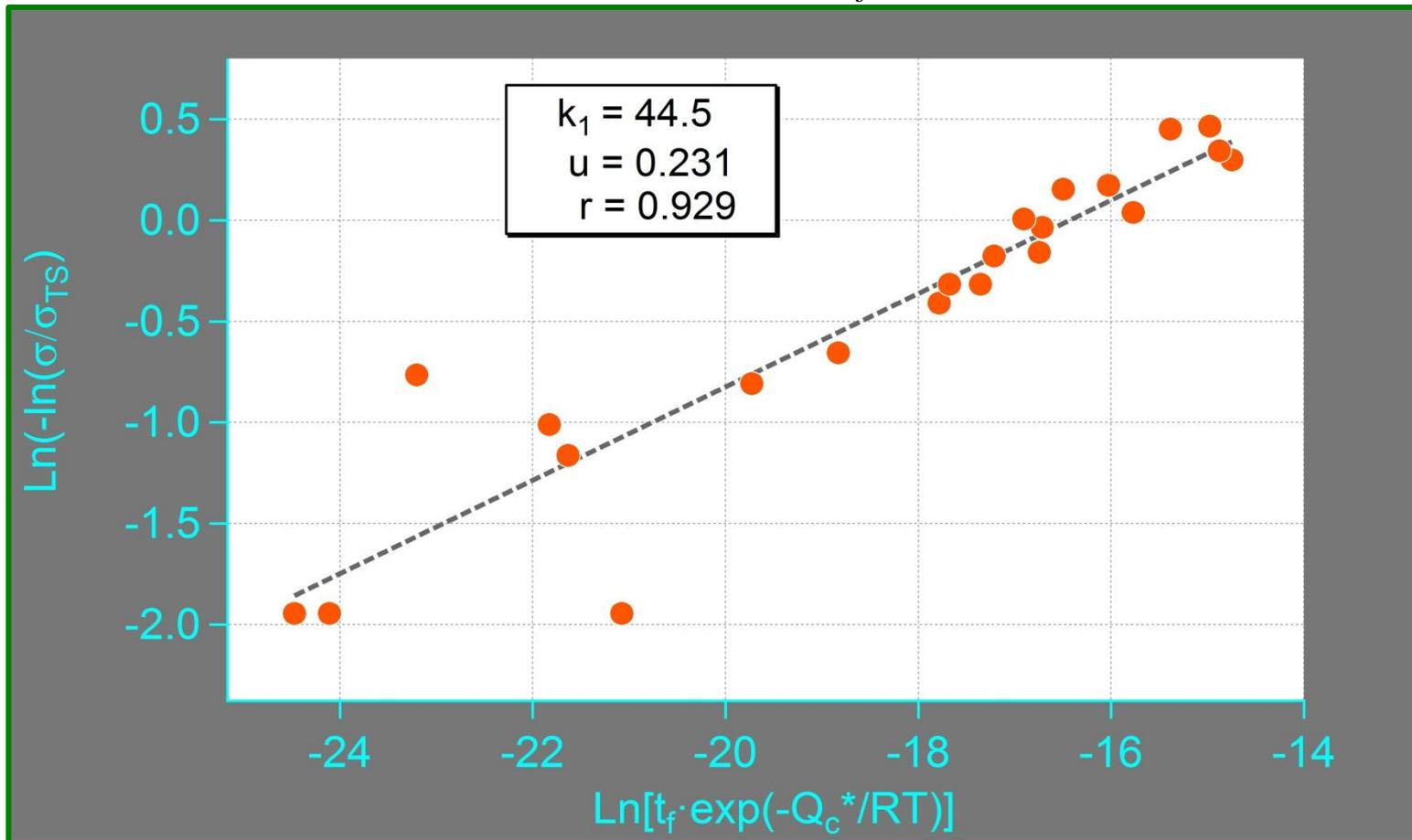
W-S Predicts 100,000 h Life for 105 MPa at 750°C for Aged Inconel 740

$$(\sigma / \sigma_{TS}) = \exp\{-k_1 [t_f \exp(-Q_c^* / RT)]^u\}$$



W-S Analysis Was Also Done for Solution-Annealed (SA) 740H

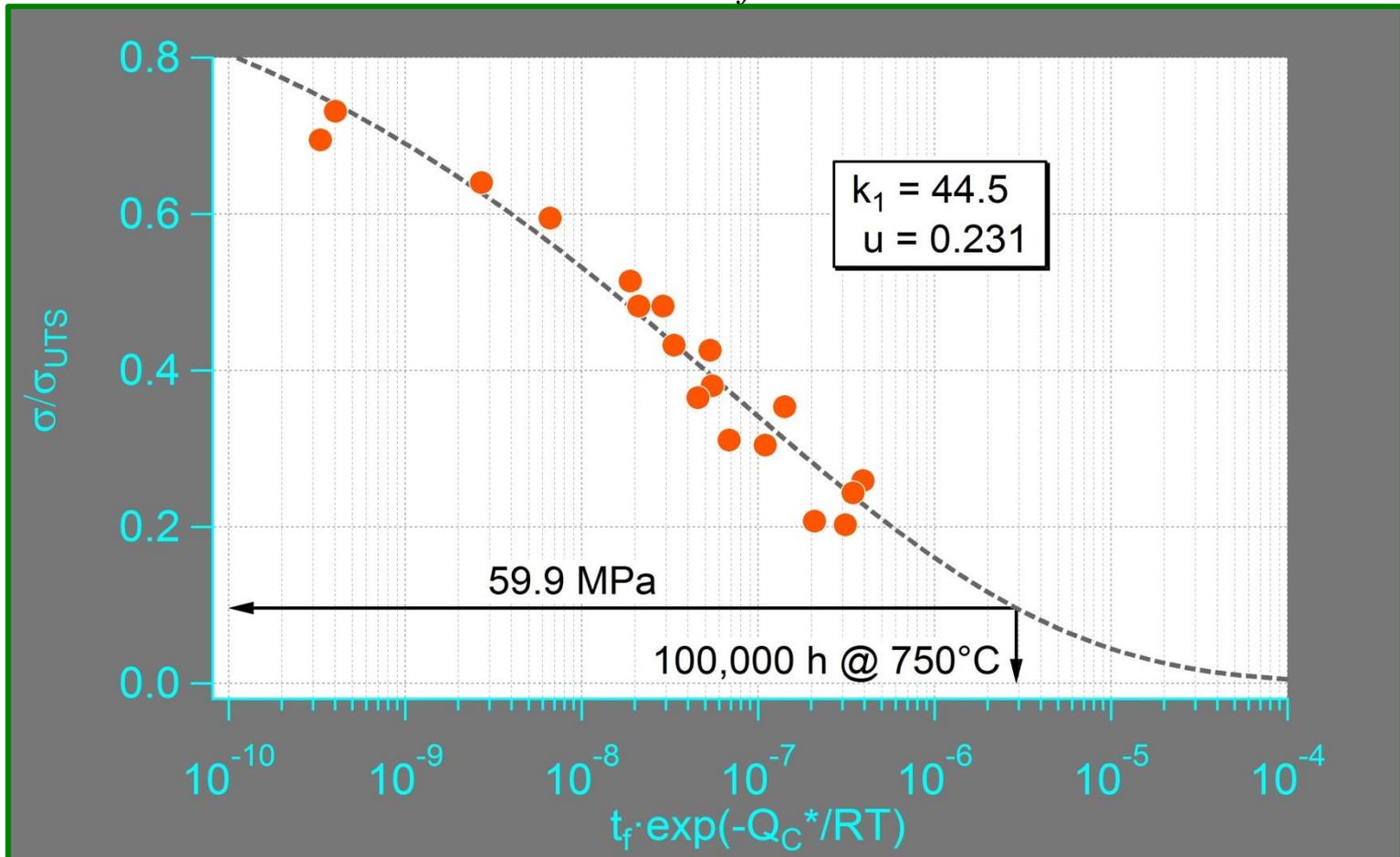
$$\ln[-\ln(\sigma / \sigma_{TS})] = \ln k_1 + u[\ln\{t_f \exp(-Q_C^* / RT)\}]$$



- k_1 : aged, 15.5 vs. SA, 44.5
- u : aged, 0.158 vs. SA, 0.231

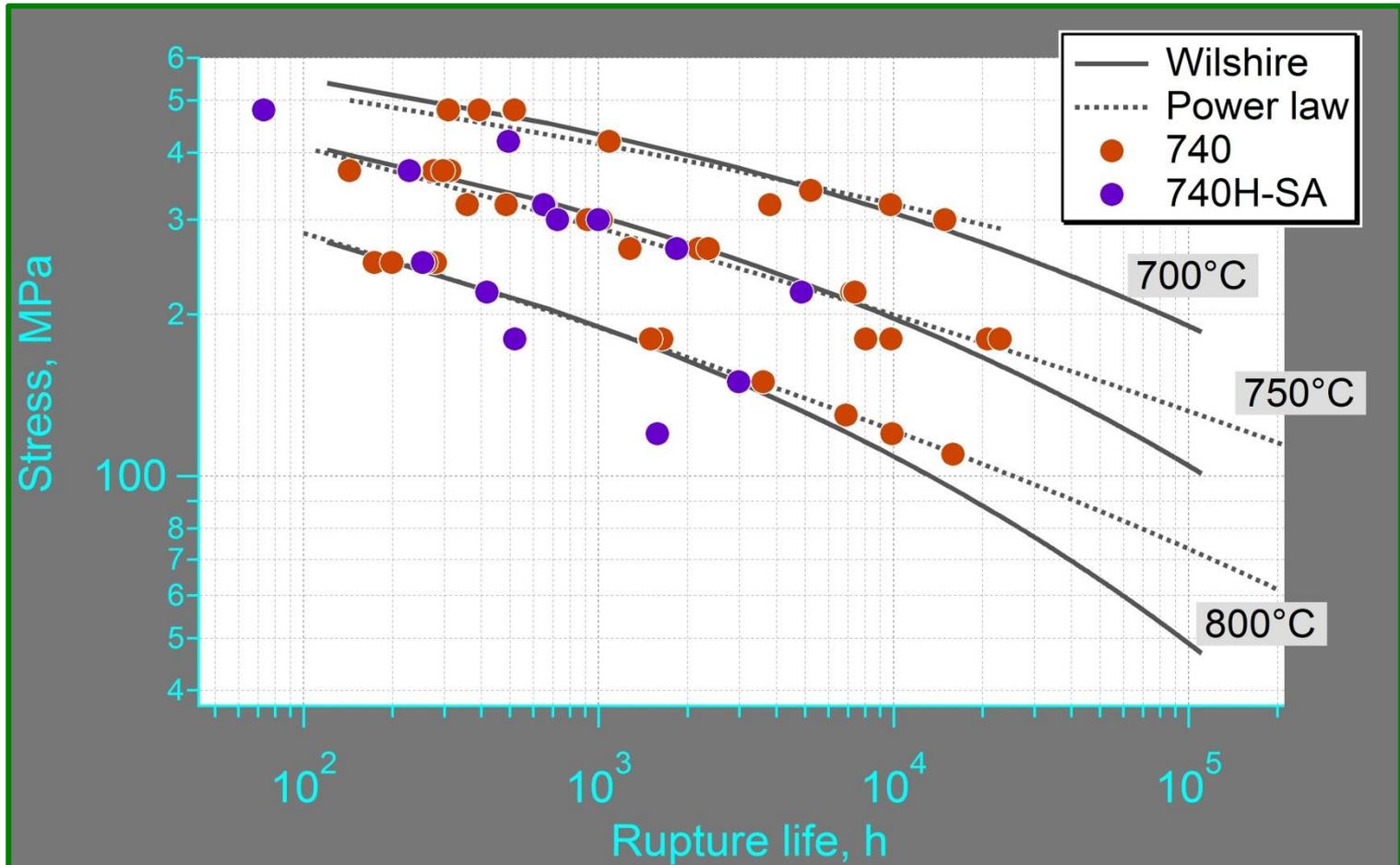
Clear Reduction in Creep Resistance of SA 740 vs. Aged 740

$$(\sigma / \sigma_{TS}) = \exp\{-k_1 [t_f \exp(-Q_c^* / RT)]^u\}$$



SA vs. aging reduces 100,000 h/750 C creep strength from 105 MPa to 60 MPa

For Inconel 740, W-S Is More Conservative than Power Law at Long Times



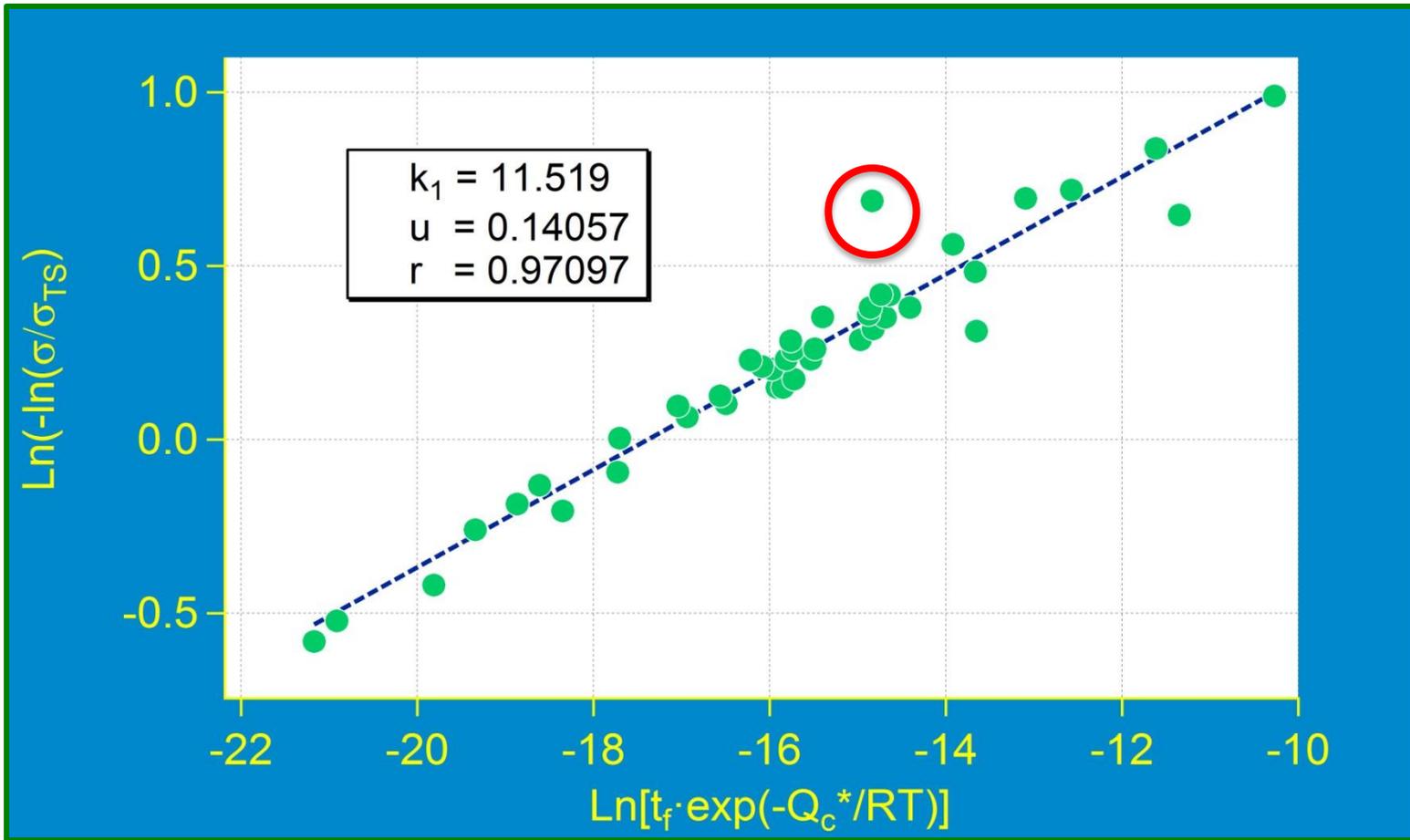
Applying W-S Analysis to Haynes 282

Source	Number of specimens	Temperature Range, °C	Stress Range, MPa	Ruture Life Range, h
GE	19	700-788	155-504	453-12,556
Haynes	19	649-982	25-586	100-10,000
AUSC Boiler	3	750-800	200-300	783-1514

- Boiler specimens were only solution annealed
- Larson-Miller parameter was used to convert data for plots of Stress-vs-Life at 700, 750, & 800°C

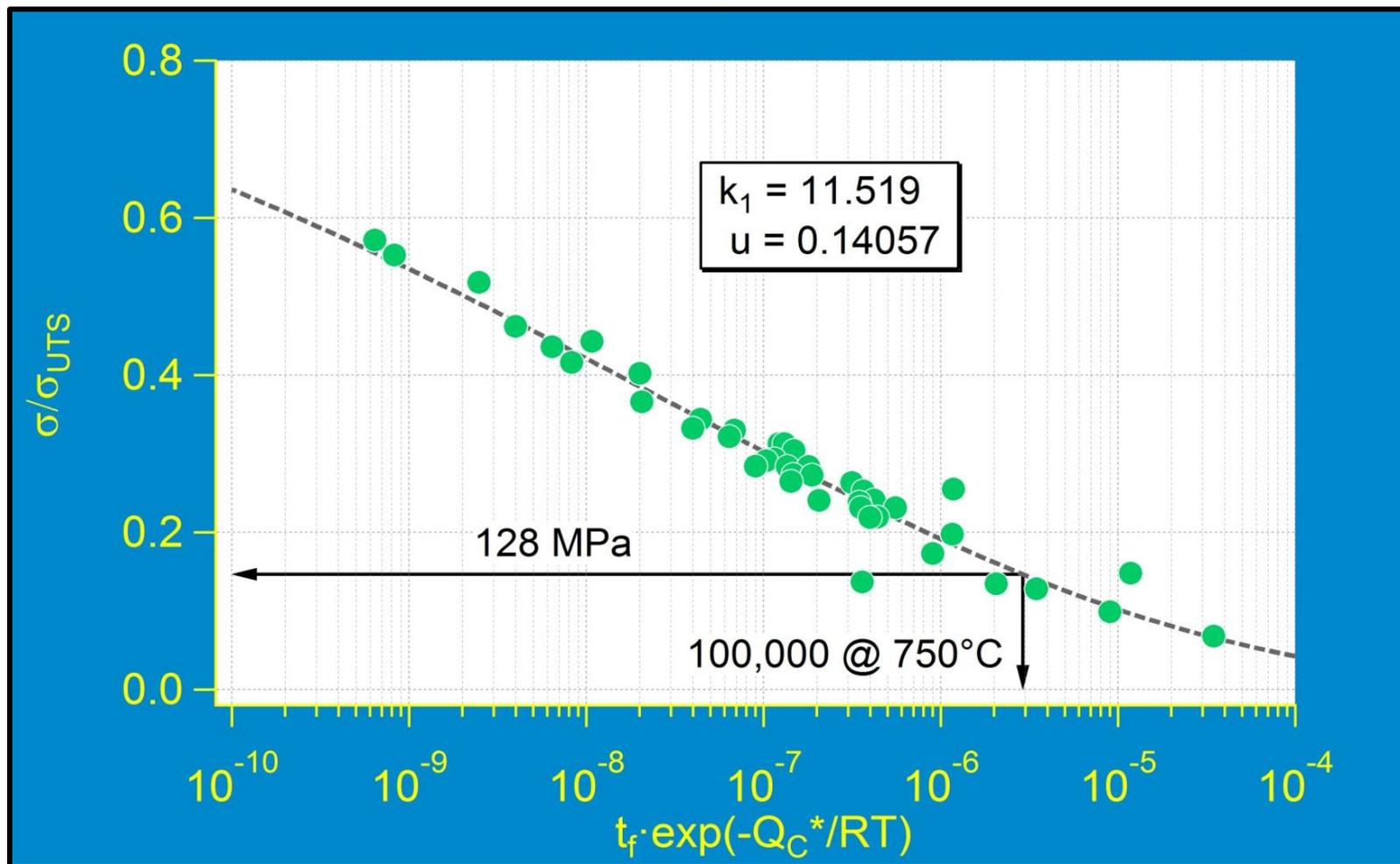
Linear Regression Yielded the Wilshire Constants, k_1 & u , for the Whole 282 Dataset

$$\ln[-\ln(\sigma / \sigma_{TS})] = \ln k_1 + u[\ln\{t_f \exp(-Q_C^* / RT)\}]$$

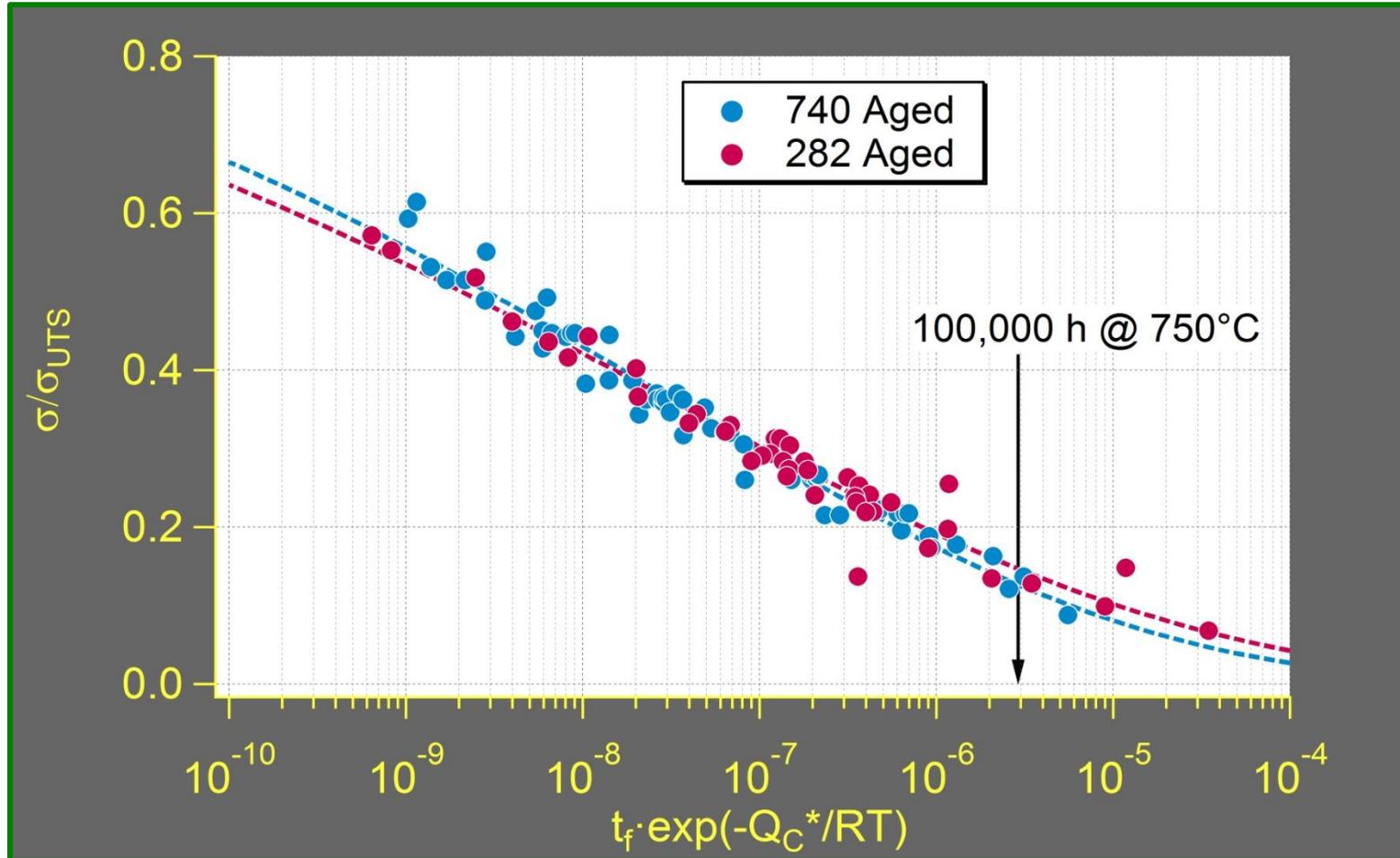


W-S Model for Aged 282 Predicts 100,000 h at 750°C and 128 MPa

$$\left(\frac{\sigma}{\sigma_{TS}}\right) = \exp\left\{-k_1 \left[t_f \exp\left(-Q_c^* / RT\right)\right]^u\right\}$$

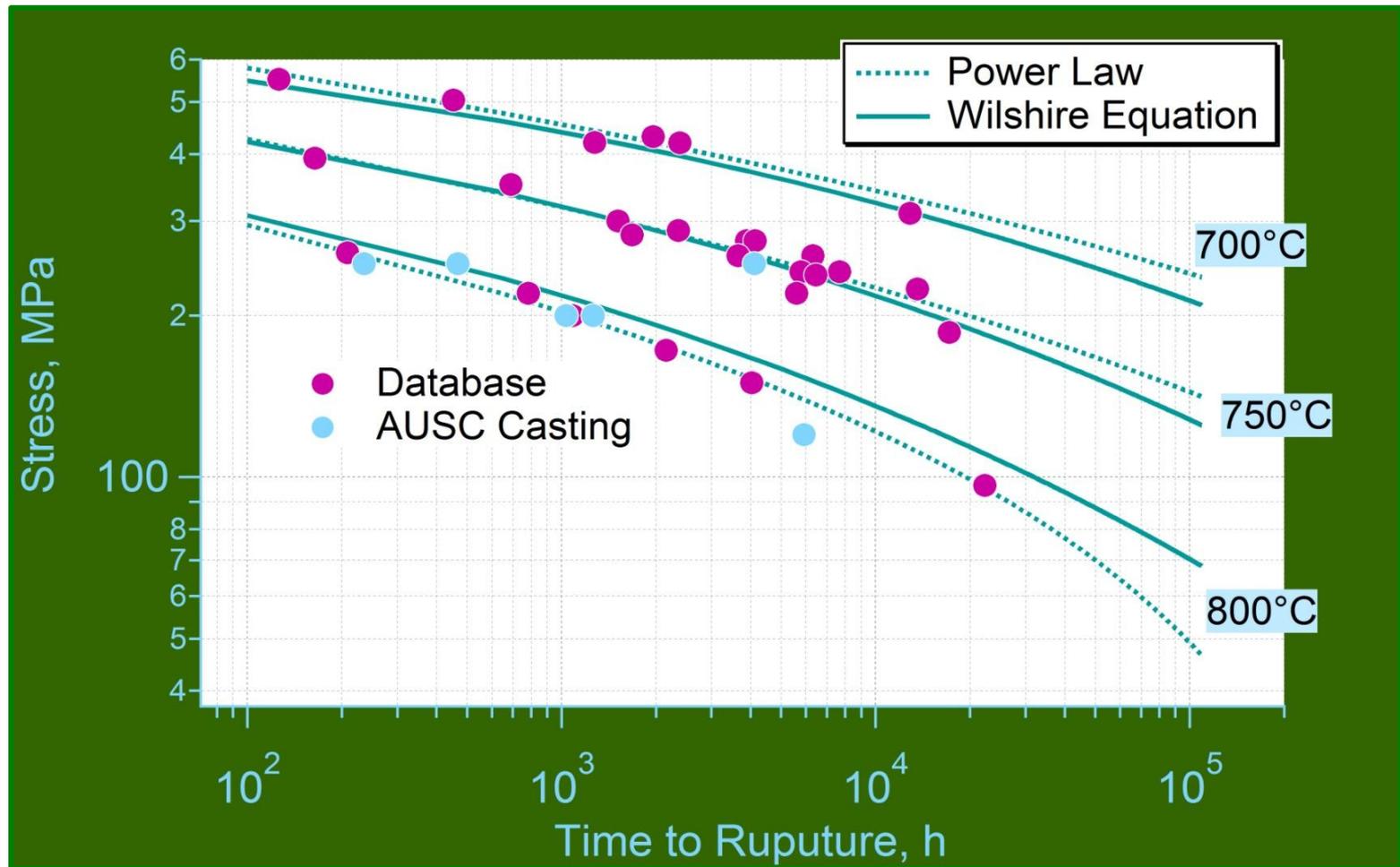


Comparison of W-S Predictions Showed Higher Strength for Aged 282 vs. 740



For 100,000 at 750 C, compared to 740 (105 MPa) the higher predicted strength of 282 (128 MPa) is consistent with its higher Mo

W-S vs Power Law Comparison for 282



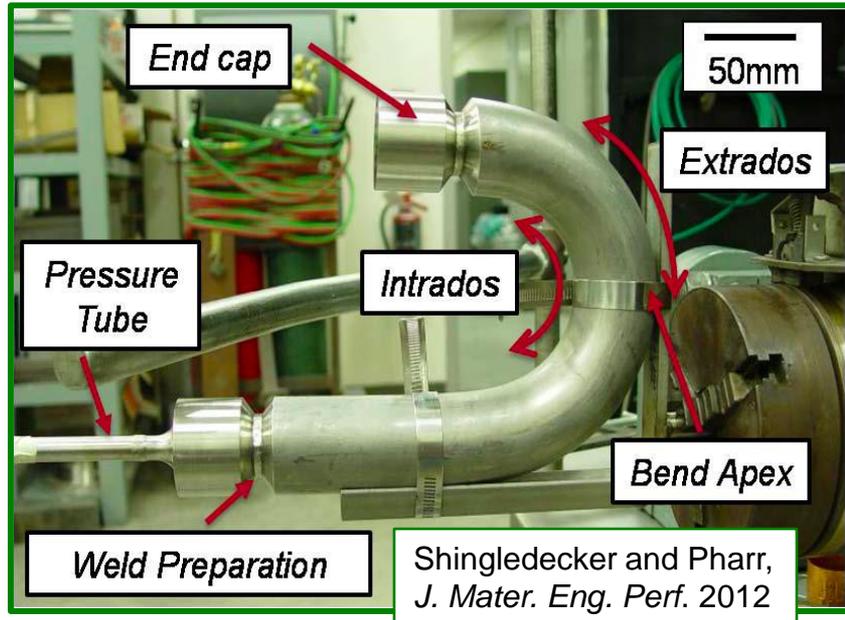
Compared to power law:

- Wilshire is more conservative at 700 C & 750 C
- Wilshire overestimates rupture life at 800 C

Power Law and W-S Creep Models

- Embody some fundamental materials behavior like diffusivity
- Use experimental data as basis for regression analyses
- Incorporation of materials behaviors is incomplete in both
 - Wilshire-Scharning uses correct boundary conditions
 - Wilshire-Scharning may be more realistic with respect to stochastic nature of the behaviors
- Predictive capabilities are compromised because of the preponderance of shorter-term data and the fact that real materials behaviors are not accurately represented

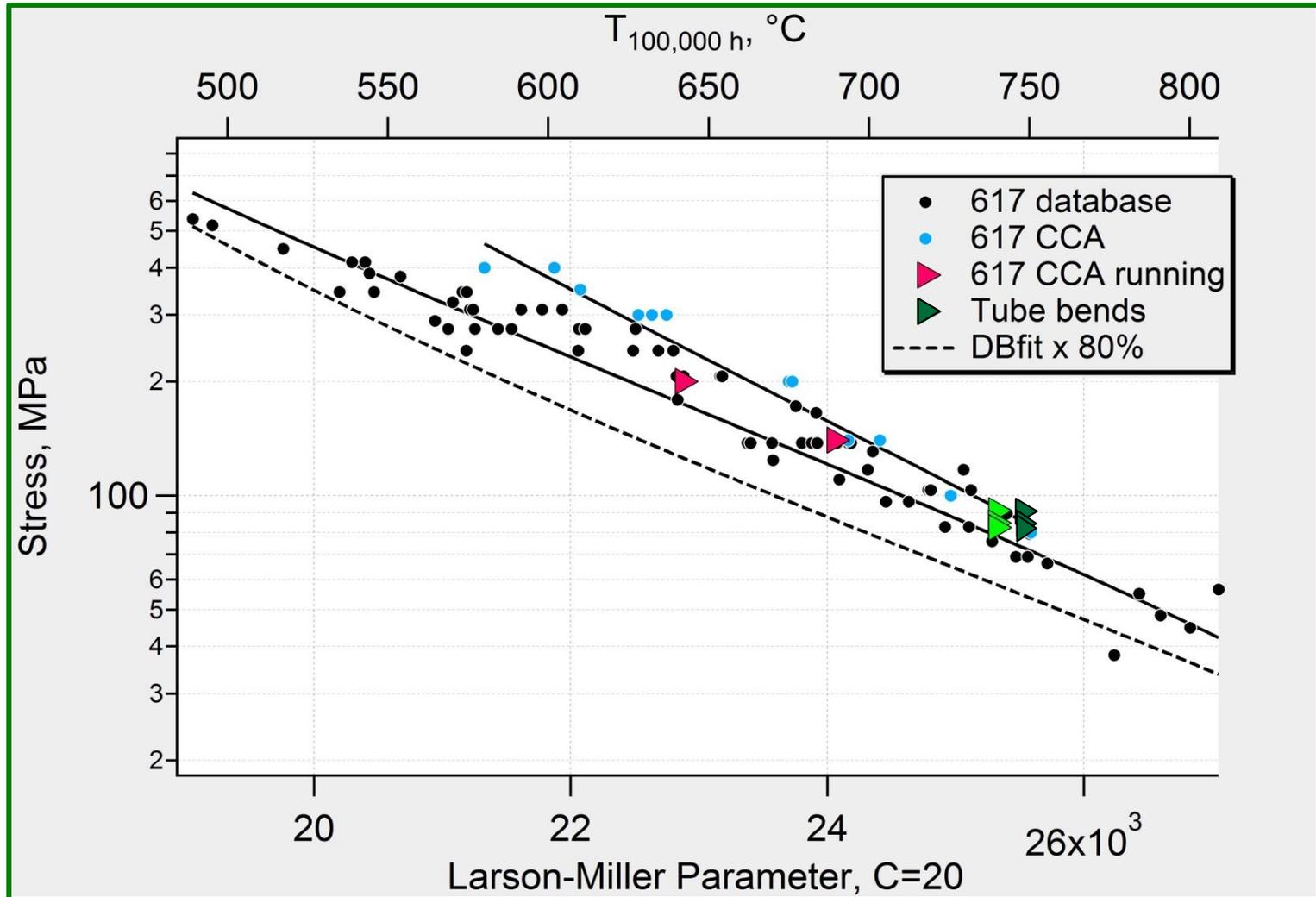
Pressurized Tube Bend Creep Tests Are Aiding Determination of Cold-Work Limits



Cold-bent tubes are being creep tested to provide guidance for determining fabrication rules for Ni-base alloys

- 740 SA tested; significant reduction in creep life; new set scheduled for testing in aged condition
- 617 running at 775 C, 5600 psi (80-90 MPa), $t \rightarrow 21,000$ h

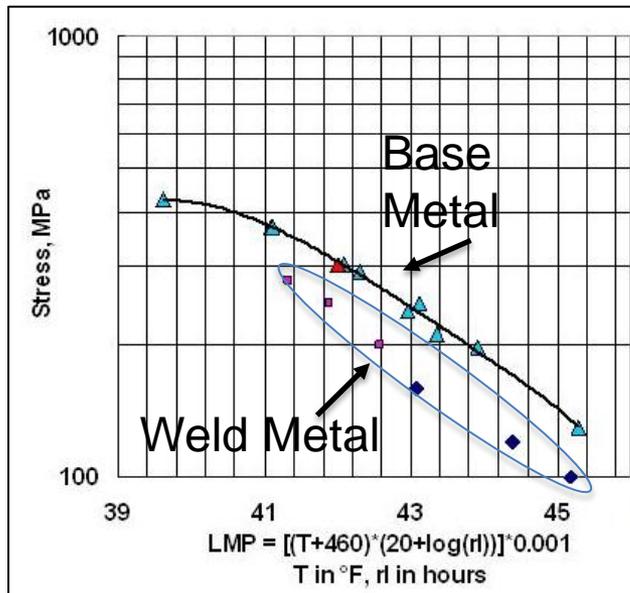
Running 617 Tube Bends Data Consistent with Wrought Behavior



Weld Strength Factors Are Being Studied

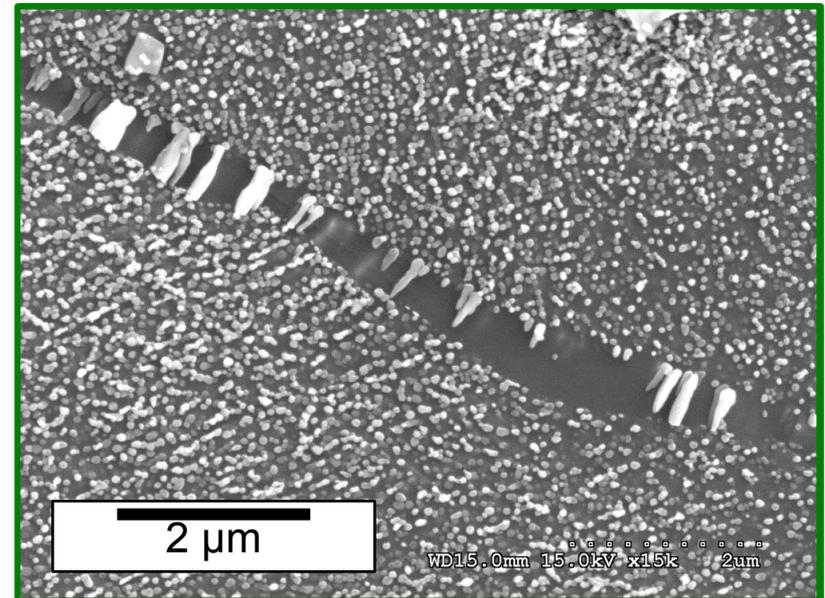


- GTAW with 740 and 282 filler metal, supplied by B&W
- 2-inch-OD x 0.4-inch-wall 740 tube



Weld strength reduction factor of 0.7

Fig. and Micros: Dan Bechetti and John DuPont, Lehigh University



γ' -Free zone along boundary toward base metal

Also Examining Welded Plate



2 Welds produced by B&W

- 740 w/282 filler metal (10 specimens)
(Plate - aged; weldment - as-welded)
- 282 w/282 filler metal (15 specimens)
(Plate - solution annealed; weldment – as-welded)

Creep-Rupture Lives Better for 282 Welds

Temp. (°C)	Stress (MPa)	Life (h)		
		740/740	740/282	282/282
700	400	168- 788	364	1333
750	220	693- 790	2589	2418
800	180	237- 646	654	1692
800	120	1664	5103	9085

Going Forth

- Pushing ahead with creep data for 282 relevant for code case (one heat)
 - Aging conditions
 - Several times at 5 temperatures
- Completing creep database for Inconel 740
- Creep-rupture testing of welded 740 and 282, microstructural analysis
- Tube bends
 - 617 at predicted life of wrought
 - Another set of aged 740 tubes will be exposed

2011 Milestones & Status:

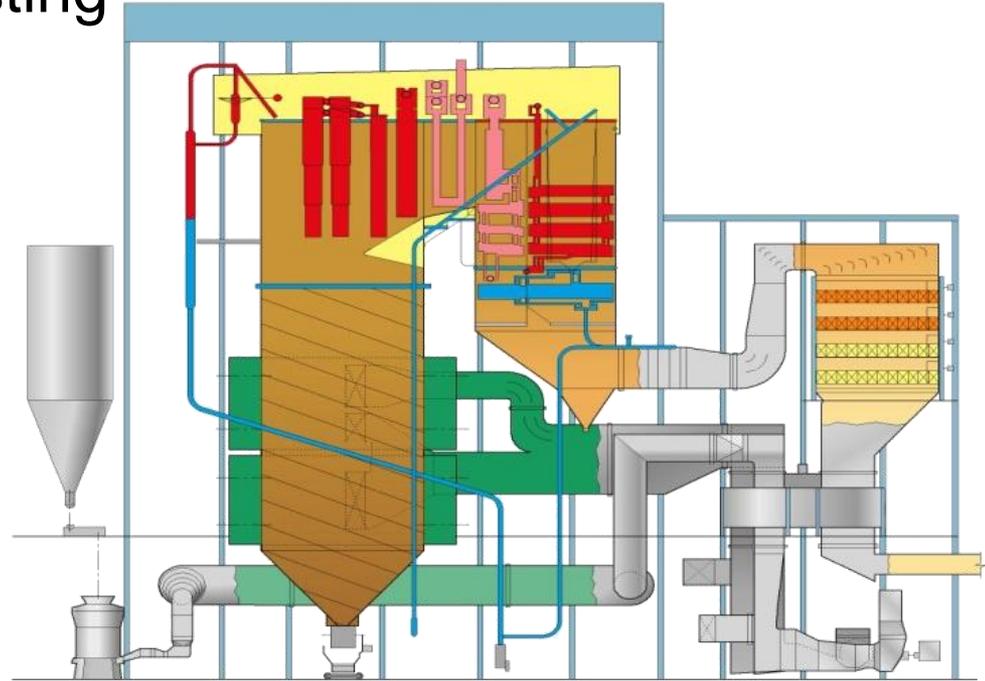
- *Results from intermediate-time tests of third heat of Inconel 740 will be summarized at Quarterly review meeting (12/10)*
Completed
- *A draft creep data package will be prepared for an ASME Code Case for Inconel 740 (06/11)*
Completed
- *Microstructure analysis of cold-worked materials will be summarized at Quarterly review meeting (09/11)*
Completed
- *Results from microstructure characterization of long-time aged 740 will be presented at Quarterly review meeting (12/11)*
Completed

2012 Milestones & Status:

- *Status of creep testing 282 will be presented at quarterly review meeting (03/12)*
Completed
- *Final analysis of creep testing 617 tube bends (06/12)*
In progress
- *Efforts to characterize WSFs for welds made with 282 filler metal will be presented at Quarterly review meeting (09/12)*
On-track
- *Effects of long-time aging on microstructure of both 740 and 282 will be summarized, reconciled with thermodynamic predictions, and presented at Quarterly review meeting (12/12)*
In progress

Substantial Progress in Qualifying Ni-based Alloys for A-USC Boiler Applications

- Long-term creep-rupture testing
 - Inconel 740
 - Alloy 282
 - Alloy 617
- Successful ASME Code Case for 740
- Weldment strength studies to minimize weld strength reduction
- Characterize, understand, and minimize deleterious cold-strain effects on creep properties

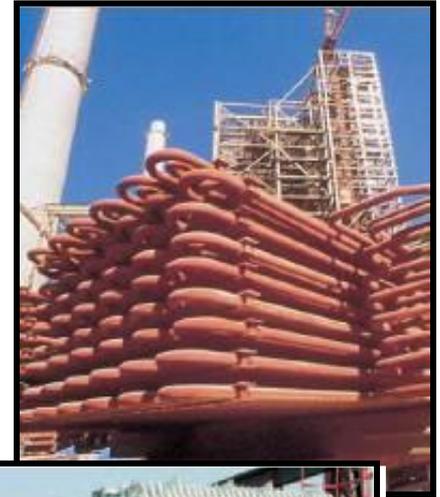


Building confidence to use new high-strength alloys

Back-Up Slides

Amount of Ni-Based Alloy Tubing Will Be Significant

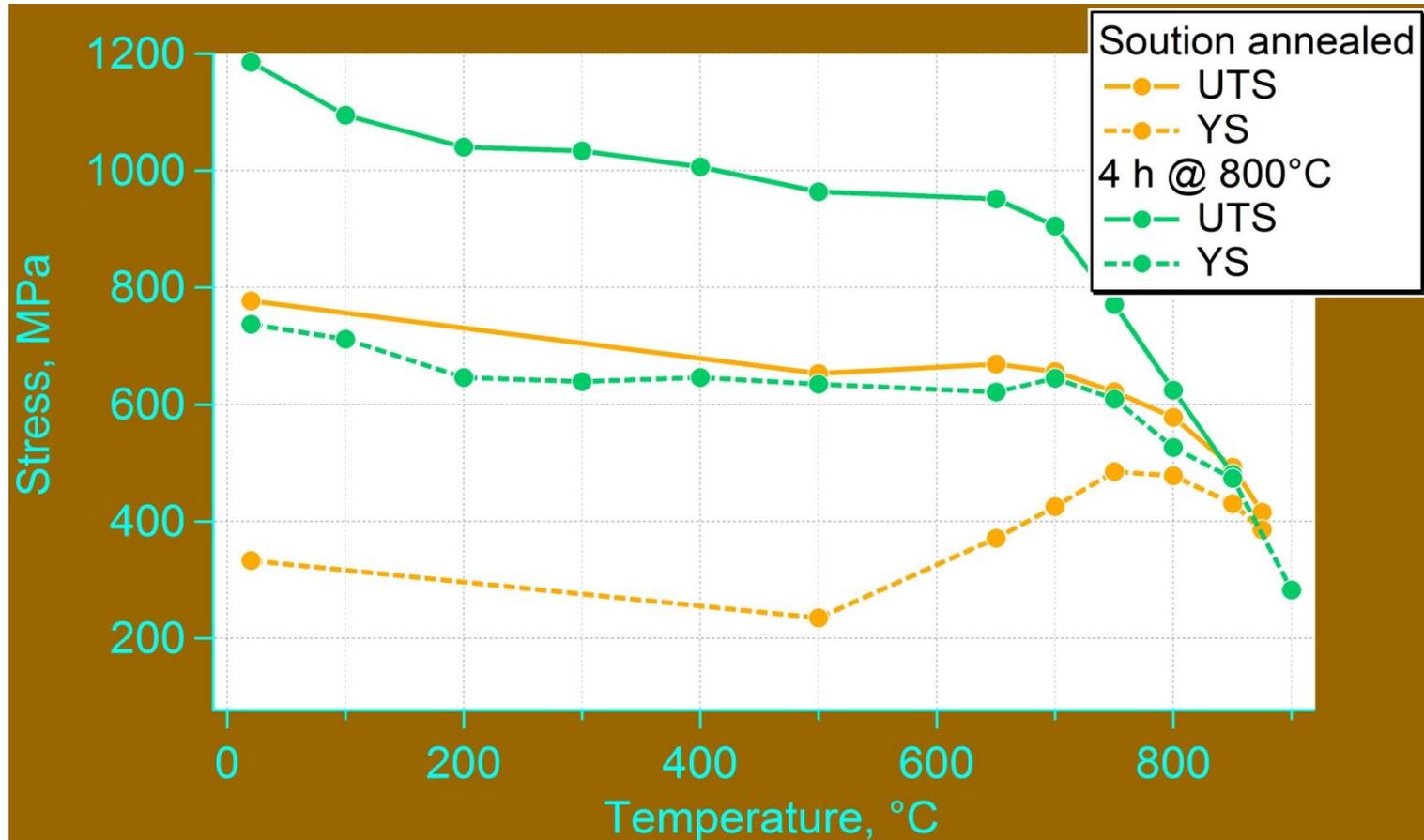
- Carbon Steel Grades – 420,000lf; 3,750,000 lbs
- T12 Alloy Steel Grade – 500,000 lbs
- T23 to T92 Alloy Grades – 2,600,000 lbs
- Traditional Stainless Steels – 1,600,000 lbs
- **Solid-solution Ni-based alloys – 1,100,000 lbs**
 - 1.750" OD X 0.400" MW
 - 2.00" OD X 0.165"/0.355" MW
- **Precip.-strengthened Ni-based – 850,000 lbs**
 - 1.750" OD X 0.290"/0.400" MW
 - 2.00 OD X 0.280"/0.400" MW



Images courtesy of The Babcock & Wilcox Company,
www.babcock.com

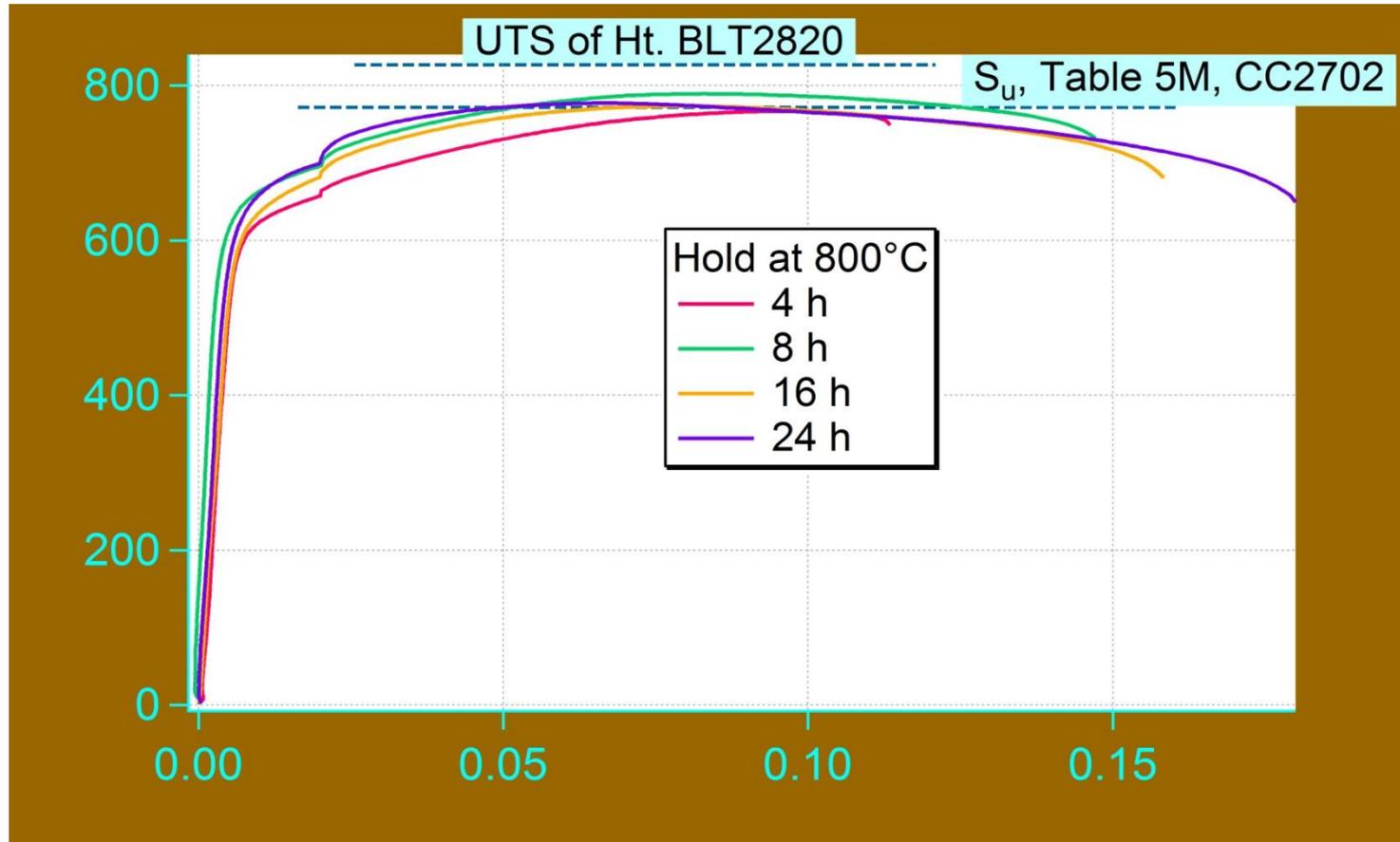
Build confidence in high-strength alloys in new applications

HV1220 Tensile data comparison: Aged vs solution annealed



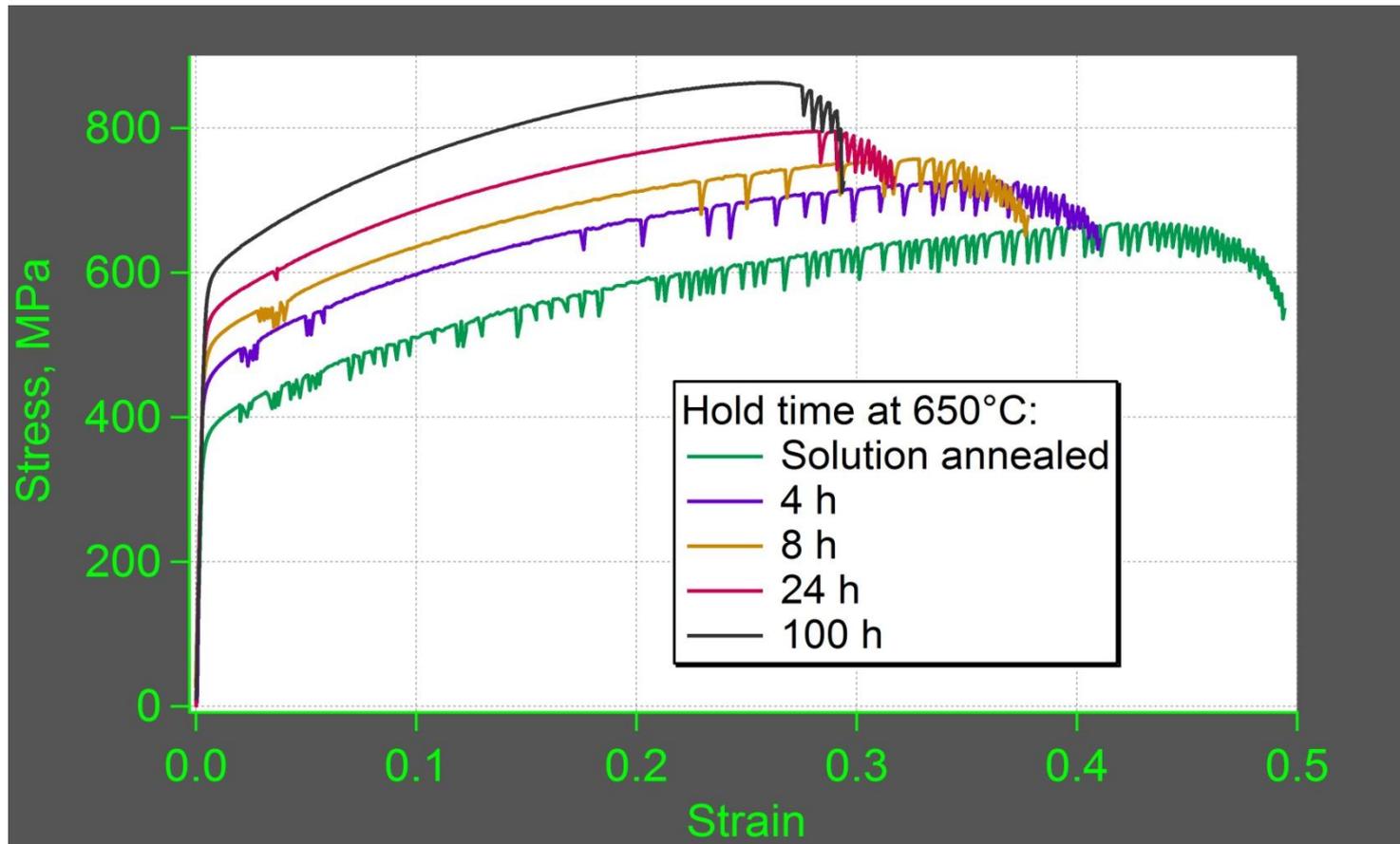
Aged condition maintains advantage over solution annealed until T approaches the γ' solvus ($\sim 980^\circ\text{C}$)

HV1220 Tensile data comparison: Aged vs CC2702



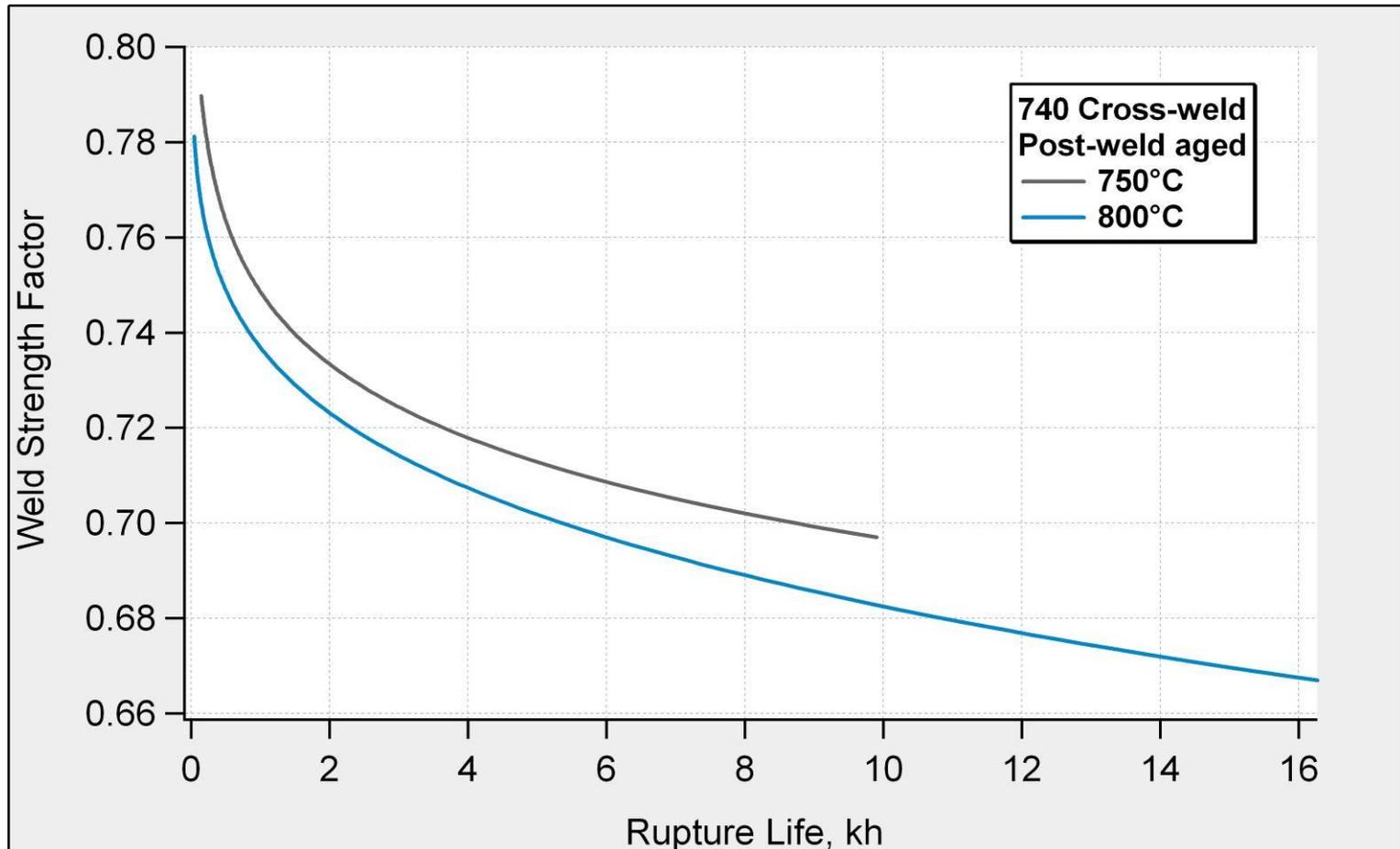
- HV1220 (740H) tensile strength is below that of non-H heats and at minimum limit of CC2702
- UTS is insensitive to aging time up to 24 h at 800°C

Definite Effect of Aging Time at 650°C



- Serrated flow informs about dislocation interactions with interstitials and precipitates
- Serrated flow diminishes as pre-test aging time increases
- In terms of UTS, 24 h @ 650 C is equivalent to 4 h @ 800 C

WSF results from GTA welded 740 tubes

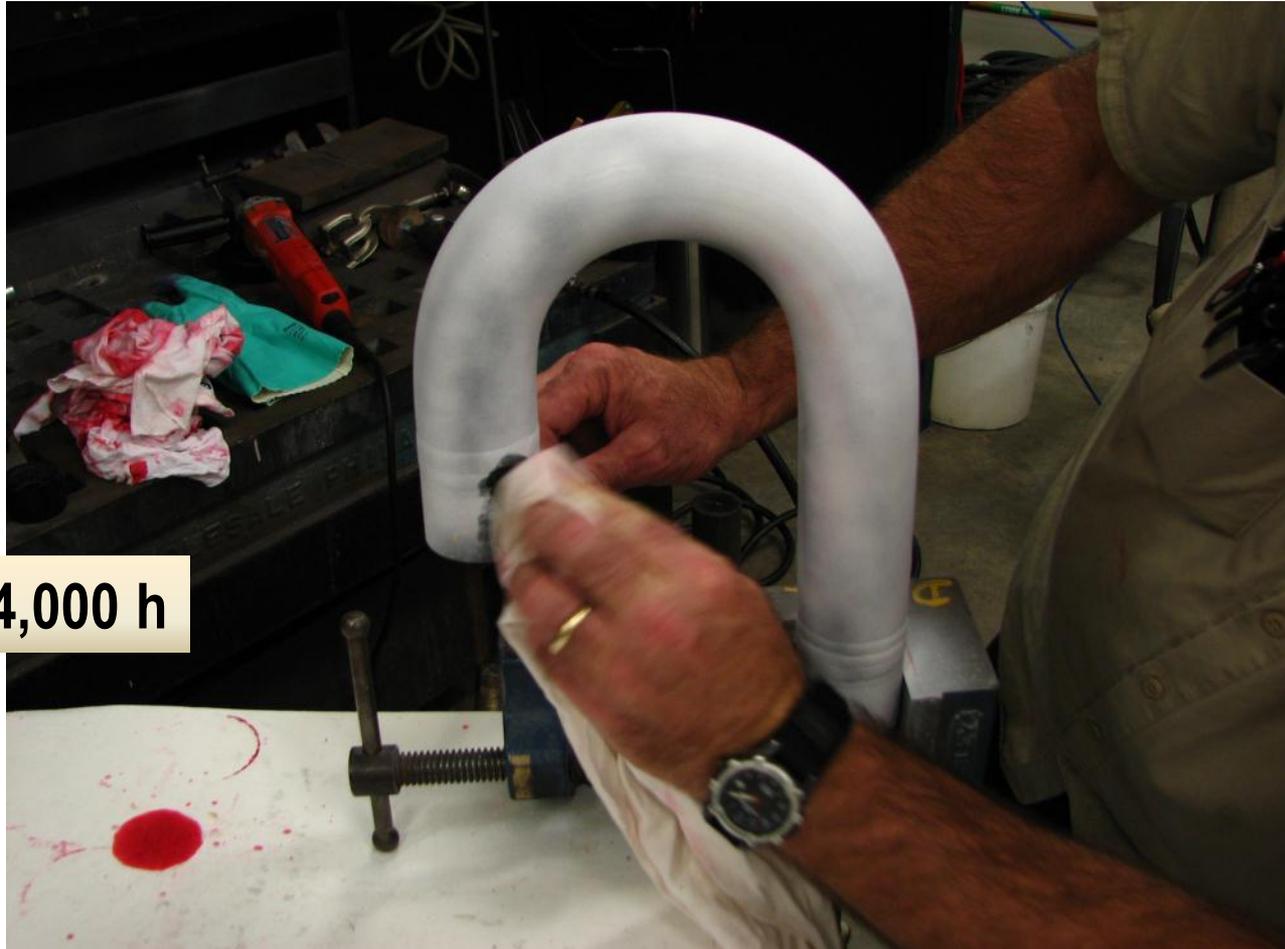


- **WSF decreases: ~ 0.1/10,000 h at both temperatures**
- **WSF averages: 750°C – 0.74; 800°C – 0.73**

Summary of CCA 617 base metal data including tubes

Specimen	Stress, MPa	°C	Life, h	LMP
617-13	400	650	1,280	21328
617-01	350	650	8,242	22075
617-02	300	650	33,155	22633
617-14	400	700	302	21873
617-04	300	700	2,377	22745
617-05	200	700	22,660	23698
617-15	300	750	105	22527
617-07	200	750	1,562	23727
617-08	140	750	7,266	24410
617-10	140	800	330	24162
617-11	100	800	1,831	24961
617-12	80	800	7,022	25587
617-03	200	650	60,672	22875
617-06	140	700	50,941	24120
B_3	91.3	775	14,344	25289
B_5	84.6	775	14,251	25285
B_675	82.4	775	14,351	25294

Dye penetrant examination indicated 617 tube bends are free of OD cracks

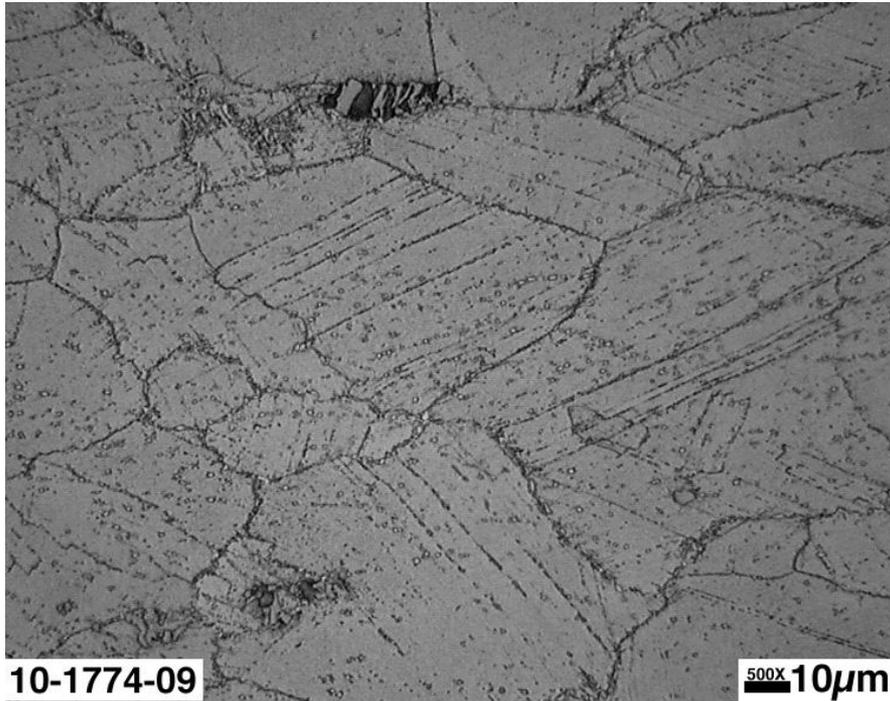


t ~ 14,000 h

- Stains and failure conditions are monitored with periodic shutdowns

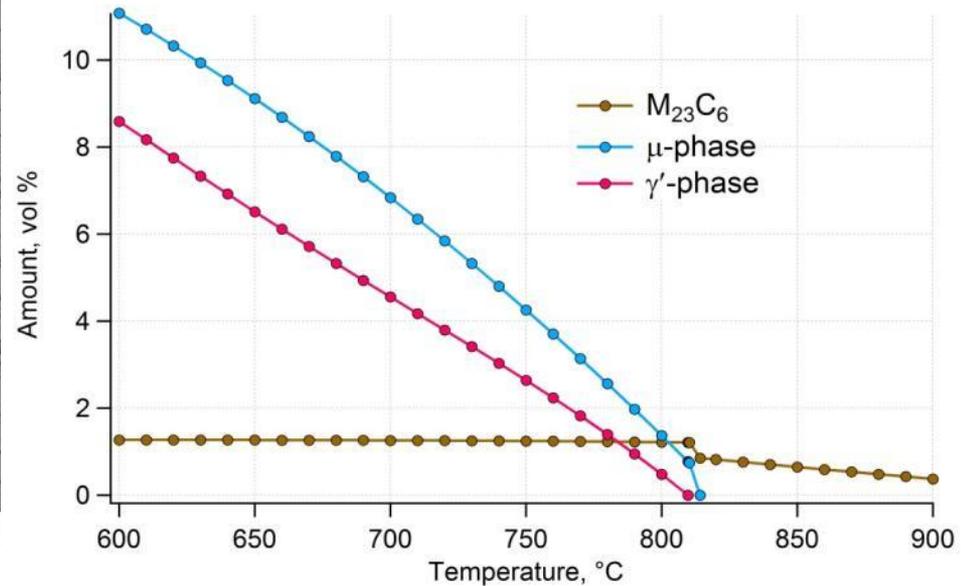
Long-time tests provide unique opportunities for understanding basic behavior

33,155 h at 650°C



At 650°C, 617 will likely contain:

- ~ 6.5% γ' - phase
- ~ 9% μ - phase



- Microstructure analysis for phase identification is in-progress

617 weldments made by Alstom are being used to characterize critical strength properties

CCA 617

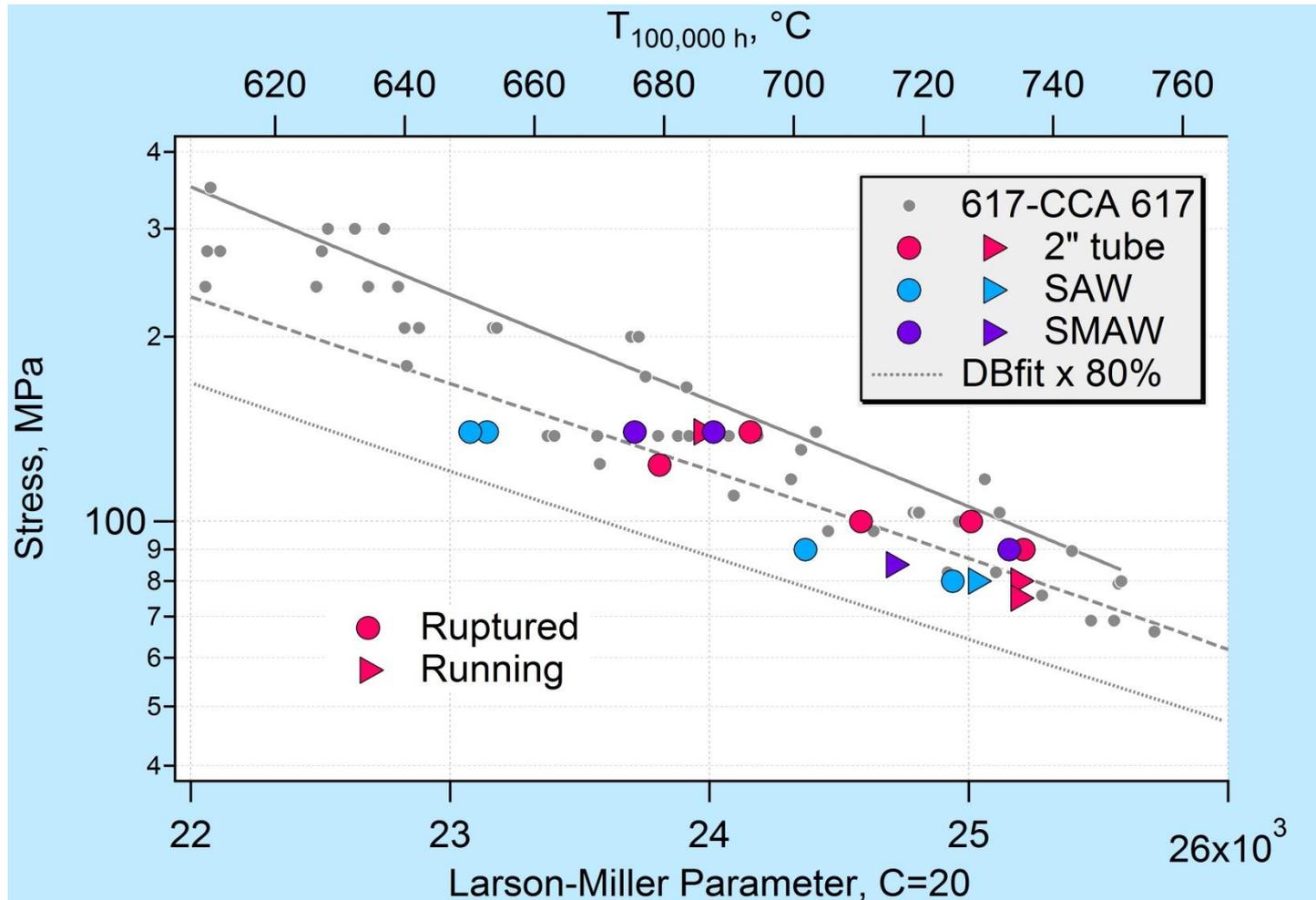
Product Form	Weld Type	Process	Filler	Comments
2-inch OD Tube	Butt	Orbital GTAW	CCA 617	Qualified, samples sent to ORNL
2-inch Plate	Butt	SAW	CCA 617	Qualified, samples sent to ORNL
		SMAW	CCA 617	Inclined plates for slag control, samples sent to ORNL. Evaluating welding suggestions received from UTP.
			Inconel 117	Weld metal fissures, needs more work

Summary of CCA 617 cross-weld rupture data from 2-inch tubes

	Spec	MPa	°C	Life, h	LMP20
Ruptured	I14-W04	140	750	4,114	24157
	I14-W05	100	750	27,923	25008
	I14-W01	123.7	800	154	23807
	I14-W02	100	800	814	24583
Running	I14-W03	140	700	38,582	23923
	I14-W06	90	750	42,744	25197
	I14-W07	80	750	39,408	25161
	I14-W08	75	750	38,367	25149

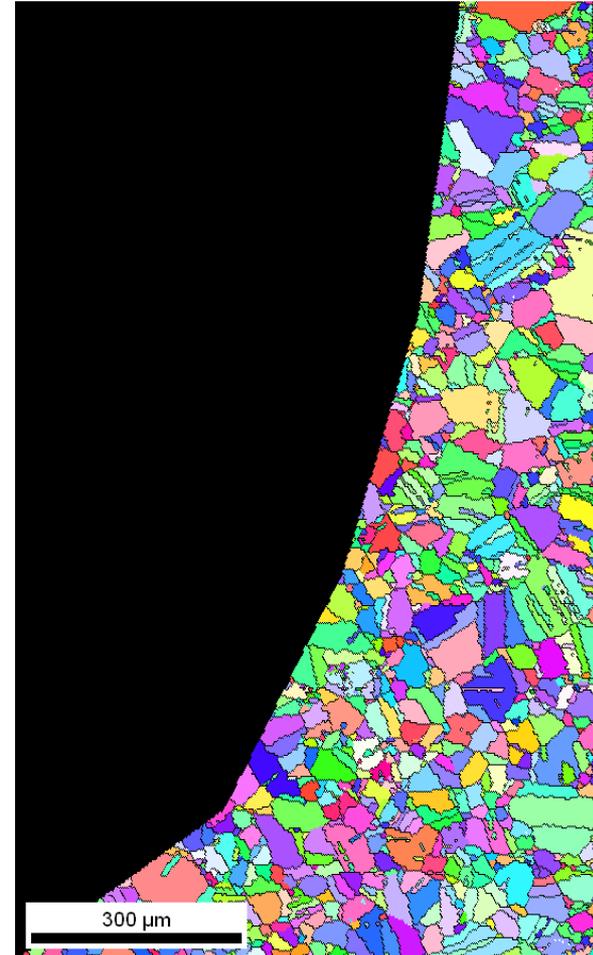
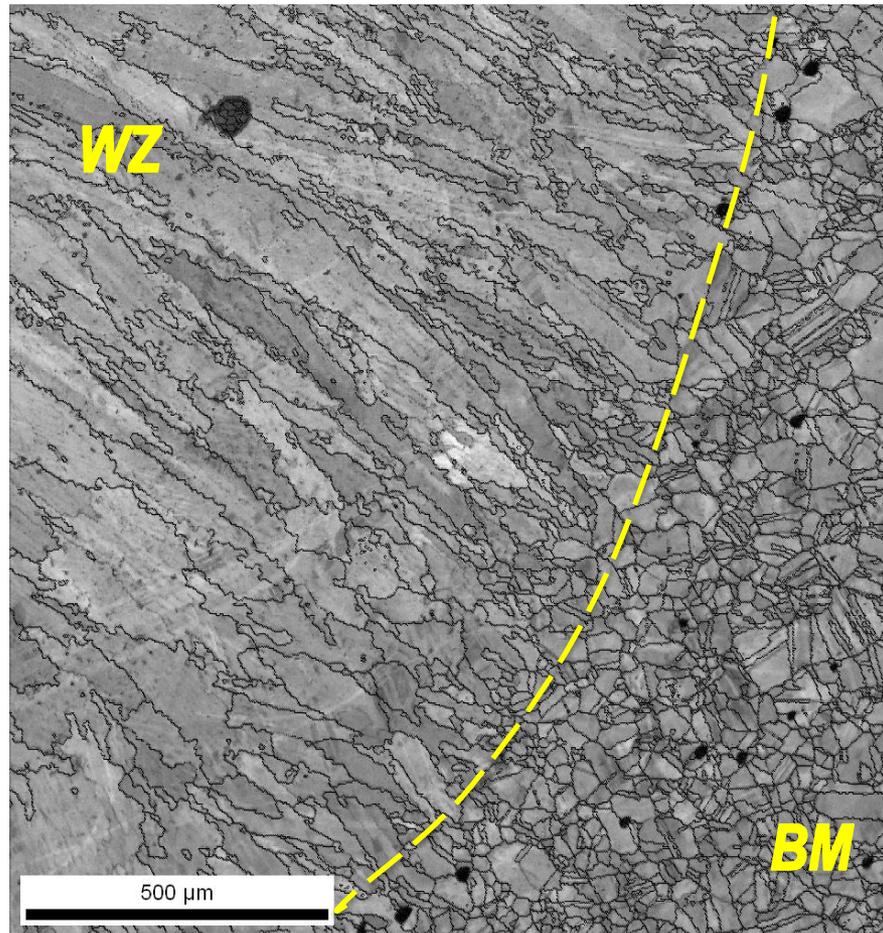
Long-time data are unique & satisfy critical needs for design and ASME code acceptance

Summary of 617 weld metal creep data



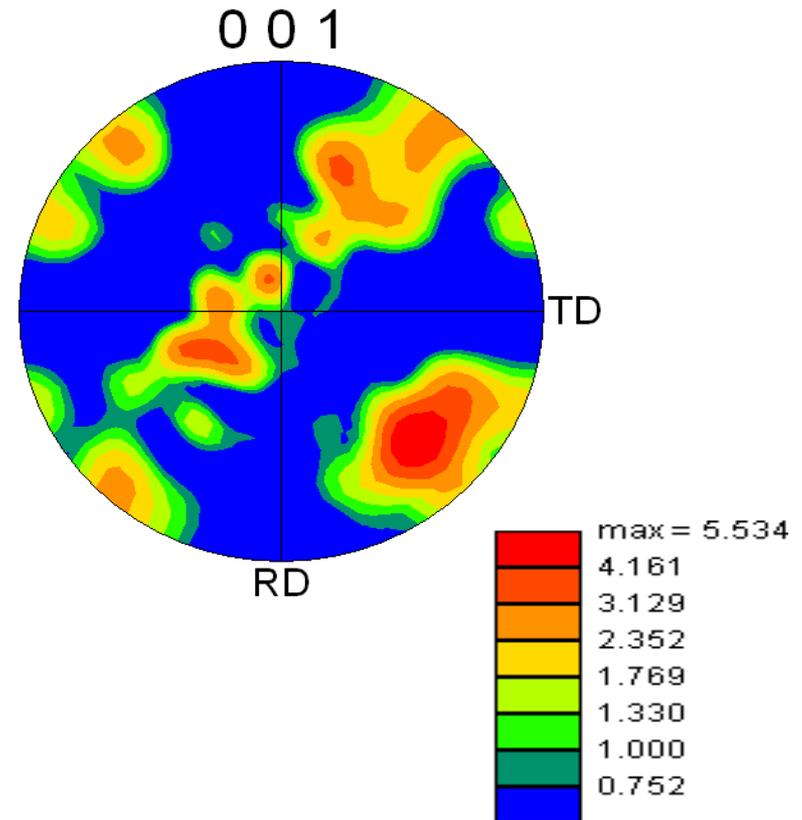
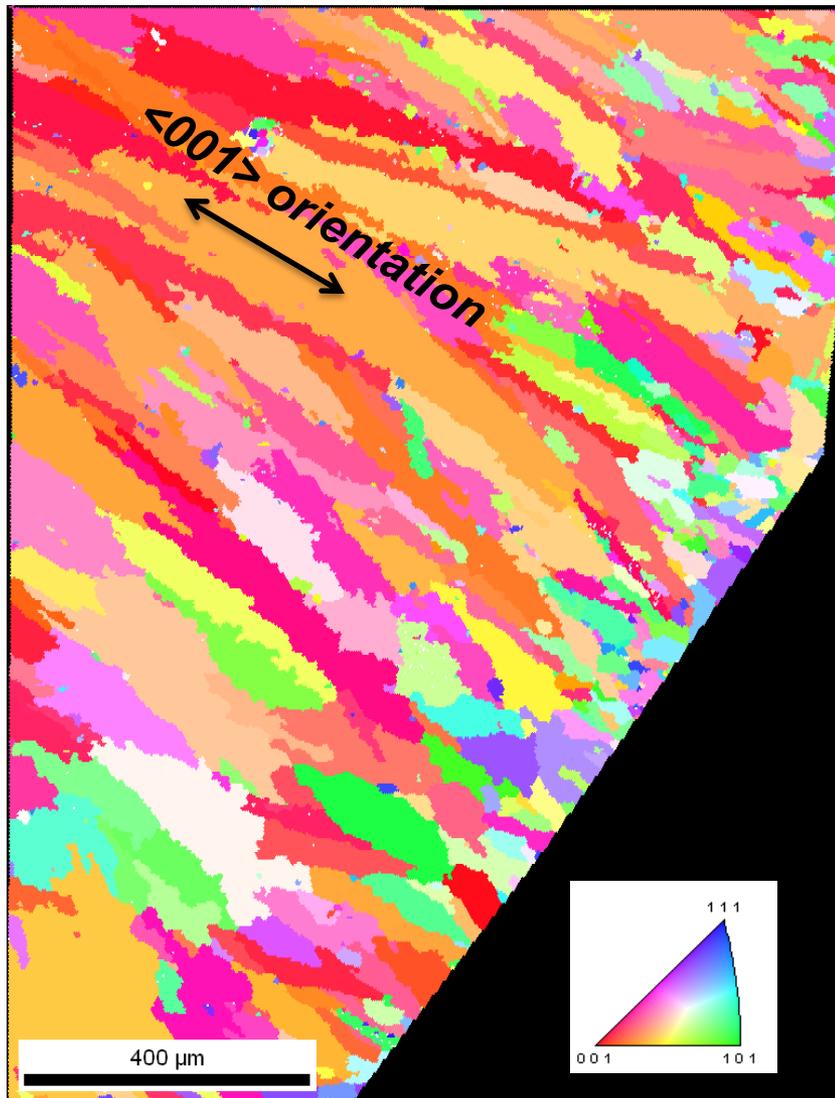
- 617 CCA data converge with 617 database above $\sim 750^{\circ}\text{C}$
- SMAW's and GTAW's have strength of base metal

OIM assessed texture differences between 740 base metal and weld deposit



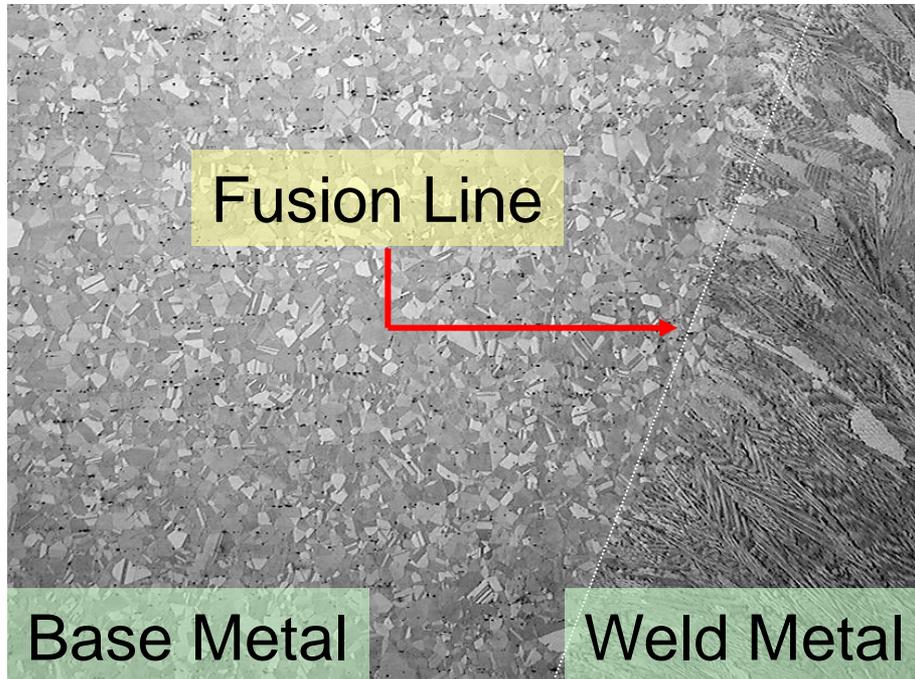
- Base metal is characterized by random crystallographic texture
- Isotropic properties are expected

Weld zones are characterized by strong crystallographic texture



- Local properties of weld deposits will not be isotropic
- Ni-based strength has strong dependence on texture

Weld Microstructures Can Be Modified By Heat Treatments

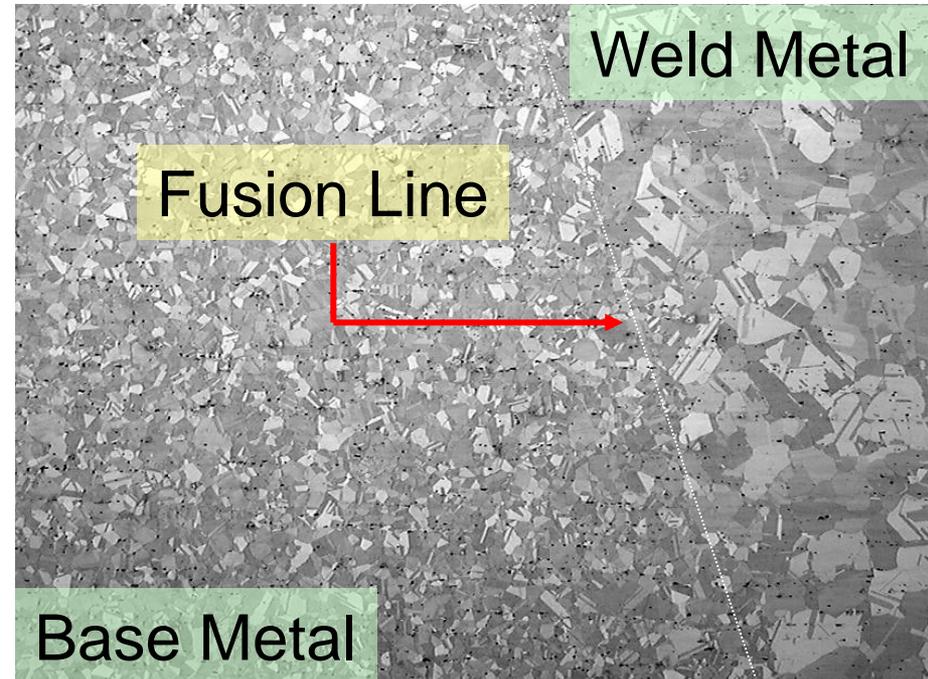


08-0670-02

1740-W02 TN 30868
800°C 180 mPa

16X 300µm

HT #1
Aged at 800°C/4 h



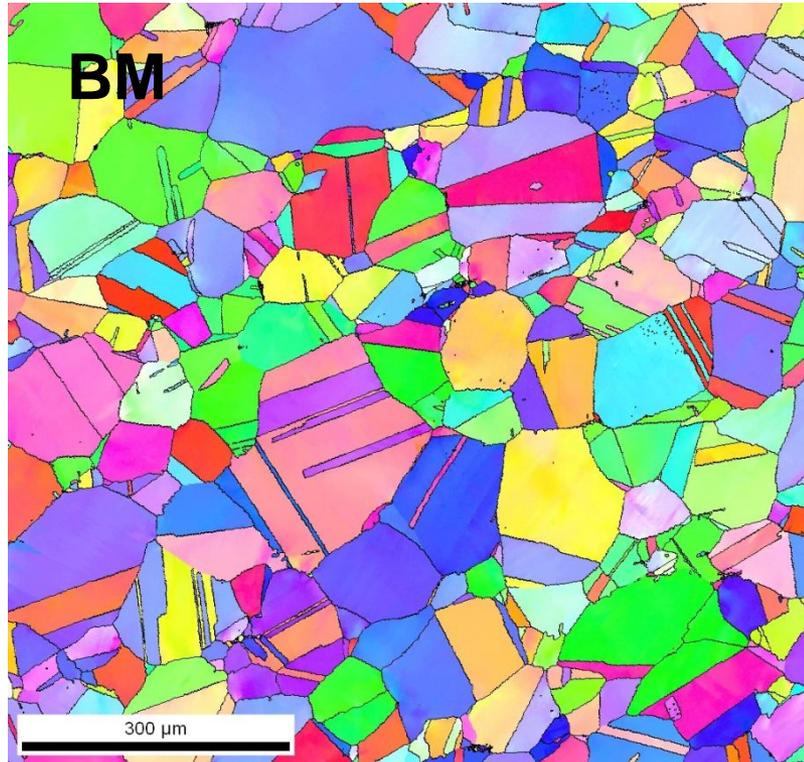
08-0671-03

1740-HT05 TN 31165 Heat # CLH 4663
800°C 180 mPa Tube Butt Weld

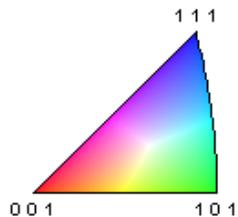
16X 300µm

HT #2
Solution anneal at 1120°C/1 h
Aged at 800°C/4 h

Solution treatment caused recrystallization and randomization



Nickel



- Benefit for rupture life at high T/low σ may be marginal