Heat Resistant 9% Cr Steels: Microstructural Stability & Creep Analysis

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NETL 2017 Project Review Meeting

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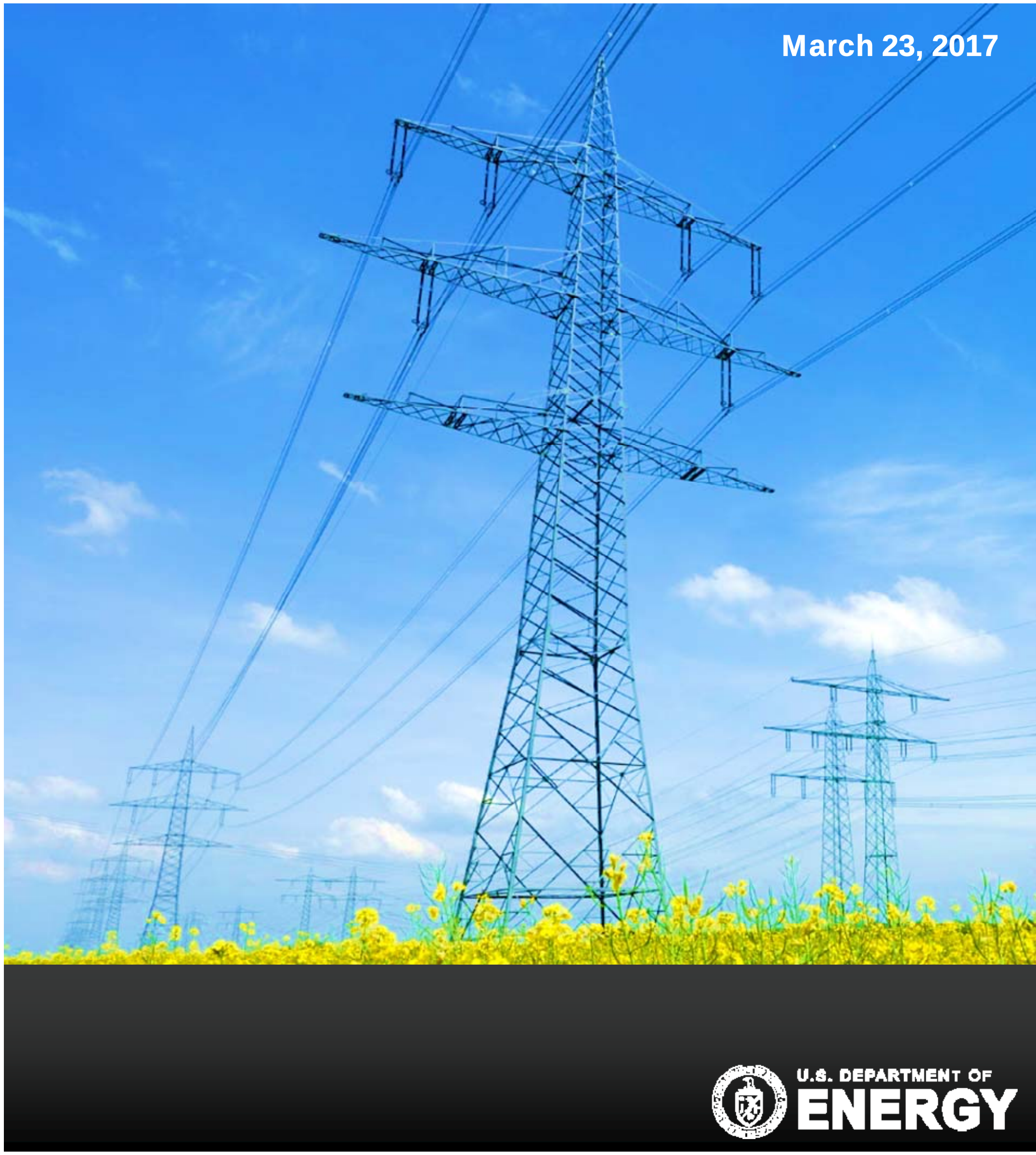
NATIONAL ENERGY TECHNOLOGY LABORATORY



Acknowledgments

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- NETL: Gordon Holcomb, Omer Dogan, Kyle Rozman, John Sears, Joe Tylczak, Chris Powell, Ed Argetsinger, Joe Mendenhall

Advanced Alloy Development

Grand Challenge

Extreme Environment Materials Program

Fossil Energy | National Energy Technology Laboratory

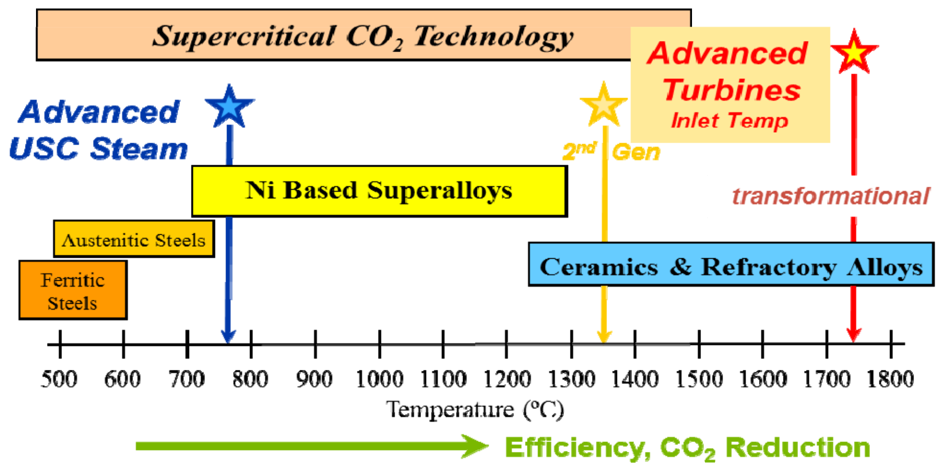
Goal:

Develop modeling methodology tools and manufacturing processes that can provide a scientific understanding of high-performance materials compatible with the hostile environments associated with advanced Fossil Energy (FE) power generation technologies.

Objective:

Materials R&D focused on structural and functional materials that will lower the cost and improve the performance of fossil-based power-generation systems.

Regis Conrad: Advanced Energy Systems Overview (April 28, 2016)



NETL Advanced Alloy Development

- Reliable materials for energy systems require effort to understand the relationship between the disposition of elements, leading to stable multi-length scale structural features that resist change over long times under very severe, and ever changing, environmental conditions.
- Complementary to this is proficiency in manufacturing these materials using relevant melting, or other, techniques that attain the desired structural features for requisite mechanical / physical performance consistent with the application.
- However, to integrate these new materials into future FE energy systems depends on the continued evolution of computational materials models, integrating them into alloy design, manufacturing and life prediction with the focus on real microstructures that can be described by a physics framework for their entire life.
- And yes. We want to do all this as cheaply as possible, using, if possible, existing infrastructure and processes!

Introduction & Background

***Heat Resistant Alloy* Development**

<u>Importance</u>

Perfect design methodology and manufacturing practice to shorten the time needed to develop advanced heat resistance alloys for transformational FE energy systems.

<u>Scope</u>

Increase the operational temperature of martensitic steels, austenitic stainless steels, and nickel superalloys for transformational FE energy systems.

<u>Expected Accomplishments</u>

FY2017: Second γ' strengthened nickel superalloy (IN740H) for use as thick wall cast components in AUSC power cycles.

Beyond: Assessment of the potential for new alloy candidate classes (e.g., HEA's, γ' strengthened Co superalloys, high yield stress SS, etc.) & process technologies (i.e., FSW, high shear materials processing, etc.) to significantly impact performance in transformational energy cycles.

https://www.youtube.com/watch?v=mnCKGI7Fnm8

General Background on Martensitic Steels

- Ferritic/Martensitic Cr steels form the backbone of current steam delivery systems.
- These alloys are less expensive to produce & in general can be recycled.
- CrMoV, NiCrMoV & steels with < 5% Cr make up the majority in tonnage in steam power plants operated < 570°C.
- In the hotter sections of the boiler & steam turbine, i.e., temperatures greater than 570°C, advanced 9-12% Cr steels will need to be used.
- At the current time, *620°C* is the approximate projected maximum use temperature due to concerns about the long-term microstructural instability of heat resistant steels.

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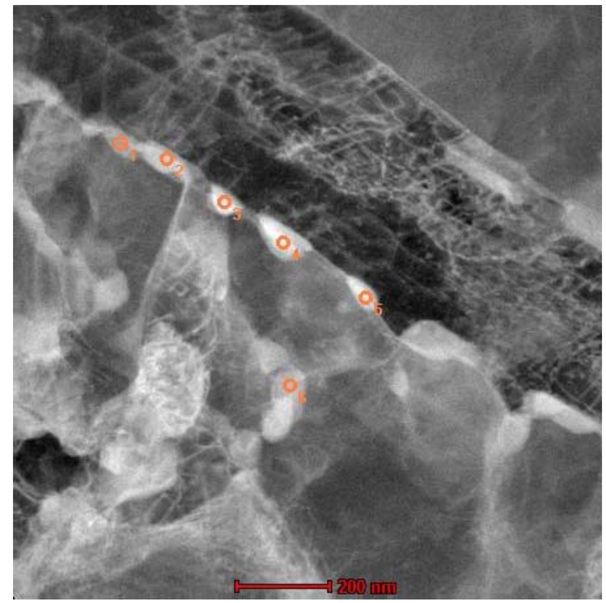
Martensitic Steel Development

1950's to date – Low alloy creep resisting steels

- 2¼CrMo; CrMoV
  - Ferritic structure, limited carbide strengthening
  - Applications up to about 540 - 570°C (maximum)



1980's development – P91 or "Modified 9Cr-1Mo" steel

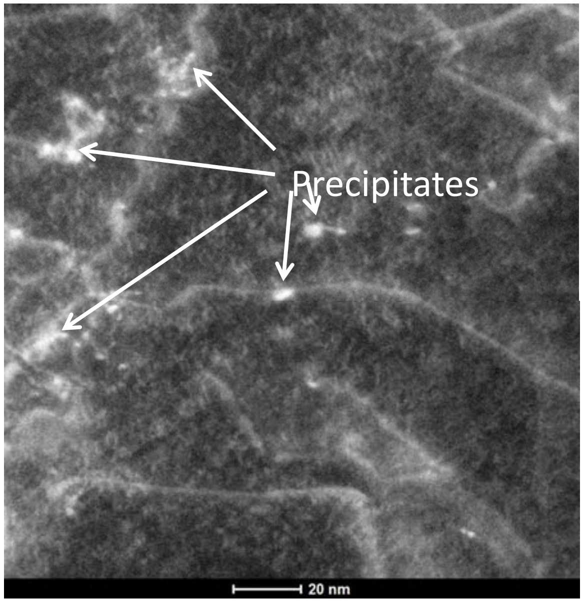
- Introduced from early 1990's onwards
- Coal plant boiler headers and drums (UK first), steam pipework and HRSG applications worldwide
  - Martensitic structure
  - Fine scale lath structure for increased creep strength
  - Carbide precipitate chains on lath boundaries
  - Vanadium modified to add finer-scale network of VN/MX precipitates
  - Applications generally up to about 580°C (or higher if at low stress)

1990 - 2000 – P92 steel (and others MARBN, CPJ-7, etc.)

- For example, replace Mo in P91 with W in P92; incorporate B: Creep strength increase in P92 compared to P91
- Applications – e.g., 600°C main steam, 620°C hot steam reheat

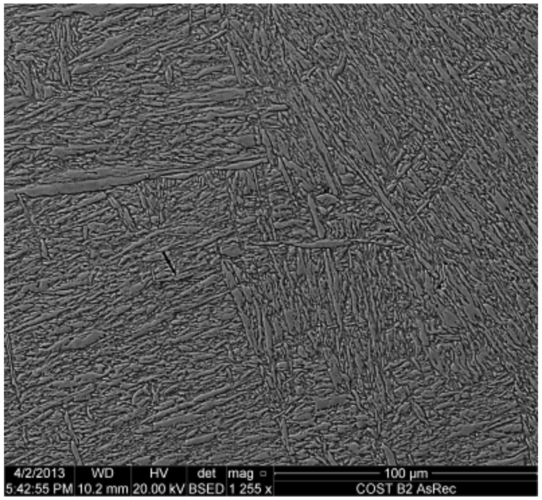
Computational / Experimental Alloy Design

- Model & design alloys using computational thermodynamics software (ThermoCalc) to develop the phases required for creep strength & to maintain the martensitic nature of the steel.
- Formulate, melt & cast alloy heats for each composition using best melting practice for alloy formulation.
- Homogenize each alloy according to its own *computationally optimized* heat treatment schedule developed from thermodynamic (ThermoCalc) & kinetic (DICTRA) modeling approach.
- Fabricate alloys into plate using standard hot forging & rolling operations.
- Develop desired microstructure features & steel strength through normalizing & tempering heat treatments.
- Assess creep & tensile properties against COST alloys (turbine) and P91 / P92 (boiler).



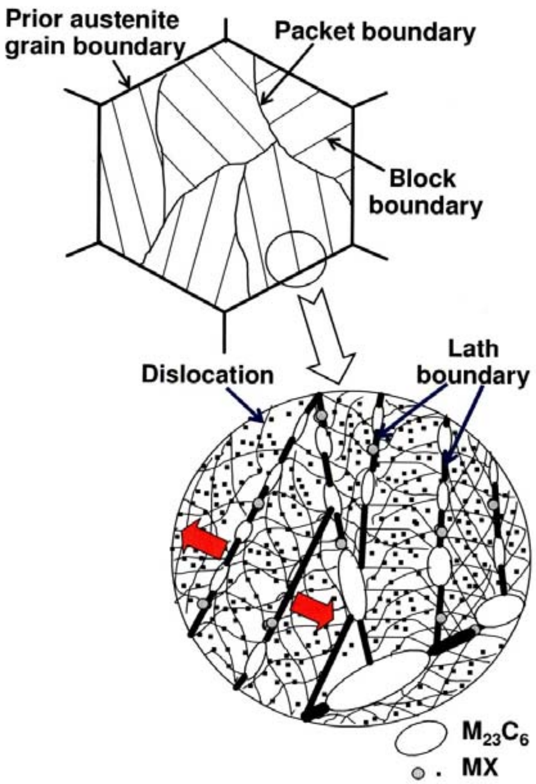
General Technical Approach

- Understand basic high temperature strengthening mechanisms & how to preserve strengthening effect through microstructural control.
- Achieve balance between the following competing effects:
  - *Necessary C, V, Nb, (and/or Ta) and N to generate MX (M: is metal; X: is C/N), thereby, slowing down dislocation movement in the matrix during creep.*
  - *Balanced amount of Mo and W for solution & precipitation hardening by* $M_{23}C_6$ *(and very small Laves phase).*
  - *Addition of Co, Cu, Mn, and/or C to suppress δ-ferrite & to provide additional precipitate strengthening (Cu) & oxidation resistance (Mn).*
  - *Addition of B to stabilize* $M_{23}C_6$ *precipitates, and thus, help to stabilize the prior austenite grain and sub-grain structures.*
  - *Higher level of Cr for oxidation resistance (e.g., must be balanced because Cr additions significantly greater than 8.5 to 9% reduce creep strength).*
  - *Addition of Si and/or RE elements to improve oxidation resistance.*



Agamennone et. al. Acta Mater.(2006), Knezevic et al. Mater. Sci. Eng. A. (2008), Wang et al. Mater. Sci. Eng. A. (2009), Yin & Jung, J. Mater. Pro. Technol. (2009), and Chilukuru et al. Mater Sci. Eng. A. (2009).

Microstructural Hierarchy of 9-12% Cr Containing Steels



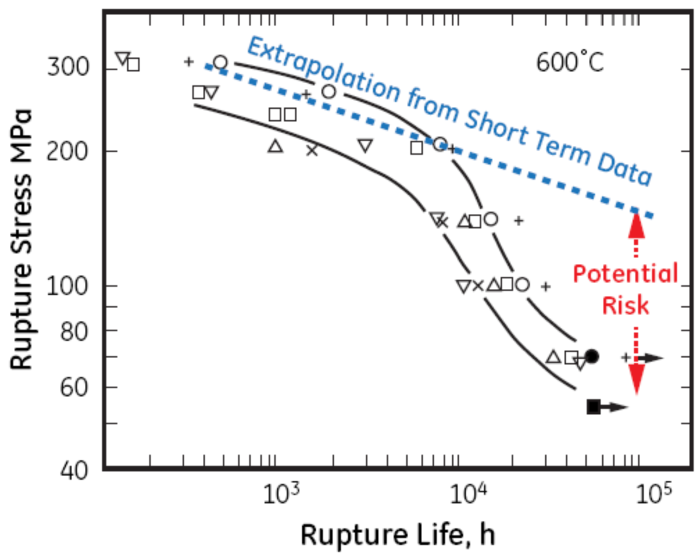
1. Prior austenite grain with associated grain boundaries.
2. Packet boundaries
3. Block boundaries
4. Lath boundaries
5. $M_{23}C_6$ carbides to stabilize lath, block, packet, and PAG boundaries
6. MX carbides to provide obstacles to dislocation motion
7. Dislocations

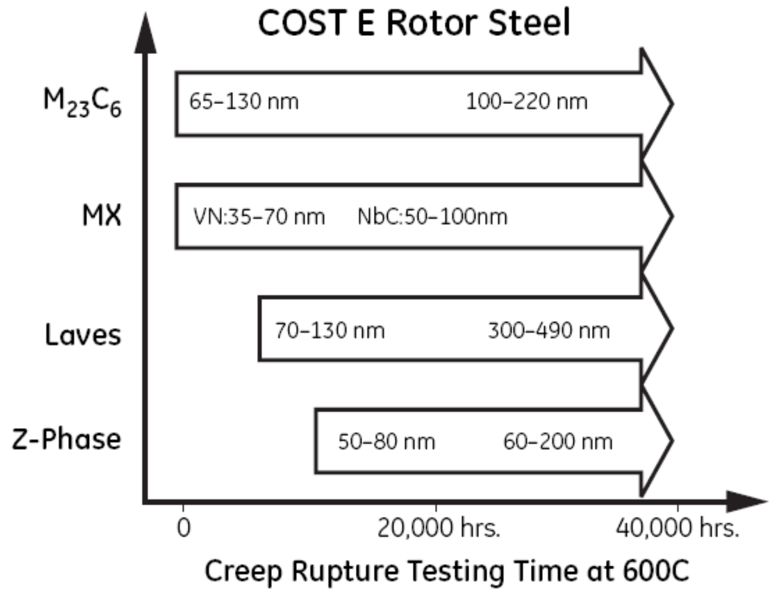
The premature breakdown of any one of these microstructural features will destabilize the entire alloy, and lead to ever increasing creep rate over time. The goal of alloy design is to slow down the destabilization of these features starting with the MX and $M_{23}C_6$ particles.

F. Abe, "Metallurgy for Long-term Stabilization of Ferritic Steels for Thick Section Boiler Components In USC Power Plants at 650°C," Proceedings of the 8th Liege Conference, (2006), pp. 965-980.

Microstructure Stability of 9-12% Cr Steels

USC Development Experience in Precipitate Instability





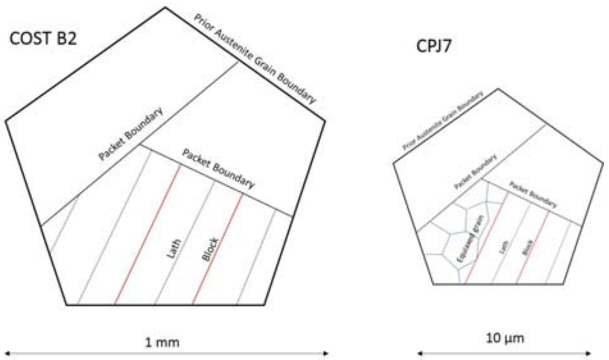
Many competing effects occur in heat resistant steels of the 9% Cr variety. Past experience has shown that the instability of any of the following, Z-phase, Laves, MX and/or $M_{23}C_6$, can cause an unexpected decrease in rupture stress as a function of time. The goal of alloy design is to slow down the destabilization of these features starting with the MX and $M_{23}C_6$ particles.

Summary of Major Commercial 9-12% Cr Steels

Commercial Turbine & Blading Alloys Compared to CPJ 7

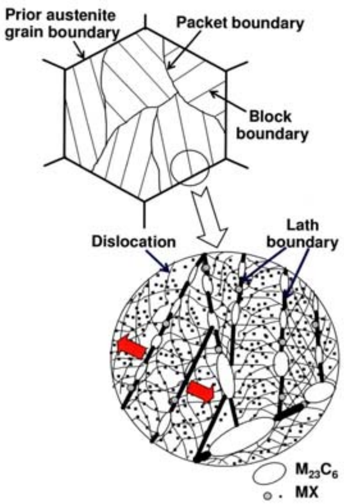
Chemistry														
Material	***C***	***Mn***	***Si***	***Ni***	***Cr***	***Mo***	***V***	***Nb***	***N***	***W***	***B***	***Co***	**Fe**	**Ta**
COST FB2	0.13	0.30	0.08	0.05	9.30	1.50	0.20	0.05	0.026		0.01	1.00	Bal	
COST E	0.12	0.45	0.10	0.74	10.40	1.10	0.18	0.045	0.05	1.00			Bal	
COST B2	0.18	0.06	0.10	0.09	9.28	1.54	0.29	0.06	0.02		0.01		Bal	
CPJ-7	0.15	0.41	0.09	0.27	9.83	1.26	0.21	0.056	0.020	0.48	0.0100	1.48	Bal	0.28
CPJ-7B	0.15	0.29	0.15	0.22	9.81	1.46	0.20	0.059	0.025	0.43	0.0078	1.53	Bal	0.20
CPJ-7C	0.16	0.47	0.11	0.22	9.95	1.34	0.19	0.061	0.022	0.49	0.0086	1.59	Bal	0.20
CPJ-7D	0.16	0.43	0.10	0.22	10.12	1.31	0.21	0.054	0.024	0.53	0.0083	1.56	Bal	0.24
CPJ-7E	0.15	0.42	0.12	0.21	9.99	1.35	0.20	0.049	0.022	0.53	0.0087	1.51	Bal	0.28

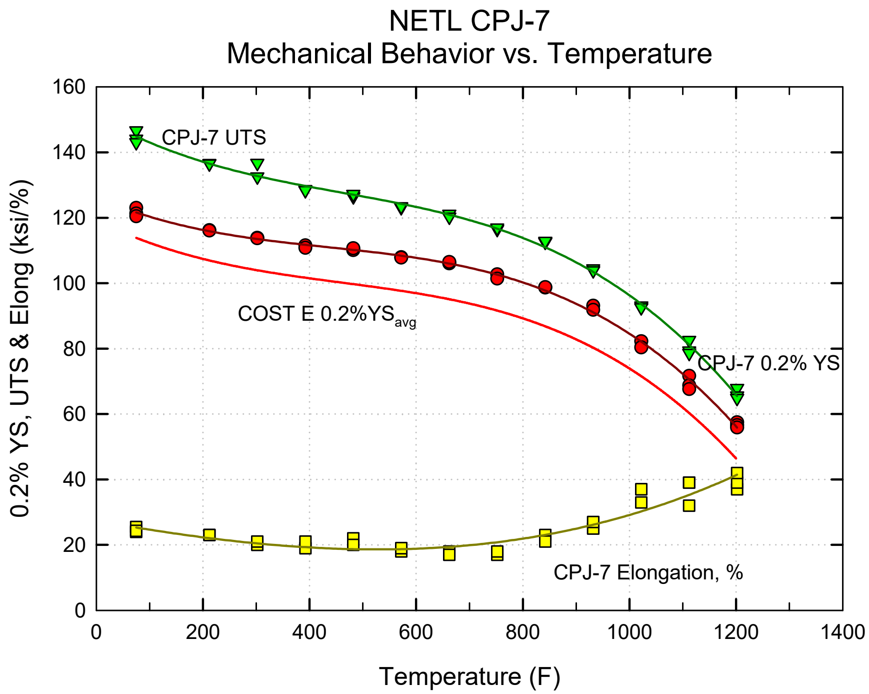
The following elements were also found in the CPJ-7 alloys: Ti (<0.004%), Al (<0.02%), P (<0.003%), Cu (<0.003%), O (<36 ppm), & S (<58 ppm).



Summary of Tensile Mechanical Behavior

Measured values for CPJ 7 versus mean 0.2% YS for COST E





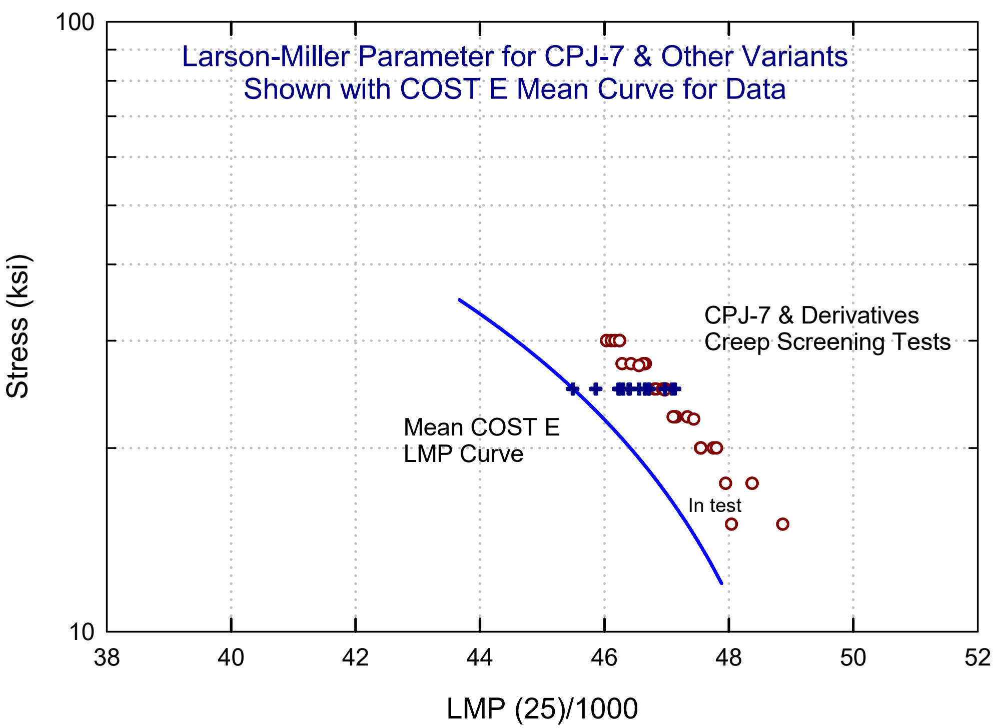
Alloy	$Mo_{(Eq)}$	C + N	B
COST FB2	1.50	0.156	100*
COST E	1.60	0.170	---
COST B2	1.54	0.200	100*
CPJ-7	1.501	0.170	100
CPJ-7B	1.675	0.175	78
CPJ-7C	1.585	0.182	86
CPJ-7D	1.575	0.185	83
CPJ-7E	1.595	0.172	87

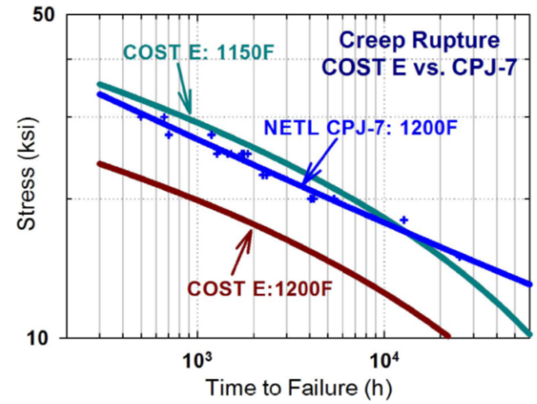
$Mo_{(Eq)}$ = % Mo + ½ % W

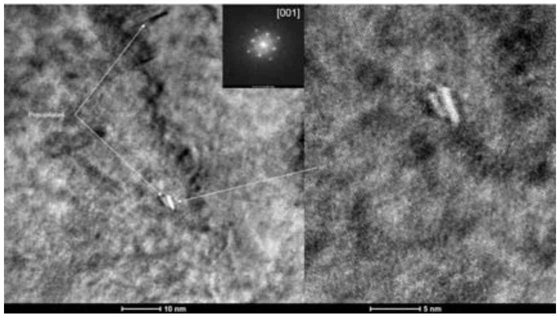
Larson-Miller Parameter

COST E versus CPJ 7

Larson-Miller Parameter plot for COST E at temperatures from 1050°F (565.5°C) to 1200°F (648.9°C). CPJ 7 testing performed at 650°C only.





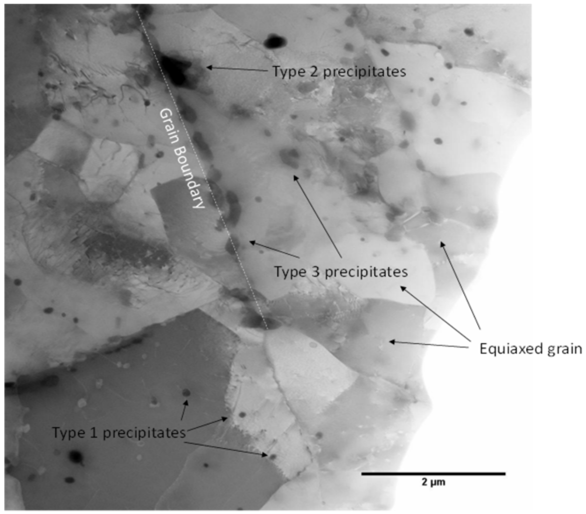


(Left) HRTEM micrograph showing fine coherent MX-type precipitates in the martensitic matrix of as-received CPJ 7. (Right) A magnified view of the lower precipitate in the left panel. The precipitate is located at the center of two high-strain (white) regions that result from lattice mismatch between the precipitate and the matrix.

Wrought CPJ 7 Martensitic 9% Cr Steel

- ❑ Identified promising chemistry for ferritic-martensitic steel, CPJ 7, through control of minor alloying additions (C, Cu, Ta), and in particular, the combined B/N levels.
- ❑ Developed manufacturing approach to consistently produce CPJ 7.
- ❑ Utilized NETL homogenization cycle in conjunction with thermo-mechanical processing to set and stabilize microstructure.
- ❑ Tested CPJ 7 chemistry robustness by varying select combinations of alloying additions: $Mo_{(eqv)}$; C + N level; B level – producing and testing four additional CPJ 7 heats, initially & many others later on.
- ❑ Assessed other minor element additions and extent of those additions on tensile and creep strength of base alloy.
- ❑ U.S. Patent awarded

Hawk, Jablonski & Cowen, *Creep Resistant High Temperature Martensitic Steel*, US 9,181,597 B1, November 10, 2015.



Cast Ferritic-Martensitic 9% Cr CPJ 7 Steel

Design Rationale Moving Forward

- Previous research identified NETL martensitic-ferritic steel CPJ 7. A *wrought* product was manufactured.
- NETL *wrought* CPJ 7 steel exhibited superior creep strength compared to commercially designed, thermo-mechanically processed and heat treated 9% Cr martensitic steels used for airfoils, rotors, and other wrought components in a steam turbine as well as piping and other thermo-mechanically processed components in the combustion boiler.
- NETL applied same alloy design rationale to develop *cast* martensitic 9% Cr steel. Subsequent alloy homogenization using NETL algorithmic approach with subsequent martensitic steel heat treatment produced *cast* version of CPJ 7 superior to any existing commercially available *cast* 9% Cr martensitic steel or derivatives.

Wrought vs. Cast Manufacturing

Wrought Manufacturing Steps:

1. Alloy Design
2. Melt Processing
3. *Homogenization*
   - Improve chemical uniformity within the matrix structure
4. Thermo-mechanical Processing
   - Physical manipulation of the grain structure for mechanical property design & refinement
   - More homogeneous "physical" structure – i.e., a more consistent & uniform grain size
5. Heat Treatment for Strength & Ductility/Fracture Toughness

Cast Manufacturing Steps:

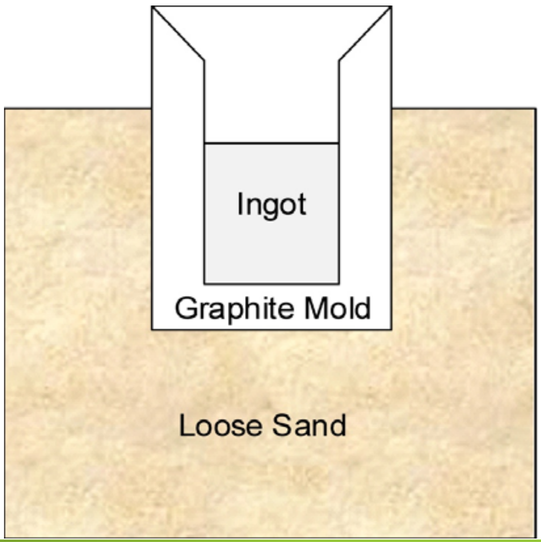
1. Alloy Design
2. Melt Processing
3. *Homogenization*
   - Improve chemical uniformity within the matrix structure
4. Heat Treatment for Strength & Ductility/Fracture Toughness

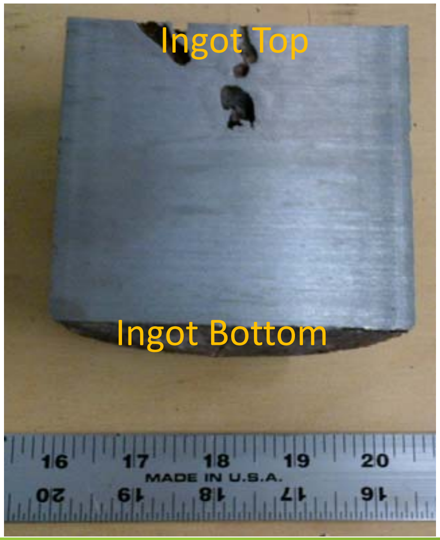
- Major difference is no manipulation of the "physical" grain structure of the resulting solid body.
- Limited ability to develop strength in the solid body except through *alloy design* & *heat treatment*.

Martensitic Steel Ingot Casting at NETL

Large-scale ingot casting for USC 650°C Power Plants

Heats of CPJ7 were formulated and cast utilizing NETL's "enhanced slow cooling" methodology. The mold was submerged in loose sand to help contain the heat of the molten steel, and thereby, slow the cooling rate substantially in order to better simulate the slow cooling conditions of a thick wall, full-size steam turbine casings. The fully heat treated ingot was then bisected along the diameter. The halves were then sectioned into 0.4" thick slabs from which 0.4" square bars were cut. From these squares round tensile bars were subsequently machined into traditional tensile/creep specimens.





Cast 9% Cr Ferritic-Martensitic Steel Chemistry

- This new *cast* 9% Cr martensitic steel has a unique chemistry, alloy design philosophy, and microstructural control (i.e., computationally based homogenization heat treatment schedule) unlike any other alloy in it's class.
- Nominal/preferred alloy chemistry:

	C	Mn	Si	Ni	Cr	Mo	V	Nb	N	W	B	Co	Fe	Ta
CPJ-7	0.15	0.40	0.10	0.30	9.75	1.25	0.20	0.06	0.020	0.50	0.0100	1.50	Bal	0.20

- Alloy design philosophy:
  - Slow down the destabilization of the various grain boundary & matrix strengthening features such as MX and $M_{23}C_6$ particles.
  - Avoid and/or postpone the formation of unwanted phases such as the Z-phase and Laves phase.
- Homogenization:
  - Induce complete chemical uniformity on the micro-scale to avoid "over rich" or "over lean" regions that could promote deleterious phase formation, thereby achieving long-term alloy stability.

Cast 9% Cr Ferritic-Martensitic Steel

Proof of Principle

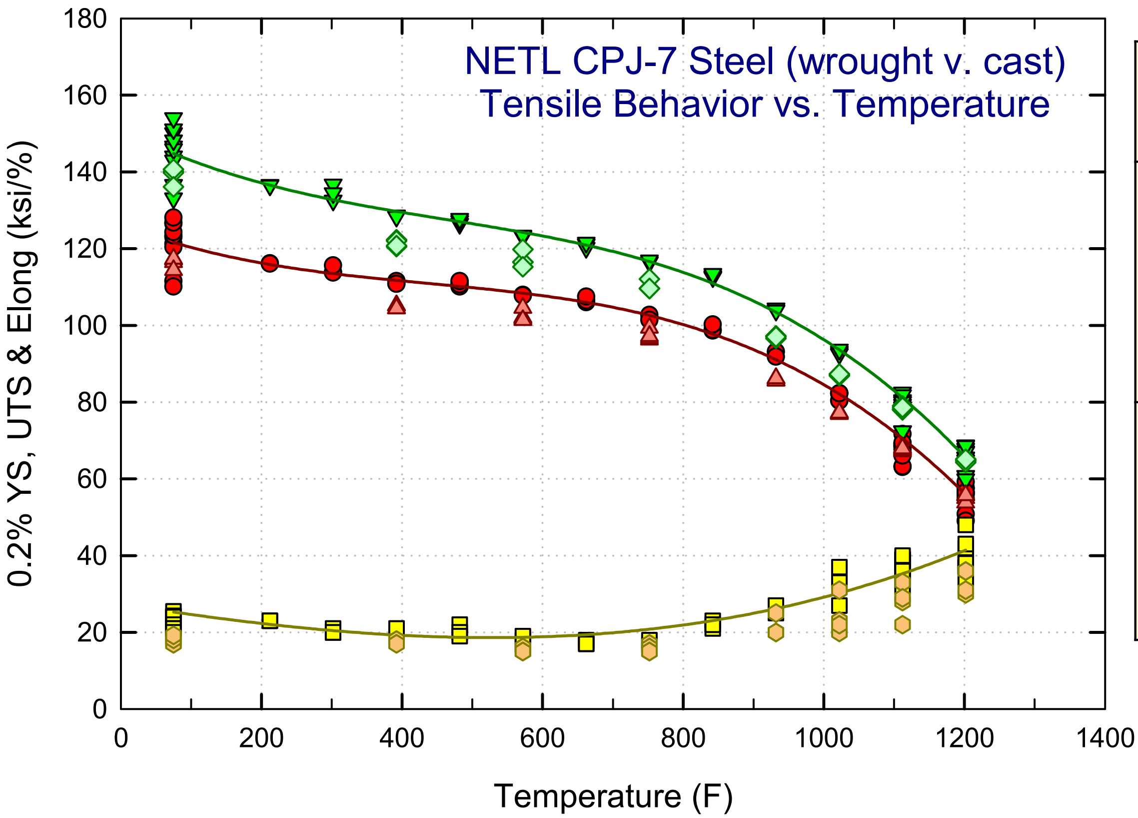
- The preferred chemistry for _cast_ CPJ 7, 9% Cr martensitic steel, was used to manufacture two heats. _No attempt was made to optimize the casting process at this time._
- After homogenization, the _cast_ CPJ 7 9% Cr steel ingot was heat treated in the following manner:

  1150°C/30 min/AC + 700°C/1 hour/AC

- Screening tensile tests were performed from material that solidified in an _equiaxed_ manner (i.e., center of the casting) as well as from material that solidified in a _columnar_ manner (i.e., exterior surface region of casting).
- Creep tests from 30 ksi to 17.5 ksi and 650°C have been performed to assess the extent of creep capability relative to commercial cast steels used in power plants, (e.g., COST CB2).
- Mechanical performance looks _very good_ – with _cast_ CPJ 7 showing outstanding mechanical performance for a casting, and similar to wrought CPJ 7.

Tensile Mechanical Behavior Cast CPJ 7 Steel

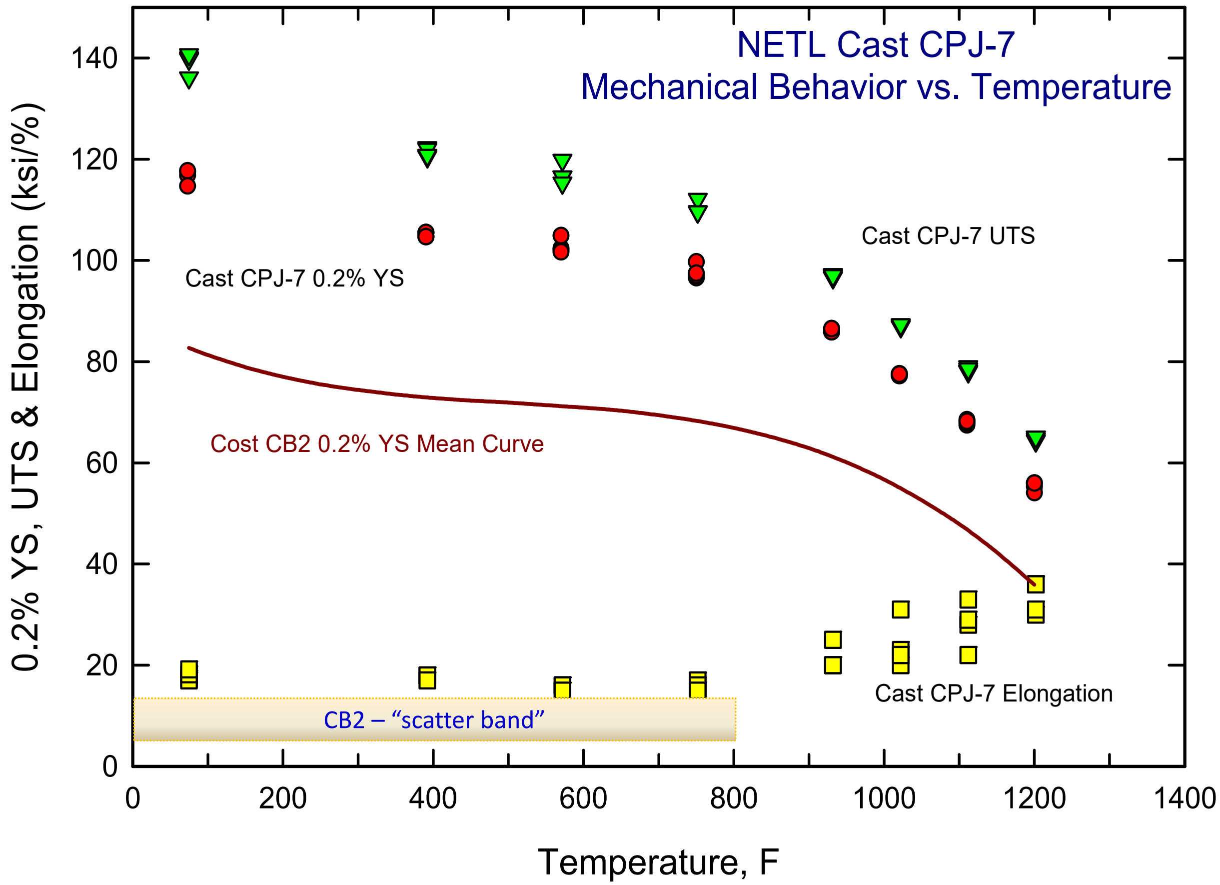
Comparison to Wrought CPJ 7 Steel



Alloy	Heat Treatment	Test Conditions (°C)	Yield Stress (MPs)	Tensile Strength (MPa)	Elongation (%)	Reduction in Area (%)
CPJ 7A Columnar	HTS+	RT	808	966	17	48
			803	964	17	42
		600	463	539	28	74
			470	545	33	76
		650	379	446	30	81
			384	449	36	80
CPJ 7A Equiaxed	HTS+	RT	809	970	18	39
			789	938	19	55
		600	466	538	22	62
			468	542	29	73
		650	371	443	31	79
			384	449	36	80

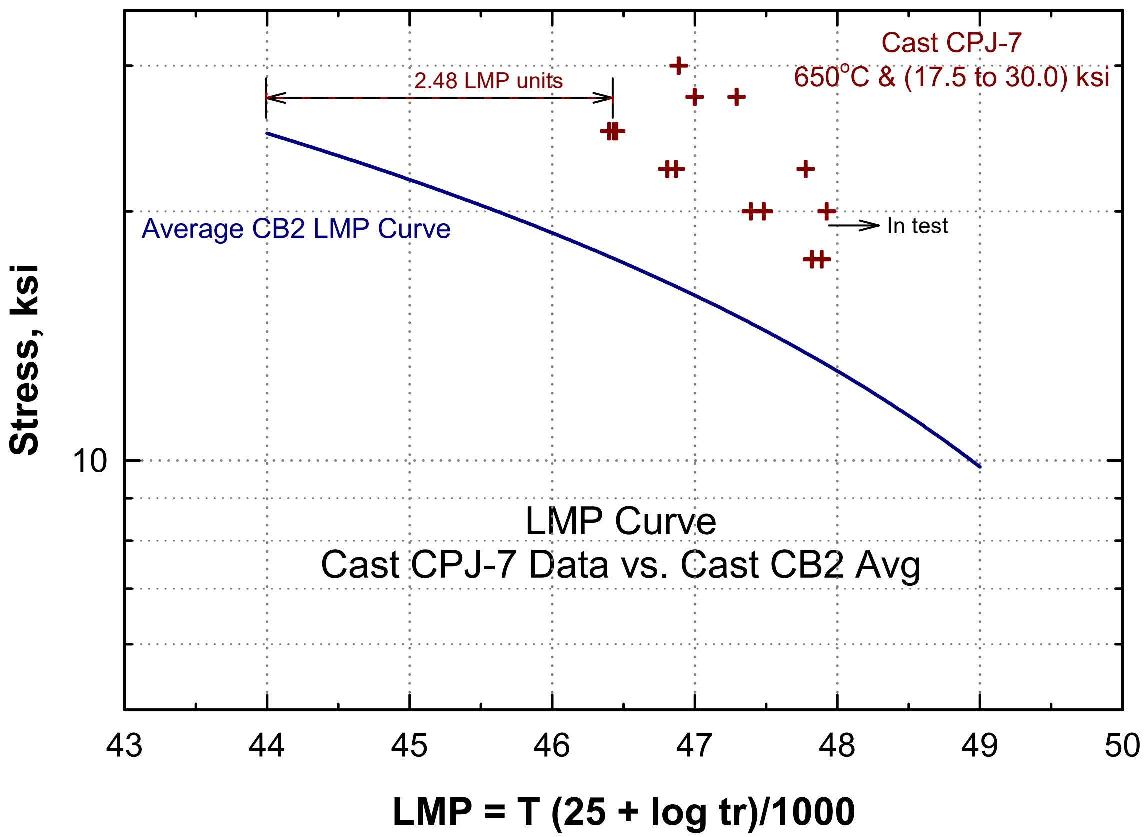
Defects more likely to be found in equiaxed region – last bit of molten metal to solidify.

Cast CPJ 7 Tensile Behavior Compared to CB2



Cast CPJ 7 vs. COST CB2

Creep Life & LMP Comparisons



Cast CPJ 7 vs. COST CB2

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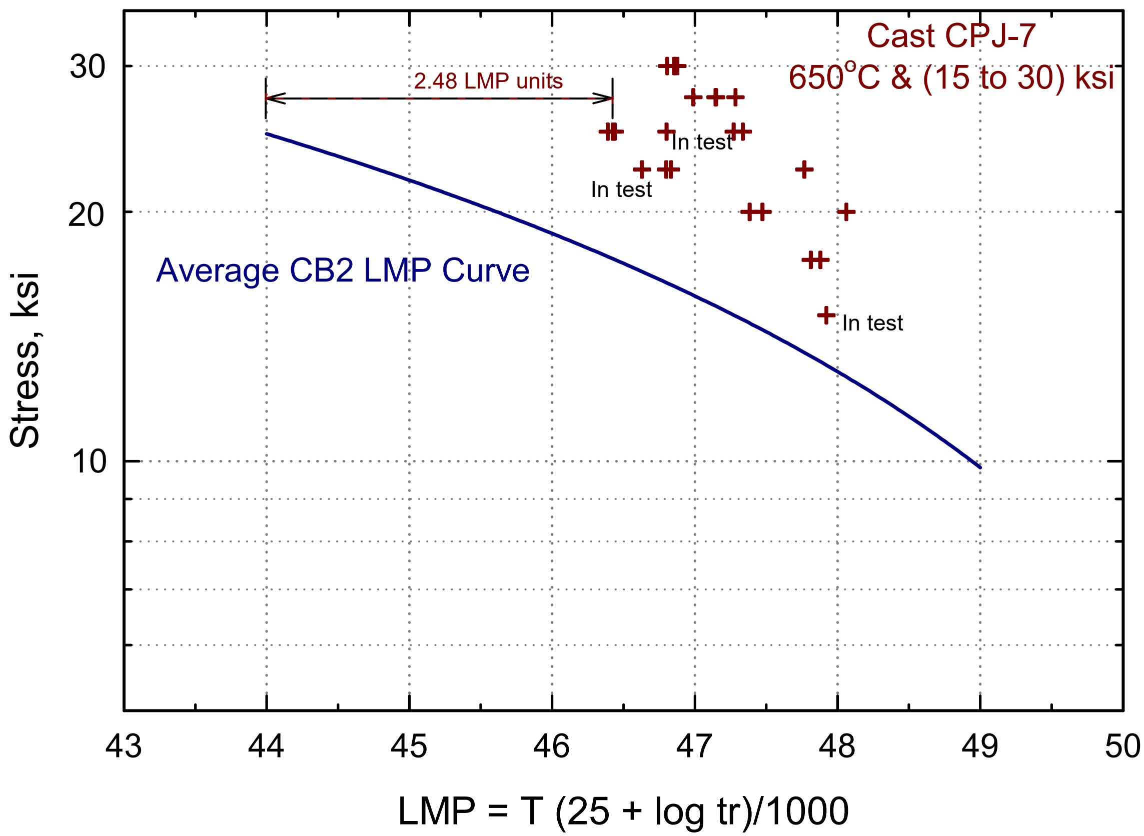
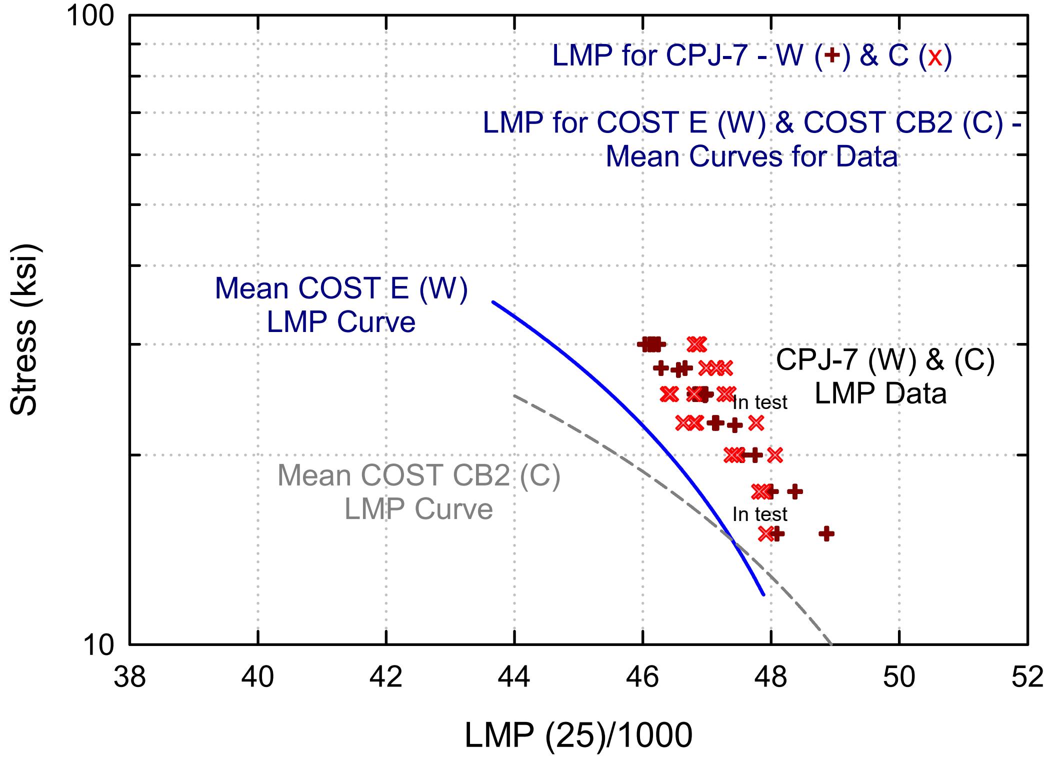


Creep Behavior Cast vs. Wrought CPJ 7 Steel

Comparison to COST E & COST CB2



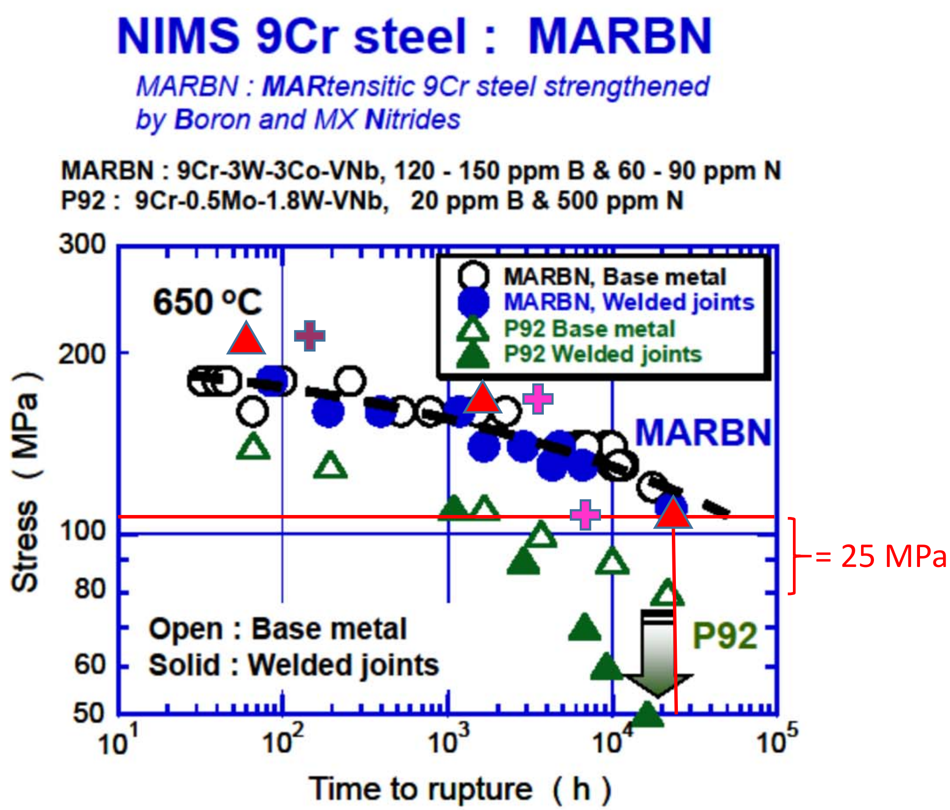
Larson-Miller Parameter plot for COST E & cast CB2 at temperatures from 1050°F (565.5°C) to 1200°F (648.9°C). CPJ-7 (cast (x) & wrought (+)) testing performed at 650°C only.

Summary & Planned Next Steps Cast CPJ 7

- Continue medium-term creep testing through 2017 and into 2018.
- Optimize casting process to produce sound castings (i.e., through the use of gating system, risers, filters, etc.).
- Produce castings suitable for welding studies (in conjunction with wrought plates of CPJ 7).
- Consider making large CPJ 7 casting via air induction melting process and/or vacuum arc remelting/electroslag remelting.
- Assess toughness & fracture energy, followed by selected fatigue screening tests at room temperature for CPJ 7 (wrought first, then castings).
- U.S. Patent awarded

  Hawk, Jablonski & Cowen, *Creep Resistant High Temperature Martensitic Steel*, US 9,556,503 B1, January 31, 2017.

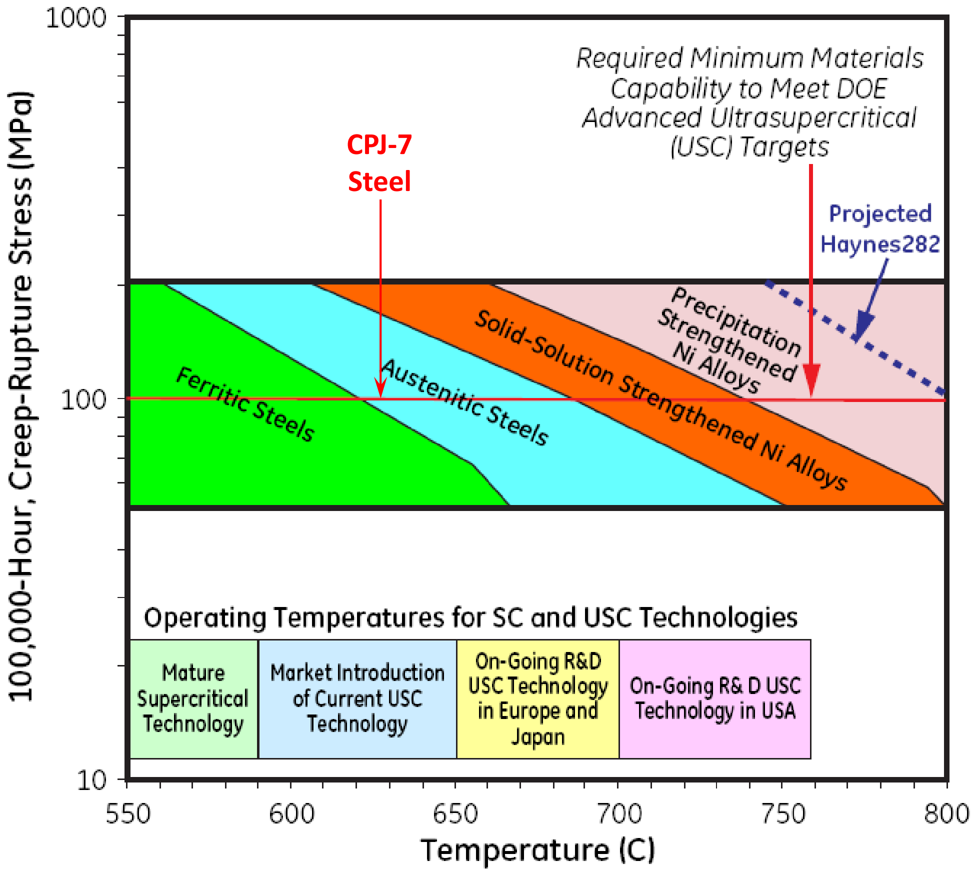
Ferritic-Martensitic MARBN-Type Steels

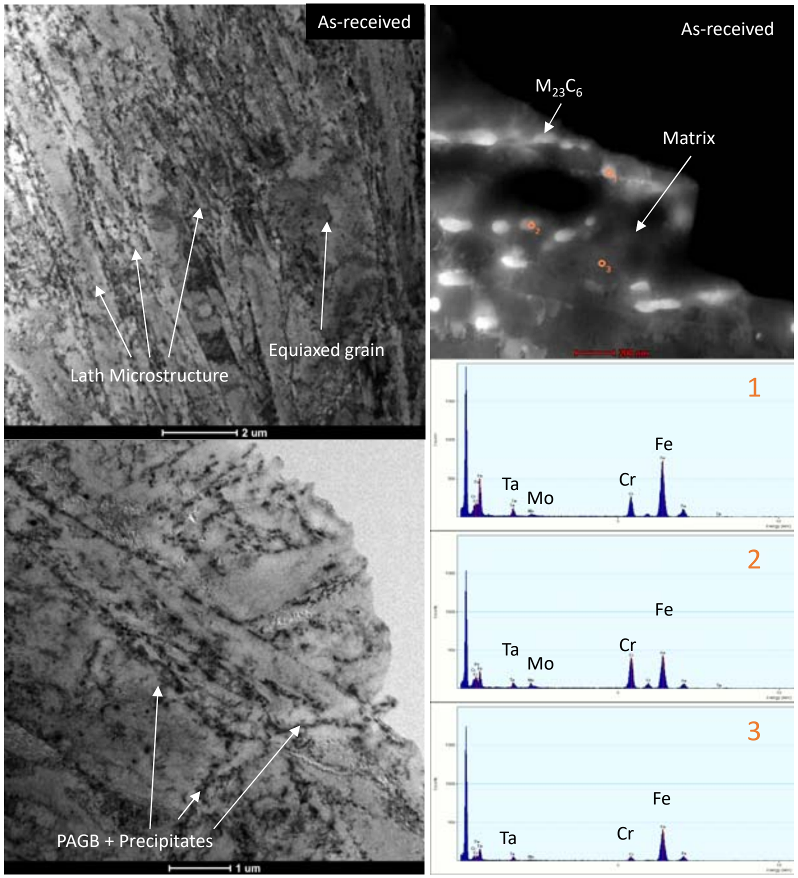


Where do the CPJ 7 steels stand with respect to other advanced 9% Cr steels?

Ferritic-Martensitic 9% Cr CPJ 7 Steel

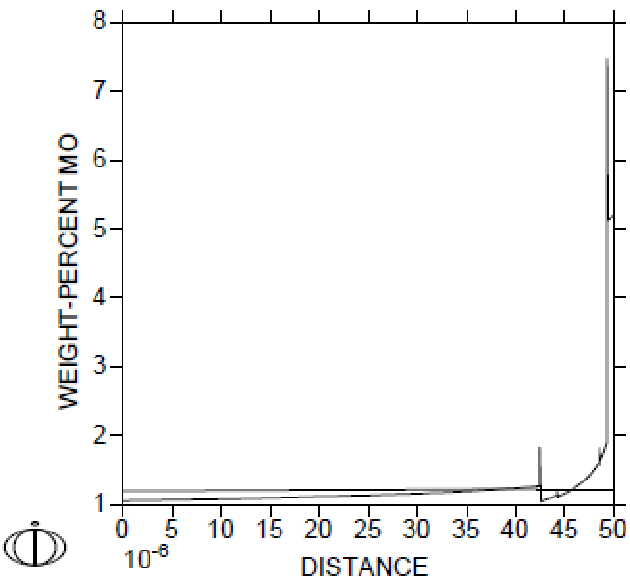
Potential for Use in USC Power Plants



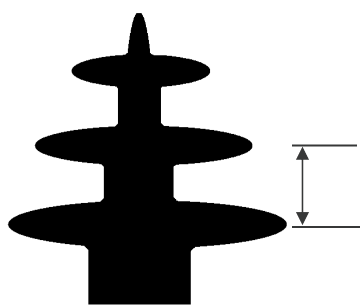


Heat Resistant Steels for 650°C Power Plants

- NETL alloy manufacturing approach focuses on homogenization step in which the incremental liquid chemistry is used to characterize the entire resulting solid inhomogeneity.
- Critical here is that the homogenization is taken to an acceptably uniform level. This is what gives the steel long term microstructural stability.



A plot of wt. % Mo vs. Distance (m) in the as-cast condition. It can be seen that there is quite significant difference in Mo weight fraction in the region equivalent to the center of, or ½, the *sdas* length.



secondary dendrite arm spacing, *sdas*

sdas approx. = 100 µm

Heat Resistant Steels for 650°C Power Plants

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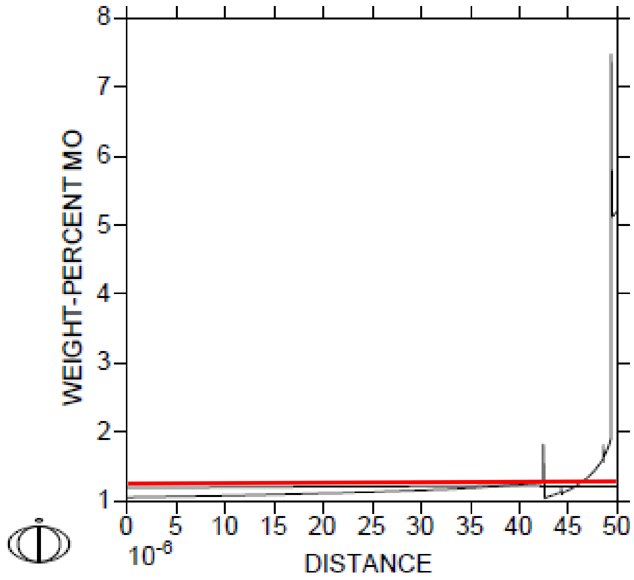
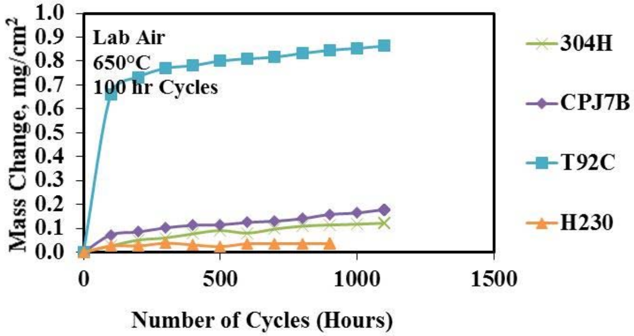
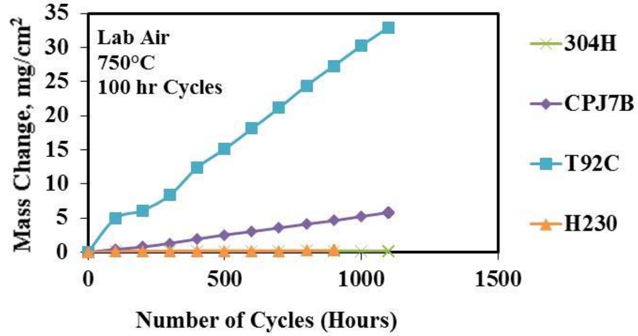


A plot of wt. % Mo vs. Distance (µm) in the as-cast and homogenized condition. After homogenization the Mo level was +/- 1% of the nominal level which was deemed adequate. Each element of the alloy was evaluated in a similar manner.

sdas approx. = 100 µm

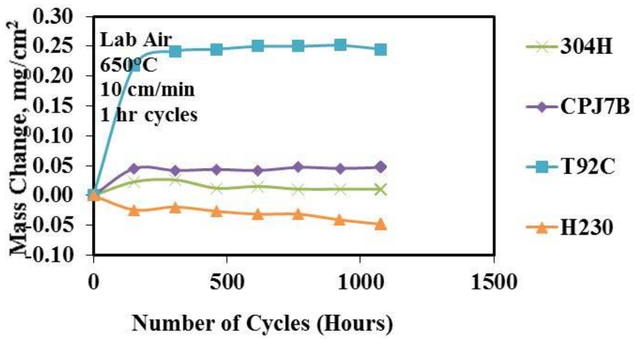
Air Oxidation with Moisture

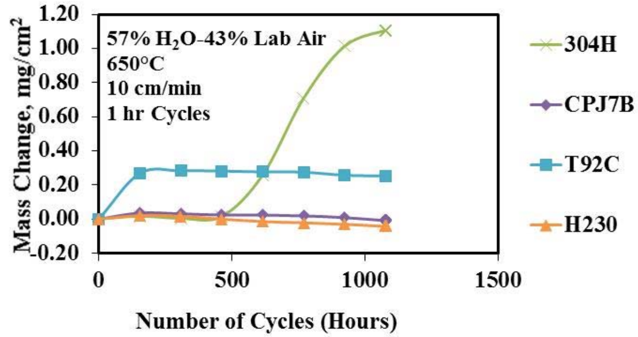




CPJ 7 performs as well as, or better than, T92 in air at 650°C & 750°C, regardless of cycling.

Water contributes to chromia evaporation and/or spalling.





Accomplishments & Future Work

- Continue short- and long-term creep testing through fall of 2017 & into 2018.
- Optimize casting process to reduce porosity & produce larger, more sound castings (i.e., through the use of gating system, risers, filters, etc.).
- Produce wrought plate & cast blocks suitable for welding studies. Explore alternative joining technologies like friction stir welding.
- Consider making large CPJ-7 casting via air induction melting process with inert gas cover. Assess limitations of approach relative to baseline data.
- Assess toughness & fracture energy, followed by selected fatigue screening tests at room temperature for CPJ-7 (wrought first, then castings).
- U.S. Patent Awarded: J.A. Hawk, P.D. Jablonski & C.C. Cowen, Creep Resistant High Temperature Martensitic Steel, US 9,556,503 B1, January 31, 2017.
- 2016 R&D 100 Award to NETL for "Computationally Optimized Heat Treatment of Metal Alloys" (Paul D. Jablonski & Jeffrey A. Hawk, November 2016, Washington, D.C.).

Thank you

Questions?

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