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Heat Resistant 9% Cr Steels: Current Status & Outlook Potential

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- NETL Advanced Alloy Development, 9% Cr Ferritic-Martensitic Steel Team: Martin Detrois, Omer Dogan, Gordon Holcomb, Slava Romanov, Kyle Rozman, Joe Tylczak, Ed Argetsinger, Joe Mendenhall, Chris Powell

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Advanced Alloy Development

Extreme Environment Materials Program

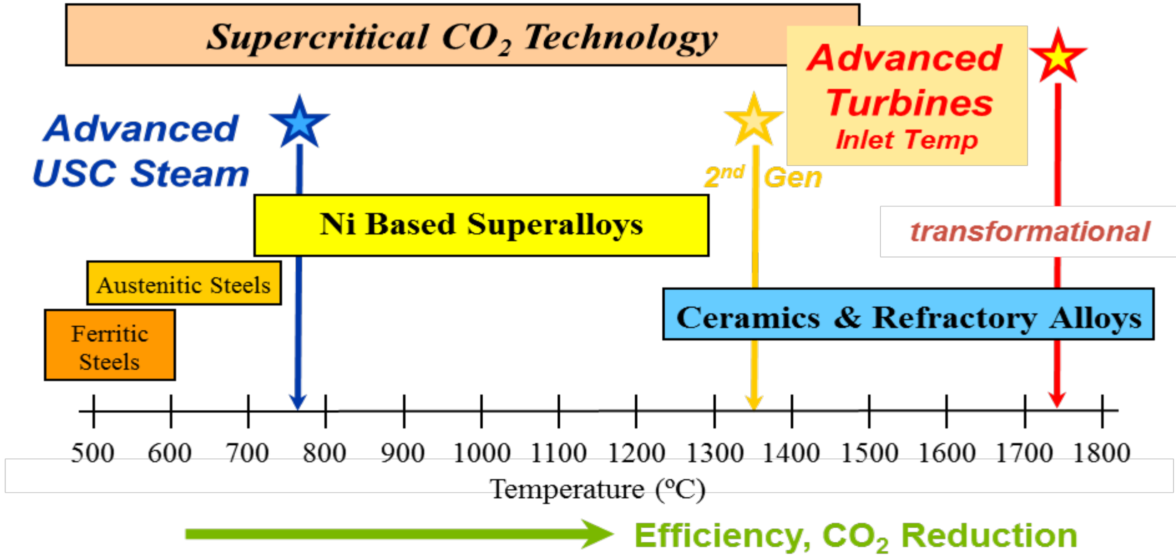
Goal:

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)



Advanced Alloy Development

- Advanced energy systems need stable materials with multi-length scale structural features that resist change over long times under very severe environmental conditions.

- Proficiency in manufacturing is incumbent to achieving these materials through relevant melting, or other, techniques that secure the desired structural features, leading to mechanical & physical performance consistent with the application.

- Integrating these materials into FE energy systems depends on the continual evolution of computational materials models, integrating them into alloy design, manufacturing, and life prediction. The focus is on real microstructures that accurately describe the physical framework for the entire component lifecycle.

- And yes. We want to do all this as cheaply as possible, using existing infrastructure and processes!

Introduction & Background

Heat Resistant Steel Development

Importance

Perfecting the design methodology and manufacturing practice for 9% Cr ferritic-martensitic steels will shorten the time needed to develop these advanced heat resistance alloys for transformational FE energy systems.

Scope

Increasing the operational temperature of 9% Cr ferritic-martensitic steels, austenitic stainless steels, and nickel superalloys will ensure the adoption of transformational FE energy systems for future coal-fired power needs.

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^{o}C, advanced 9-12% Cr steels are used exclusively.
- At the current time, ~620°C is the maximum use temperature due to concerns about the long-term microstructural instability of these steels (Z-phase).

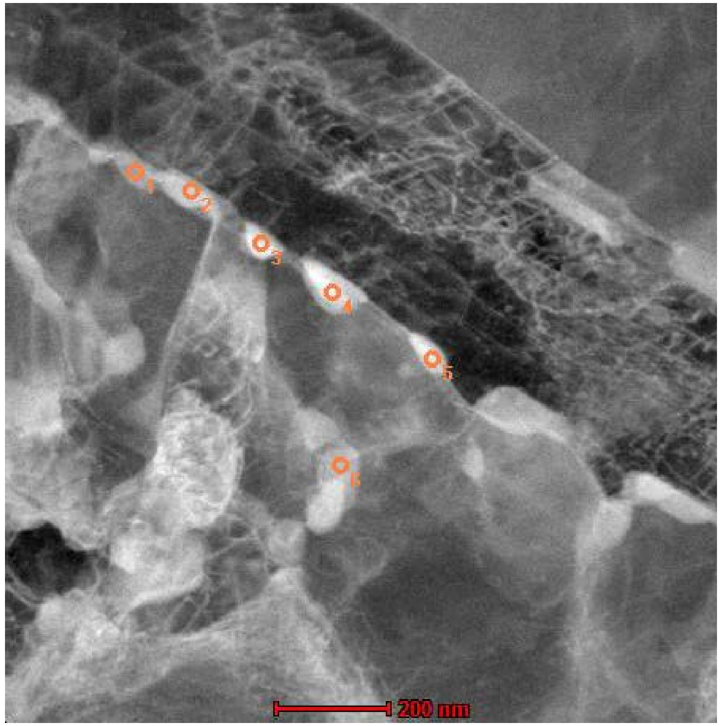
Martensitic Steel Development

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)

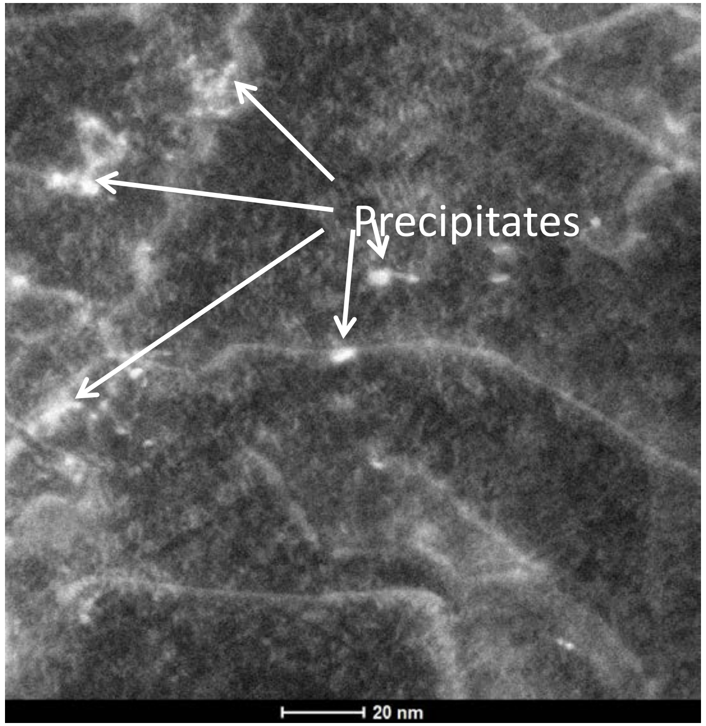


1990 – 2010: P92 steel (others MARBN-type steels, SAVE12, CPJ7, JMP, etc.)

- 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

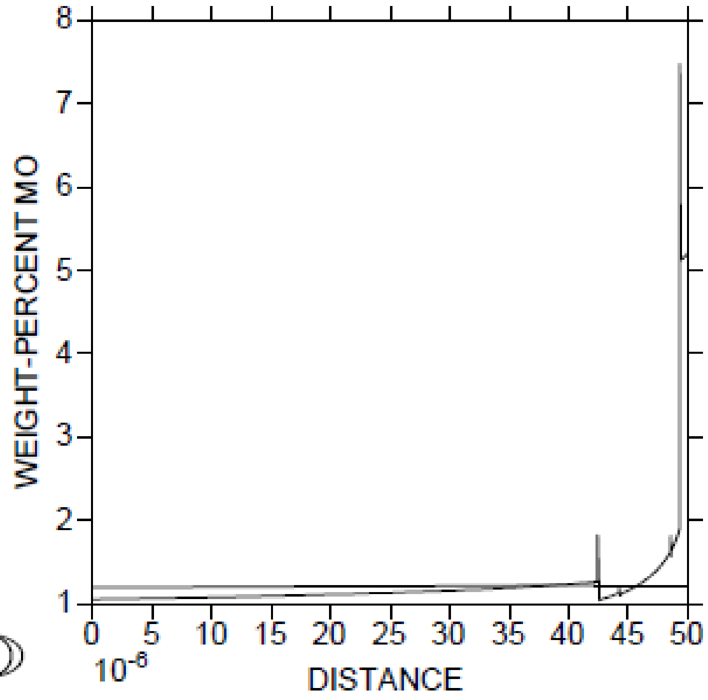
Computational/Experimental Alloy Design

- 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/SAVE12 (boiler).



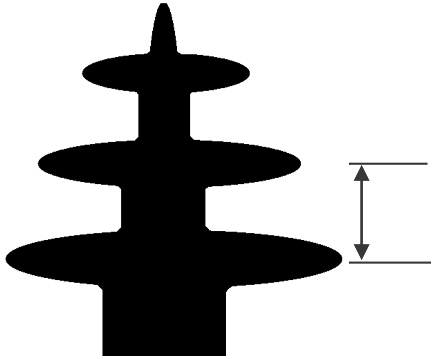
Heat Resistant Steels for 650°C Power Plants

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



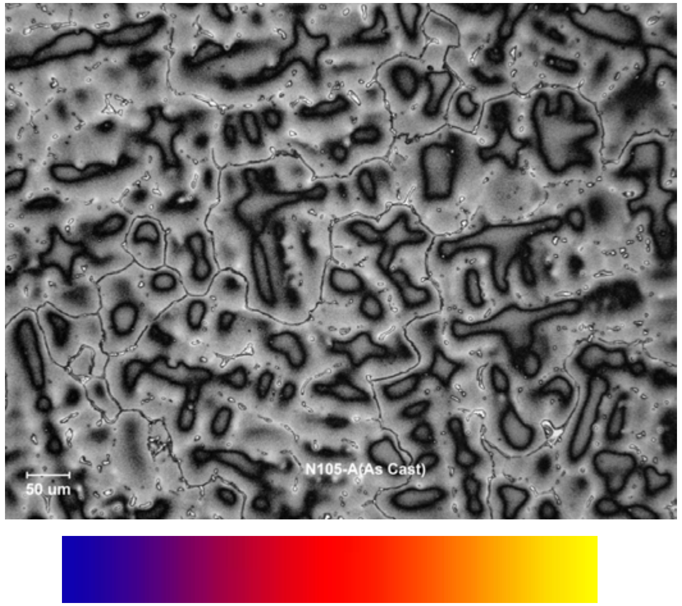
sdas approx. = 100 µm

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*

As-cast



Heat Resistant Steels for 650°C Power Plants

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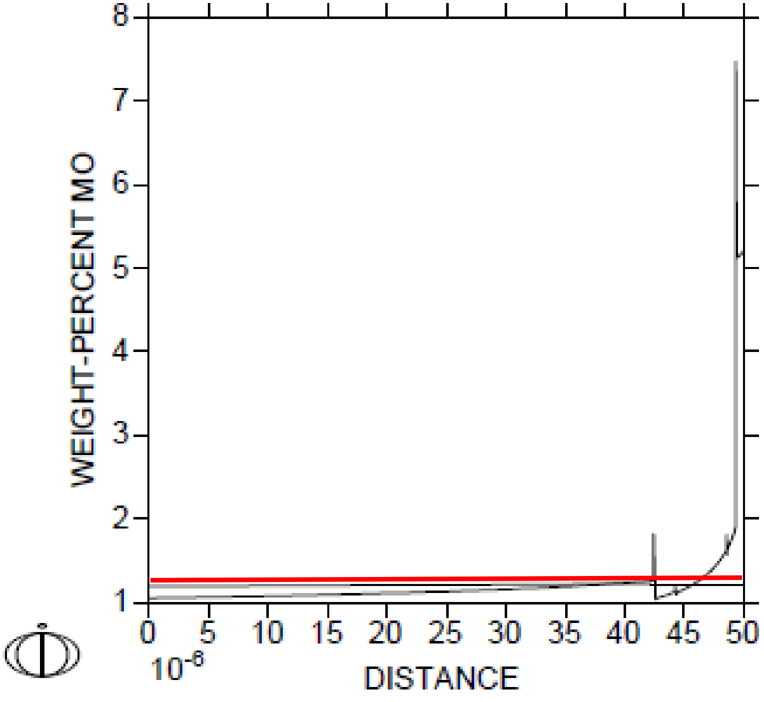
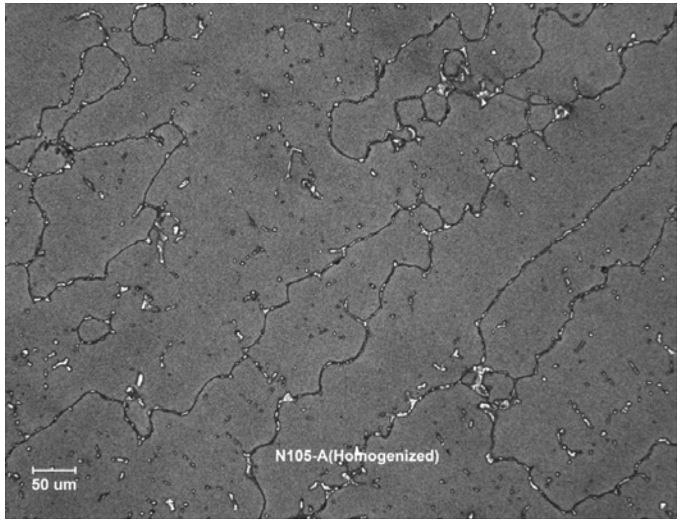


sdas approx. = 100 µm

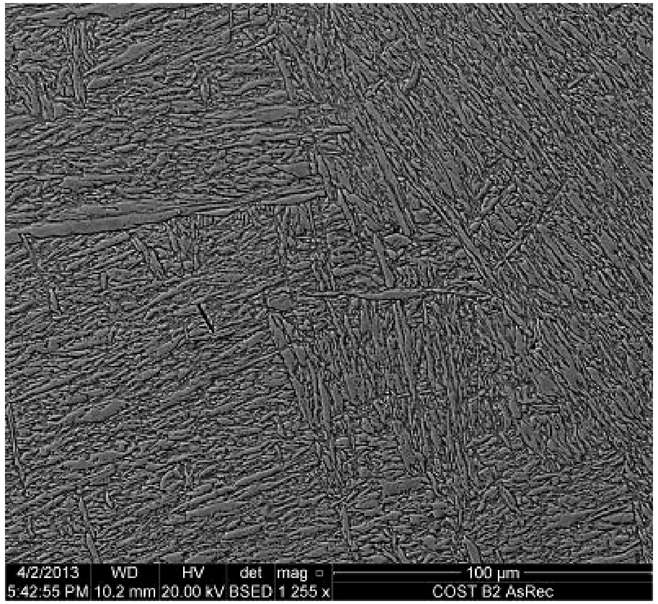
A plot of wt. % Mo vs. Distance (µm) in the as-cast and homogenized condition. After homogenization the Mo level was +/- 1% of the nominal level which was deemed adequate. Each element of the alloy was evaluated in a similar manner.

Homogenized



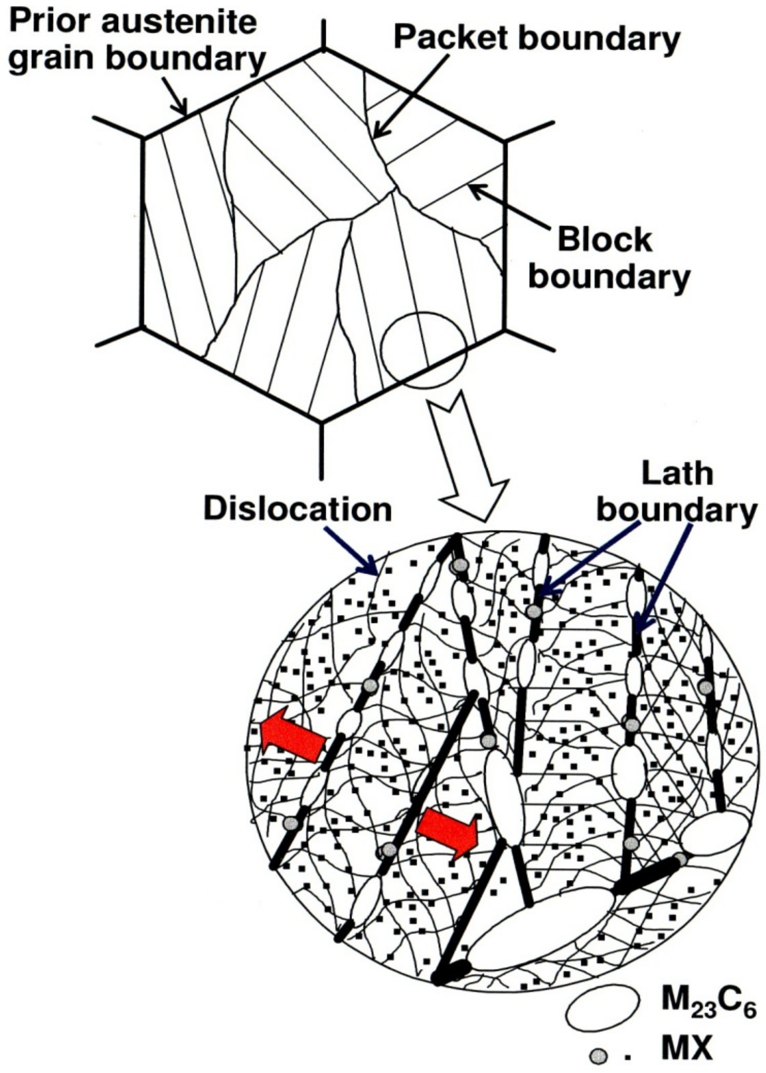
General Technical Approach

- 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).

Feature Hierarchy of 9-12% Cr Containing Steels

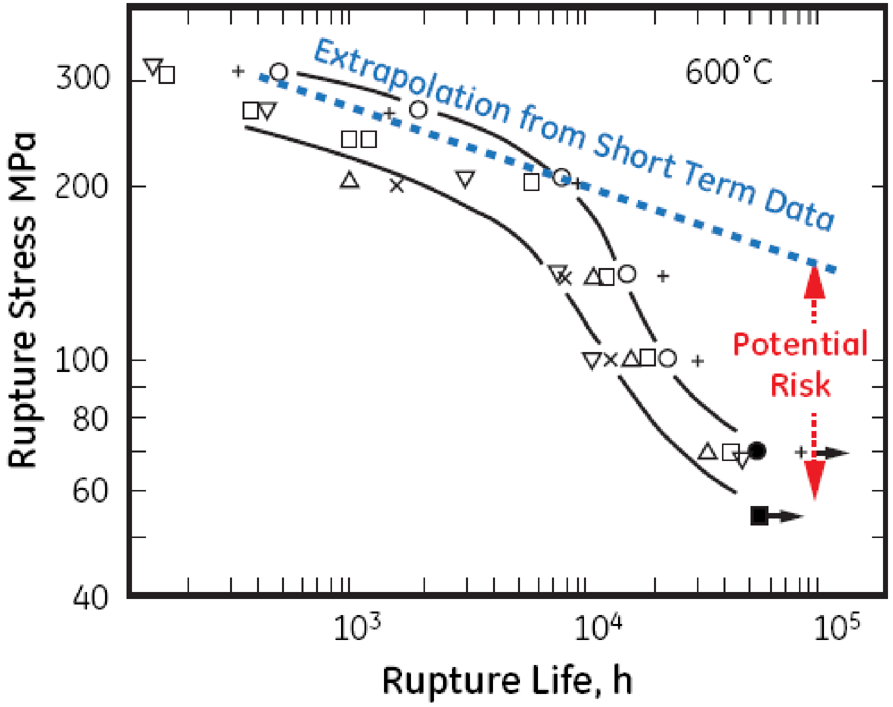


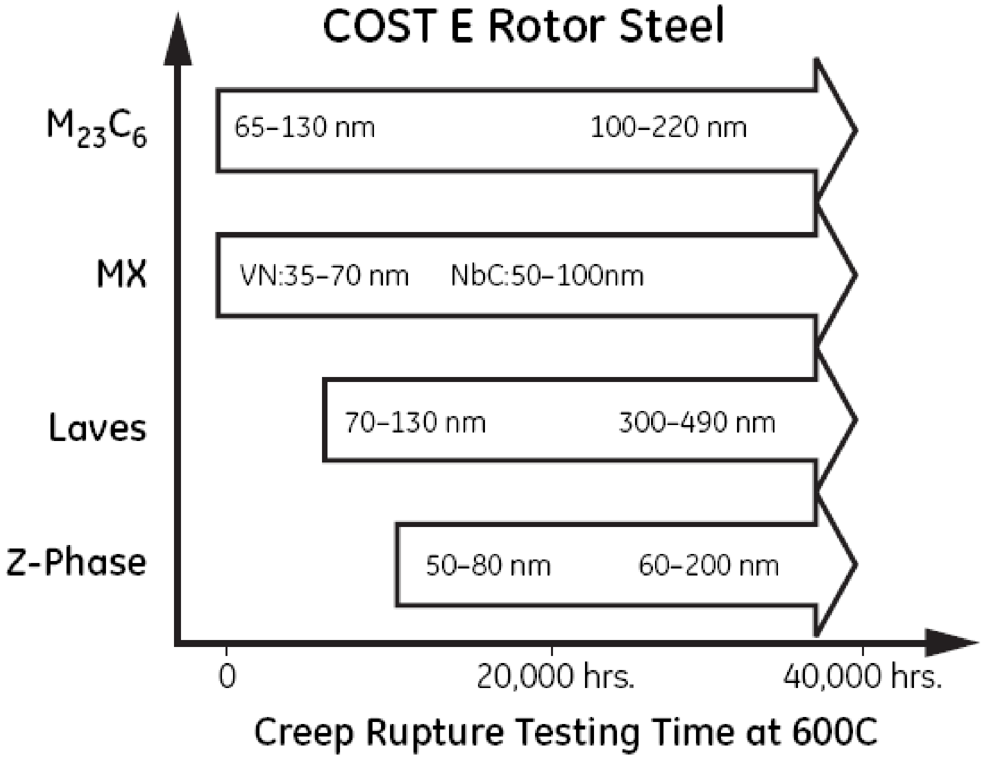
1. Prior austenite grain with associated grain boundaries.
2. Packet boundaries
3. Block boundaries
4. Lath boundaries
5. $M_{23}C_6$ carbides to stabilize lath, block, packet, and PAG boundaries
6. MX carbides to provide obstacles to dislocation motion
7. Dislocations

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



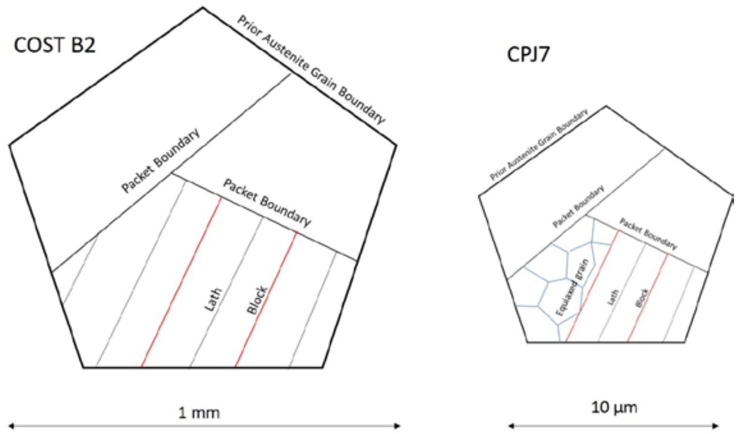


Many competing effects occur in heat resistant steels of the 9% Cr variety. Past experience has shown that the instability of any of the following, Z-phase, Laves, MX and/or $M_{23}C_6$, can cause an unexpected decrease in rupture stress as a function of time. The goal of alloy design is to slow down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

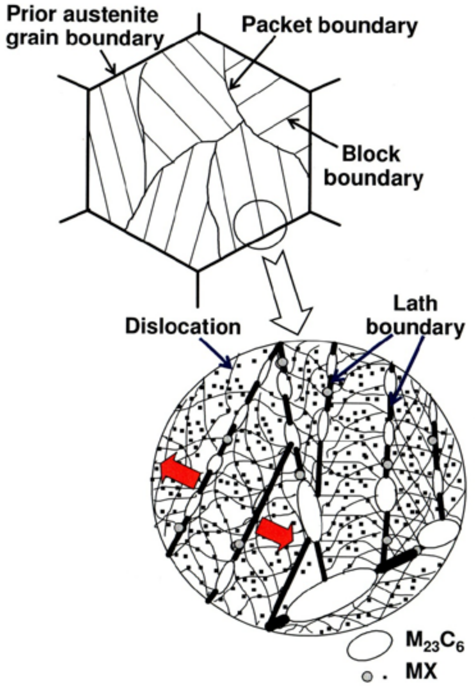
Summary of Major Commercial 9-12% Cr Steels

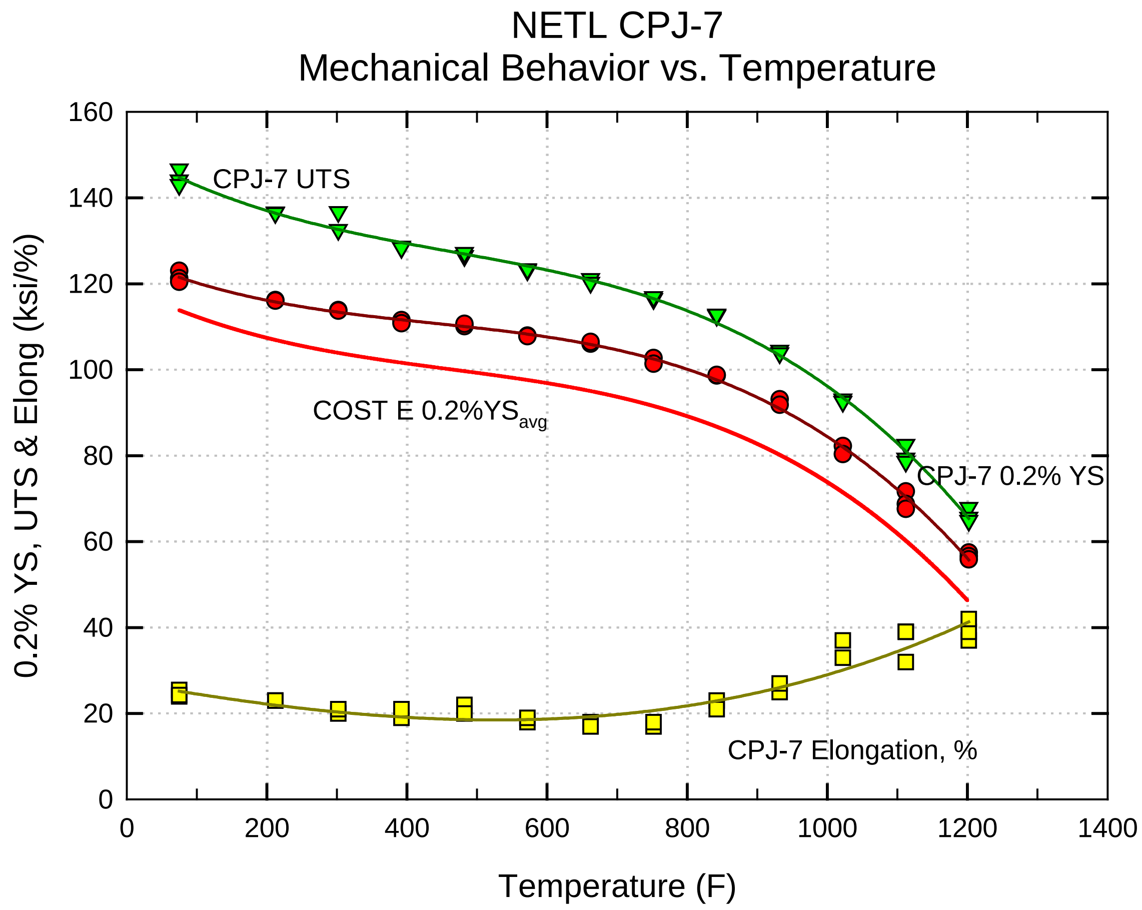
Chemistry													
Material	***C***	***Mn***	***Si***	***Ni***	***Cr***	***Mo***	***V***	***Nb***	***N***	***W***	***B***	***Co***	**Fe**	**Ta**
COST FB2	0.13	0.30	0.08	0.05	9.30	1.50	0.20	0.05	0.026		0.01	1.00	Bal	
COST E	0.12	0.45	0.10	0.74	10.40	1.10	0.18	0.045	0.05	1.00			Bal	
COST B2	0.18	0.06	0.10	0.09	9.28	1.54	0.29	0.06	0.02		0.01		Bal	
CPJ7	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
CPJ7B	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
CPJ7C	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
CPJ7D	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
CPJ7E	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 CPJ7 Tensile Mechanical Behavior





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*
CPJ7	1.501	0.170	100
CPJ7B	1.675	0.175	78
CPJ7C	1.585	0.182	86
CPJ7D	1.575	0.185	83
CPJ7E	1.595	0.172	87

Mo$_{(Eq)}$ = % Mo + ½ % W

Selected CPJ7 Chemistry Modifications

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**	
CPJ7	**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**
CPJ7B	**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**
CPJ7C	**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**
CPJ7D	**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**
CPJ7E	**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**
CPJ8A	**0.15**	**0.42**	**0.10**	**0.28**	**10.64**	**0.50**	**0.21**	**0.056**	**0.034**	**0.51**	**0.0089**	**2.93**	**Bal**	**0.27**
CPJ9	**0.14**	**0.40**	**0.08**	**0.27**	**10.63**	**0.51**	**0.20**	**0.055**	**0.020**	**0.52**	**0.0087**	**2.94**	**Bal**	**< 0.003**
CPJ10	**0.15**	**0.43**	**0.11**	**0.21**	**10.03**	**1.37**	**0.22**	**0.058**	**0.028**	**0.51**	**0.0093**	**1.59**	**Bal**	**0.16**
CPJ11	**0.15**	**0.41**	**0.10**	**0.23**	**10.18**	**1.35**	**0.21**	**0.051**	**0.022**	**0.60**	**0.0097**	**1.59**	**Bal**	***0.16***
CPJ12	**0.15**	**0.42**	**0.10**	**0.23**	**10.62**	**0.54**	**0.19**	**0.054**	**0.030**	**0.48**	**0.0097**	**4.67**	**Bal**	**0.18**
CPJ13	**0.15**	**0.45**	**0.10**	**0.27**	**10.53**	**0.53**	**0.24**	**0.055**	**0.033**	**0.51**	**0.0088**	**6.16**	**Bal**	**0.26**
CPJ14	**0.15**	**0.44**	**0.10**	**0.26**	**10.74**	**0.52**	**0.20**	**0.053**	**0.038**	**0.50**	**0.0095**	**8.23**	**Bal**	**0.19**

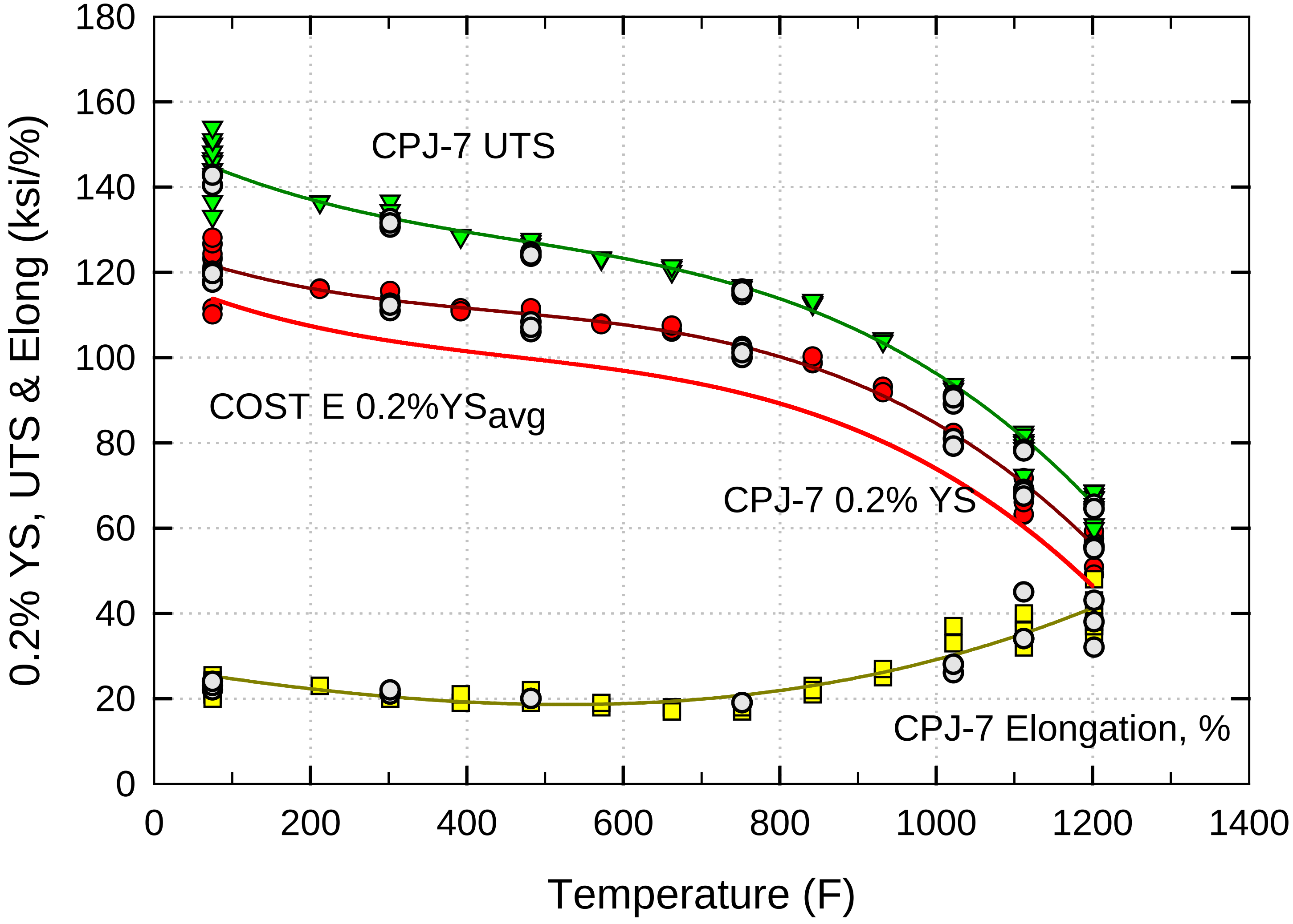
The following elements were also found in the CPJ Steels: Ti (<0.004%), Al (<0.02%), P (<0.003%), O (<36 ppm), S (<58 ppm) and Cu (CPJ-7 = 0.003% & CPJ (8A-14) ≤ 0.03%).

Blue: Cu effect; Red: Co effect; Green: no Ta (#9) or Hf substituted for Ta (#11)

Matrix of CPJ7-type Chemistry Modifications

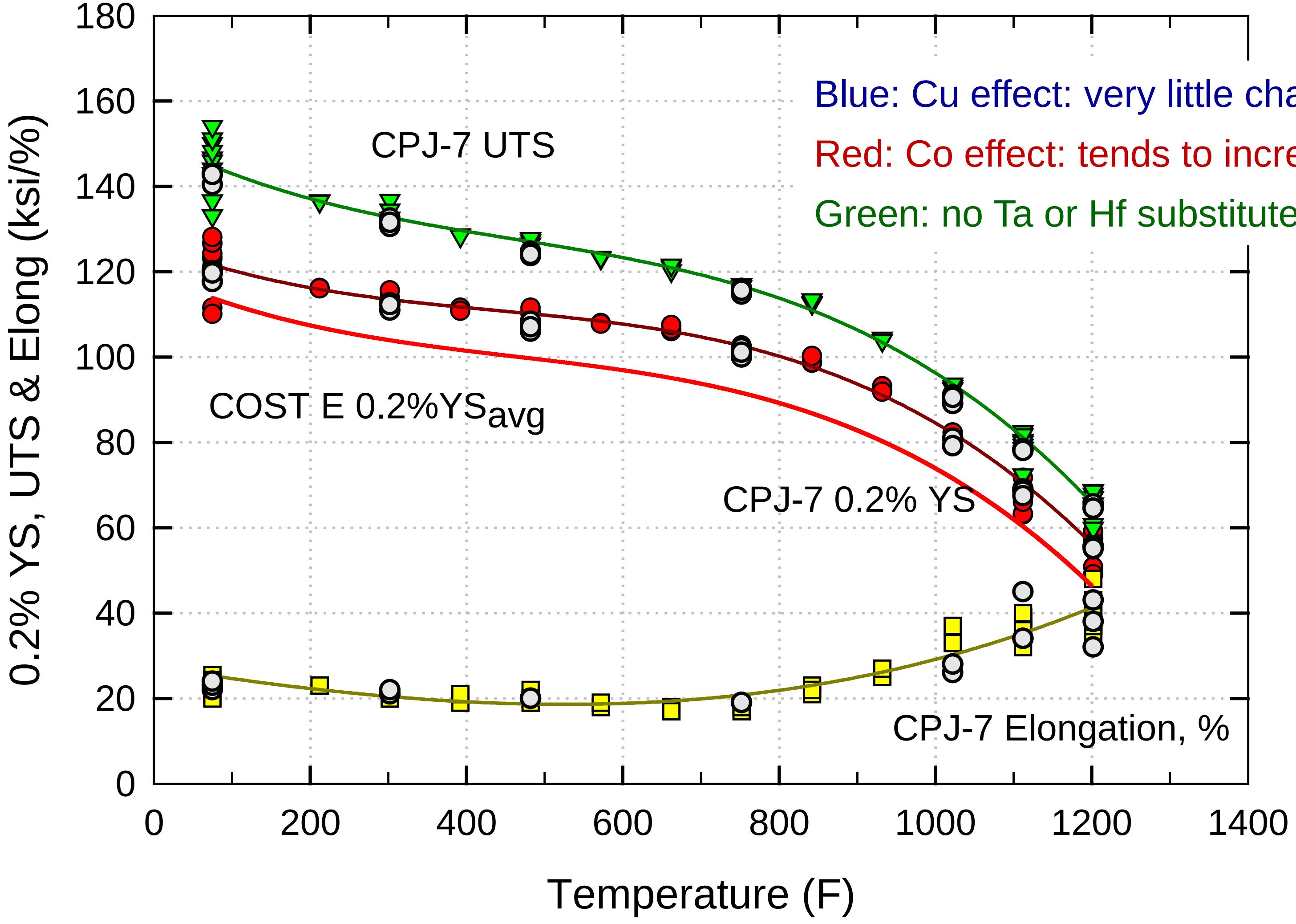
ID	Mn	Si	Cr	Ni	Co	Mo	W	Nb	Ti	Al	Fe	Cu	Ta	Hf	Re	V	C	O	N	P	S	B
#	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%		Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	ppm	ppm	Wt%	ppm	ppm
1	0.480	0.24	10.08	0.070	2.93	0.01	0.025	0.053	0.095	0.013	BAL	0.003	0.003			0.21	0.10	92	111	0.001	60	100
2	0.490	0.26	10.08	0.060	0.01	1.53	0.010	0.057	0.097	0.013	BAL	0.003	0.001			0.21	0.10	72	96	0.001	60	100
3	0.508	0.261	10.111	0.080	2.931	0.010	0.037	0.054	0.010	0.017	BAL	0.003	0.145			0.206	0.18	30	161	0.001	60	100
4.1	0.406	0.087	9.833	0.270	1.479	1.262	0.482	0.056	0.004	0.016	BAL	0.003	0.279			0.209	0.15	36	200	0.001	50	100
4.2	0.288	0.150	9.812	0.217	1.529	1.464	0.428	0.059	0.004	0.005	BAL	0.003	0.202			0.204	0.15	29	252	0.003	58	78
4.3	0.473	0.111	9.953	0.224	1.588	1.342	0.493	0.061	0.004	0.009	BAL	0.003	0.198			0.194	0.16	34	222	0.003	55	86
4.4	0.430	0.101	10.121	0.215	1.557	1.312	0.526	0.054	0.004	0.010	BAL	0.003	0.244			0.212	0.16	36	245	0.001	58	83
4.5	0.421	0.117	9.993	0.206	1.505	1.325	0.530	0.049	0.004	0.014	BAL	0.003	0.280			0.199	0.15	32	221	0.001	58	87
4.6	0.430	0.106	10.034	0.214	1.585	1.365	0.508	0.058	0.004	0.005	BAL	0.031	0.155			0.219	0.15	64	278	0.003	59	93
4.7	0.405	0.065	9.963	0.310	1.467	1.263	0.484	0.056	0.001	0.013	BAL	0.028	0.377			0.202	0.15	66	222	0.001	38	92
4.8	0.393	0.055	9.986	0.310	1.480	1.262	0.480	0.056	0.001	0.012	BAL	0.026	0.310			0.206	0.15	73	208	0.001	42	90
4.9	0.406	0.071	9.969	0.310	1.472	1.262	0.491	0.056	0.003	0.014	BAL	0.027	0.368			0.207	0.15	67	176	0.001	38	89
4.10	0.471	0.096	9.847	0.270	1.458	1.261	0.484	0.057	0.002	0.011	BAL	0.294	0.280			0.208	0.15	32	239	0.001	56	104
4.11	0.414	0.078	9.875	0.270	1.467	1.268	0.472	0.056	0.001	0.017	BAL	0.006	0.269		0.115	0.202	0.15	32	238	0.001	58	102
5	0.415	0.101	10.639	0.280	2.933	0.504	0.513	0.056	0.003	0.013	BAL	0.033	0.266			0.205	0.15	50	341	0.001	60	89
6	0.403	0.084	10.629	0.270	2.937	0.505	0.517	0.055	0.010	0.012	BAL	0.031	0.003			0.203	0.14	75	200	0.001	64	87
7	0.410	0.101	10.176	0.227	1.586	1.347	0.596	0.051	0.004	0.005	BAL	0.042	0.005	0.160		0.213	0.15	47	215	0.002	59	97
8	0.422	0.099	10.618	0.234	4.673	0.539	0.479	0.054	0.004	0.005	BAL	0.043	0.177			0.190	0.15	28	296	0.002	67	97
9	0.452	0.101	10.527	0.269	6.158	0.527	0.508	0.055	0.004	0.011	BAL	0.037	0.260			0.237	0.15	28	328	0.002	67	88
10	0.443	0.013	10.740	0.260	8.226	0.524	0.498	0.053	0.004	0.005	BAL	0.037	0.185			0.197	0.15	23	379	0.001	75	95
11	0.413	0.084	9.875	0.260	0.012	1.262	0.479	0.056	0.003	0.016	BAL	0.002	0.266			0.205	0.15	43	244	0.001	50	83
12	0.409	0.057	9.975	0.310	2.949	1.267	0.458	0.062	0.001	0.013	BAL	0.026	0.355			0.208	0.15	72	221	0.001	39	75
13	0.403	0.054	9.969	0.310	0.736	1.269	0.468	0.061	0.002	0.013	BAL	0.027	0.361			0.210	0.15	74	238	0.001	36	75
14	0.419	0.088	9.893	0.270	1.460	0.502	0.515	0.054	0.002	0.011	BAL	0.295	0.233			0.206	0.15	50	221	0.001	50	113
15	0.411	0.085	9.866	0.270	1.466	0.506	0.511	0.055	0.001	0.017	BAL	0.003	0.274		0.100	0.205	0.15	27	236	0.001	59	106
16	0.412	0.078	9.111	0.270	1.474	1.370	0.476	0.056	0.002	0.014	BAL	0.033	0.346			0.206	0.15	28	226	0.001	59	85
17	0.510	0.229	9.085	0.190	2.942	0.100	2.914	0.062	0.001	0.014	BAL	0.003	0.010			0.202	0.15	27	193	0.001	59	104
18	0.511	0.257	9.085	0.180	2.926	0.101	2.894	0.065	0.001	0.014	BAL	0.003	0.003			0.208	0.15	21	230	0.001	67	121
19	0.512	0.240	9.080	0.180	2.928	0.100	2.897	0.063	0.001	0.016	BAL	0.032	0.349			0.203	0.15	22	222	0.001	60	101

Summary of CPJ7 Tensile Mechanical Behavior



Based on selected CPJ7 chemistry modifications.

Summary of CPJ7 Tensile Mechanical Behavior



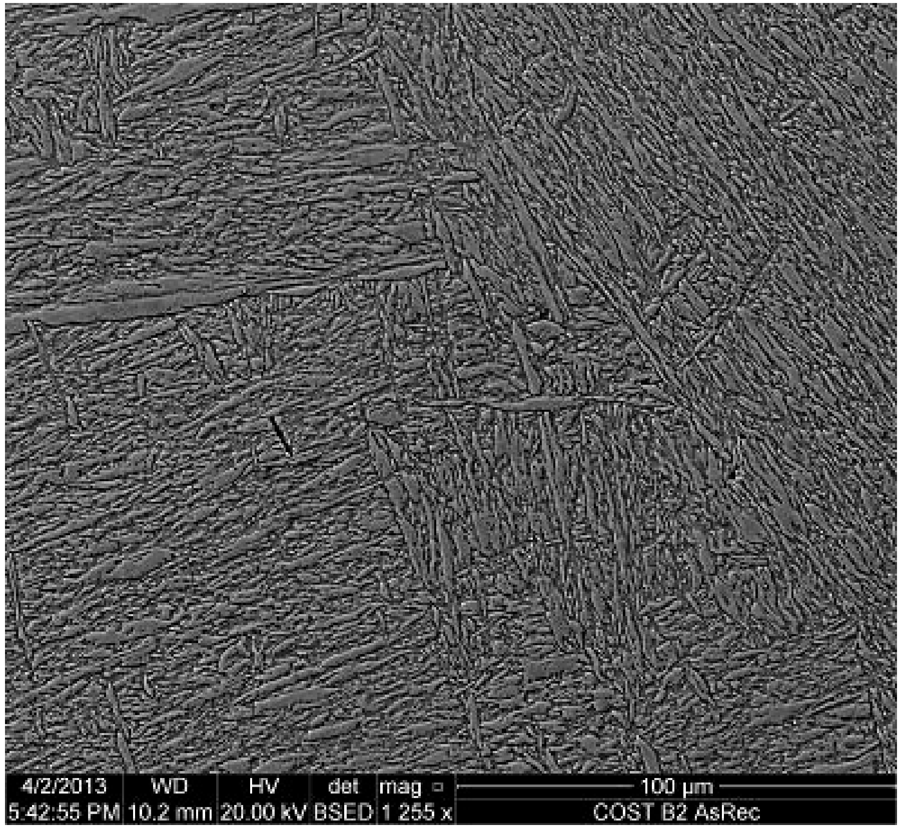
Blue: Cu effect: very little change in tensile behavior (CPJ7 & 10)

Red: Co effect: tends to increase tensile strength relative to CPJ7

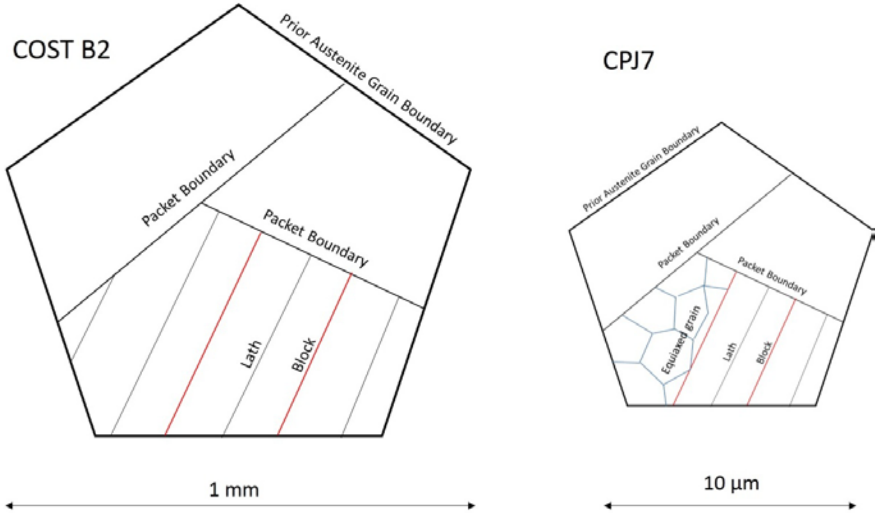
Green: no Ta or Hf substituted for Ta: lower tensile strength relative to CPJ7

Based on selected CPJ7 chemistry modifications.

Summary of CPJ7 Microstructure Features



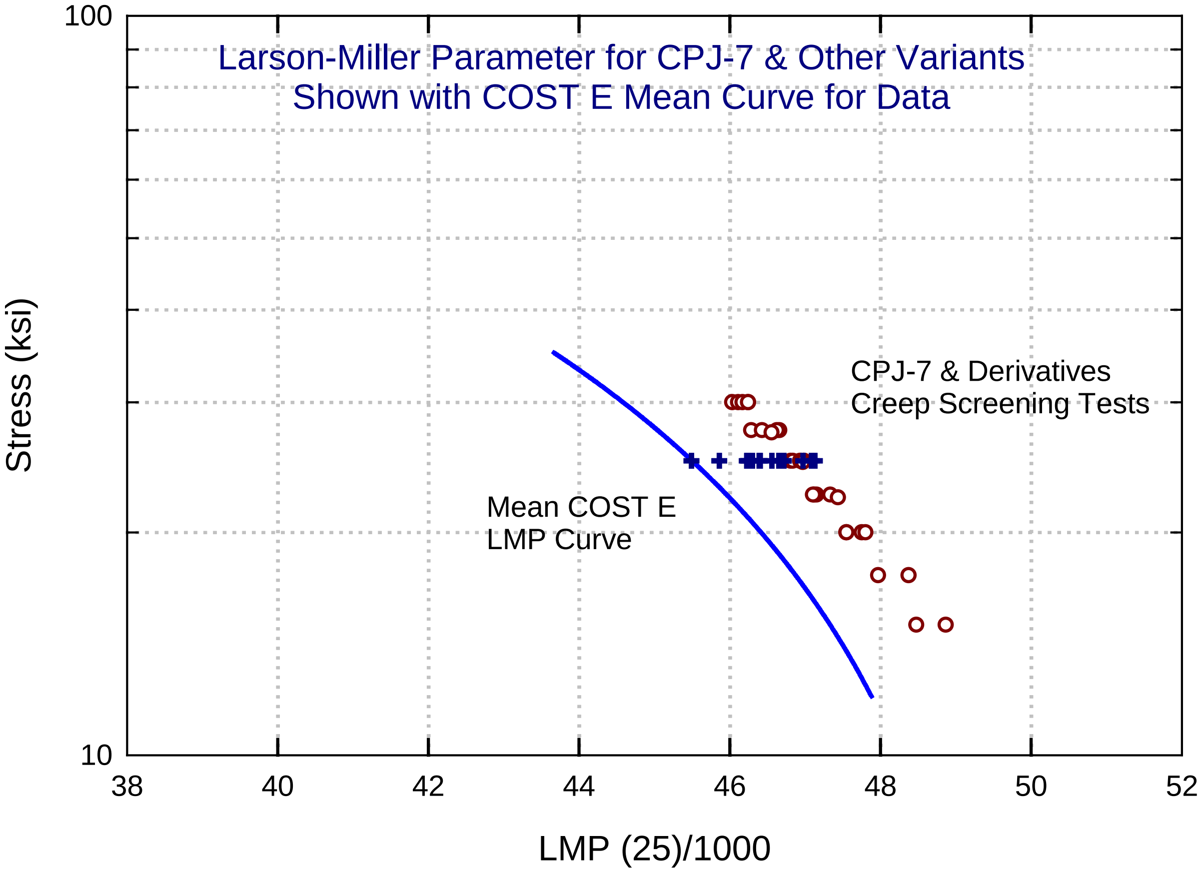
Murayama et al., VaTech, as part of the NETL-RUA Innovative Process Technologies, 2011-2012.

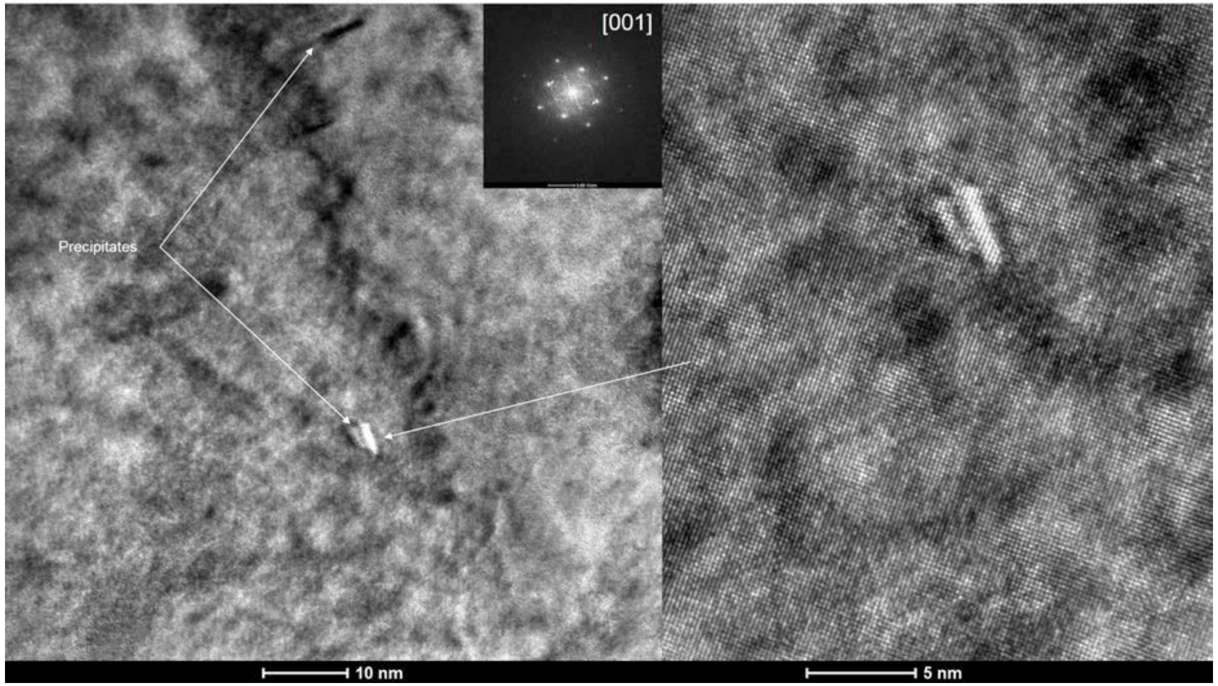


Microstructure Feature	COST B2	CPJ-7
Matrix Phase	Martensite	Martensite + Retained Ferrite or Recrytallized Grains
Prior Austenite Grain (PAG)	1 mm	6 – 15 µm
Lath Size	1 – 2 µm	1 – 2 µm
Precipitates	$M_{23}C_6$	$M_{23}C_6$ + Laves
Precipitate Location	Grain Boundaries (GB)	GB + Grain Interiors
Dislocation Density	High (due to martensitic transformation)	Mixed – Low in equiaxed grain regions & high in martensitic regions
Probable Creep Resistance Mechanisms	Boundary precipitates & high dislocation density*	Boundary precipitates, including Laves*

Larson-Miller Parameter

Larson-Miller Parameter plot for COST E at temperatures from 1050°F (565.5°C) to 1200°F (648.9°C). CPJ7 testing performed at 650°C only.

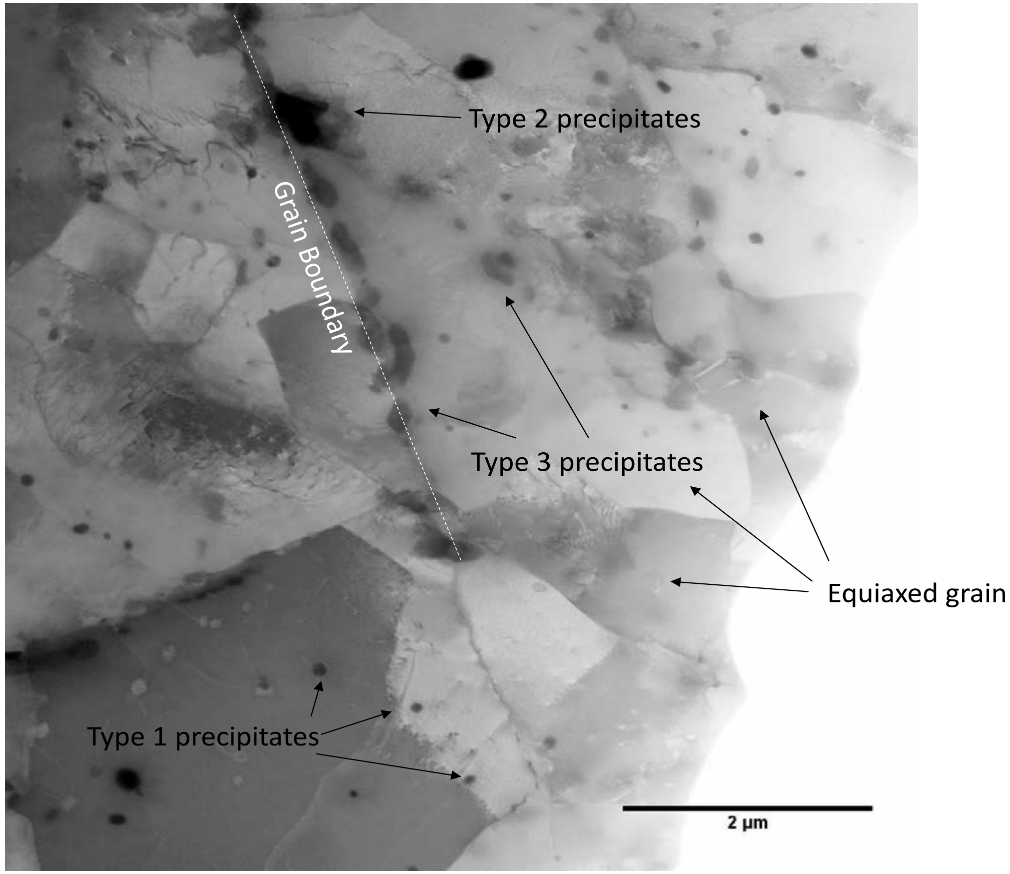




(Left) HRTEM micrograph showing fine coherent MX-type precipitates in the martensitic matrix of as-received CPJ7. (Right) A magnified view of the lower precipitate in the left panel. The precipitate is located at the center of two high-strain (white) regions that result from lattice mismatch between the precipitate and the matrix.

Wrought CPJ7 Martensitic 9% Cr Steel

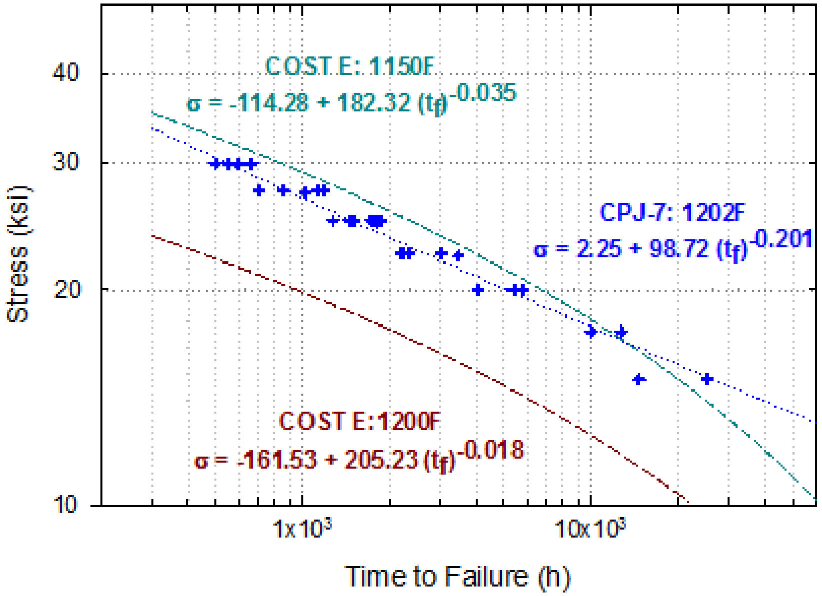
- ☐ Identified promising chemistry for ferritic-martensitic steel, CPJ7, through control of minor alloying additions (C, Cu, Ta), and in particular, the combined B/N levels.
- ☐ Developed manufacturing approach to consistently produce CPJ7.
- ☐ Utilized NETL homogenization cycle in conjunction with thermo-mechanical processing to set and stabilize microstructure.
- ☐ Tested CPJ7 chemistry robustness by varying select combinations of alloying additions: $Mo_{(eqv)}$; C + N level; B level – producing and testing four additional CPJ7 heats, initially & many others later on.
- ☐ Assessed other minor element additions and extent of those additions on tensile and creep strength of CPJ7 base alloy.



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

Cast Ferritic-Martensitic 9% Cr CPJ7 Steel

- Previous research identified NETL martensitic-ferritic steel CPJ7. A wrought product was manufactured.
- NETL wrought CPJ7 steel exhibited superior creep strength compared to commercially designed, thermo-mechanically processed & 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 the same alloy design rationale to develop cast martensitic 9% Cr steel. Alloy homogenization using NETL algorithmic approach with subsequent martensitic steel heat treatment produced cast version of CPJ7 superior to any existing commercially available cast 9% Cr martensitic steel or derivatives.



Wrought vs. Cast Manufacturing

<ins>Wrought Manufacturing Steps:</ins>

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

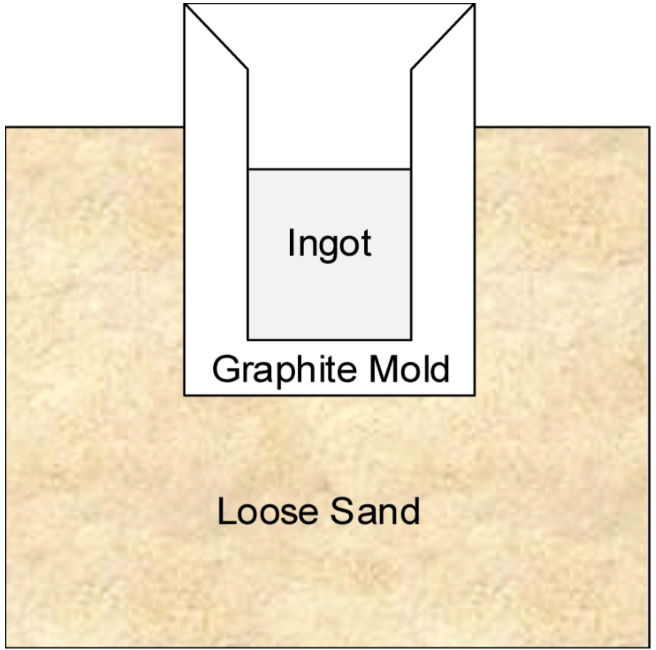
<ins>Cast Manufacturing Steps:</ins>

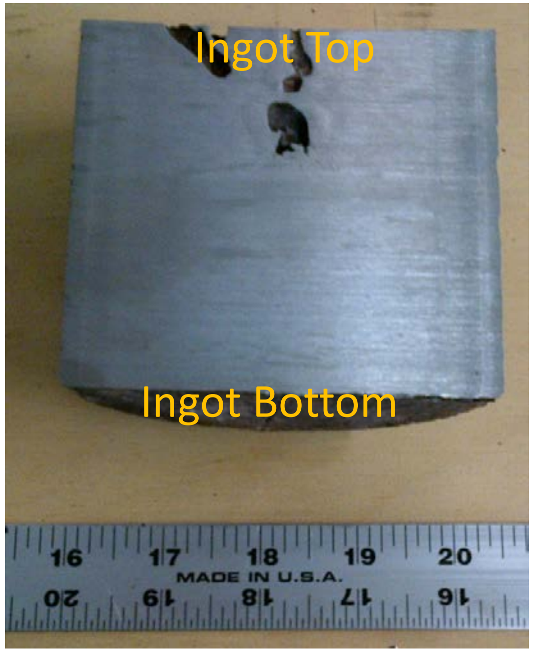
1. Alloy Design
2. Melt Processing
3. *Homogenization*
    - Improve chemical uniformity within the matrix structure
4. Heat Treatment for Strength & Ductility/Fracture Toughness

- ➢ 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

Heats of CPJ-7 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

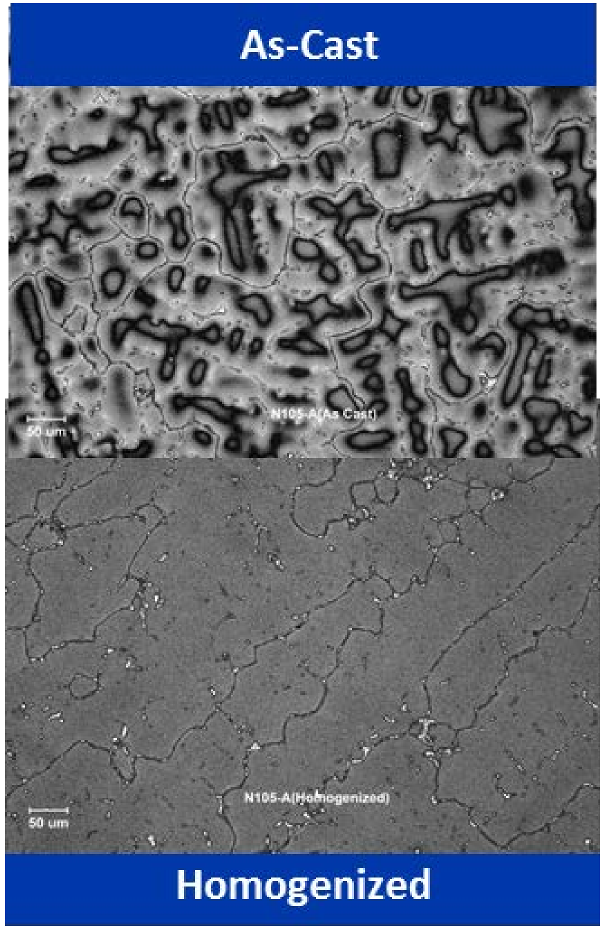
- This new cast 9% Cr martensitic steel has a unique chemistry, alloy design philosophy, and microstructural control (i.e., computationally based homogenization heat treatment schedule) unlike any other alloy in it's class.
- Nominal/preferred alloy chemistry:

	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.

Summary of Homogenization Step for Castings

	Residual Inhomogeneity		
Section Size	<10%	<5%	<1%
	Maximum Heat Treat Furnace Temperature - 1250°C		
Up to 5″	1125°C/1 h + 1250°C/3 h	1125°C/1 h + 1250°C/4 h	1125°C/1 h + 1250°C/8 h
5-8″	1125°C/2 h + 1250°C/5 h	1125°C/2 h + 1250°C/8 h	1125°C/2 h + 1250°C/18 h
> 8″	1125°C/2 h + 1250°C/10 h	1125°C/2 h + 1250°C/14 h	1125°C/2 h + 1250°C/30 h
	Maximum Heat Treat Furnace Temperature - 1200°C		
Up to 5″	1125°C/1 h + 1200°C/6 h	1125°C/1 h + 1200°C/8 h	1125°C/1 h + 1200°C/16 h
5-8″	1125°C/2 h + 1200°C/10 h	1125°C/2 h + 1200°C/16 h	1125°C/2 h + 1200°C/32 h
> 8″	1125°C/2 h + 1200°C/20 h	1125°C/2 h + 1200°C/30 h	1125°C/2 h + 1200°C/62 h



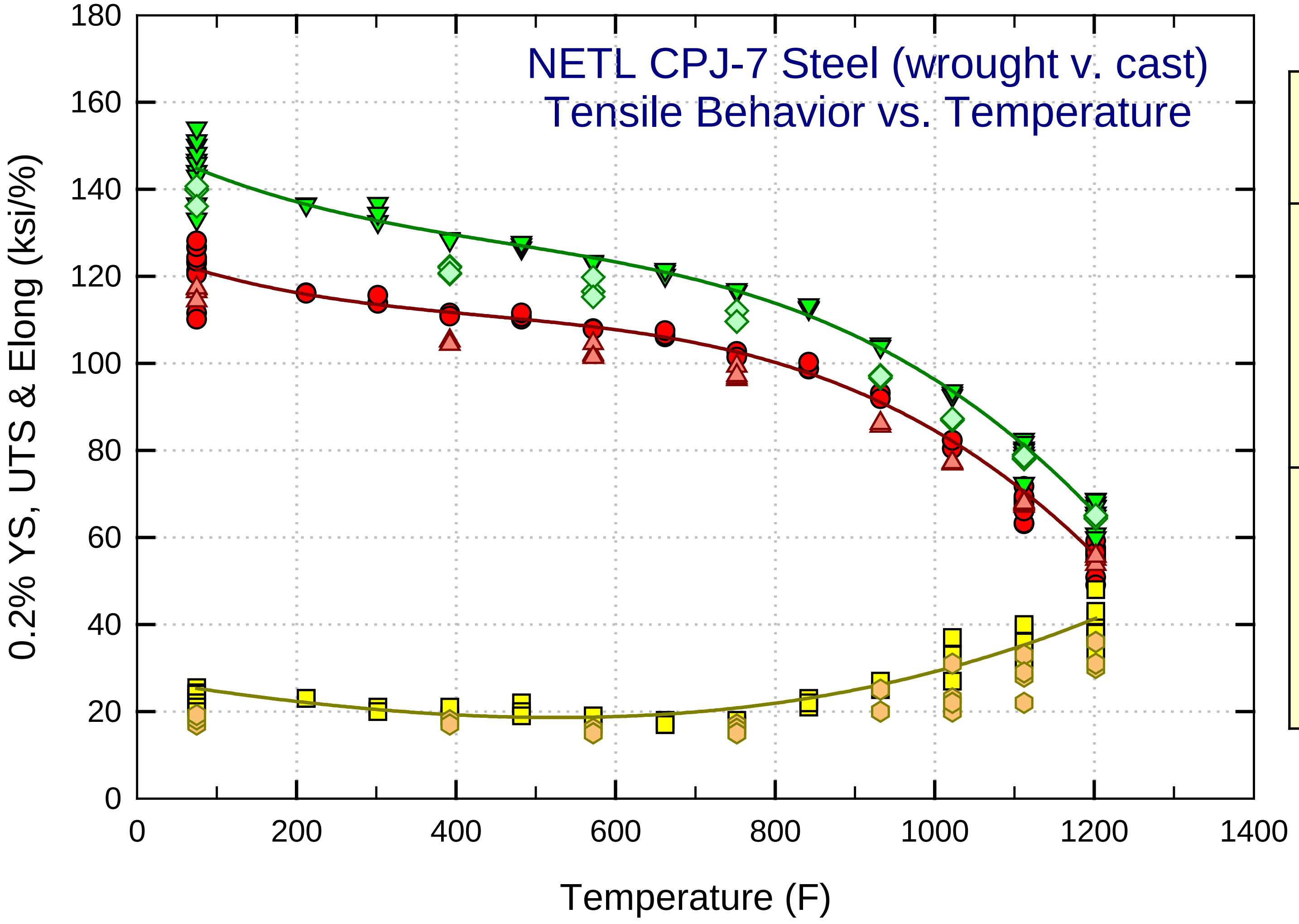
Cast 9% Cr Ferritic-Martensitic Steel

- ☐ The preferred chemistry for cast CPJ7, 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 CPJ7 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 CPJ7 showing outstanding mechanical performance for a casting, and similar to wrought CPJ7.

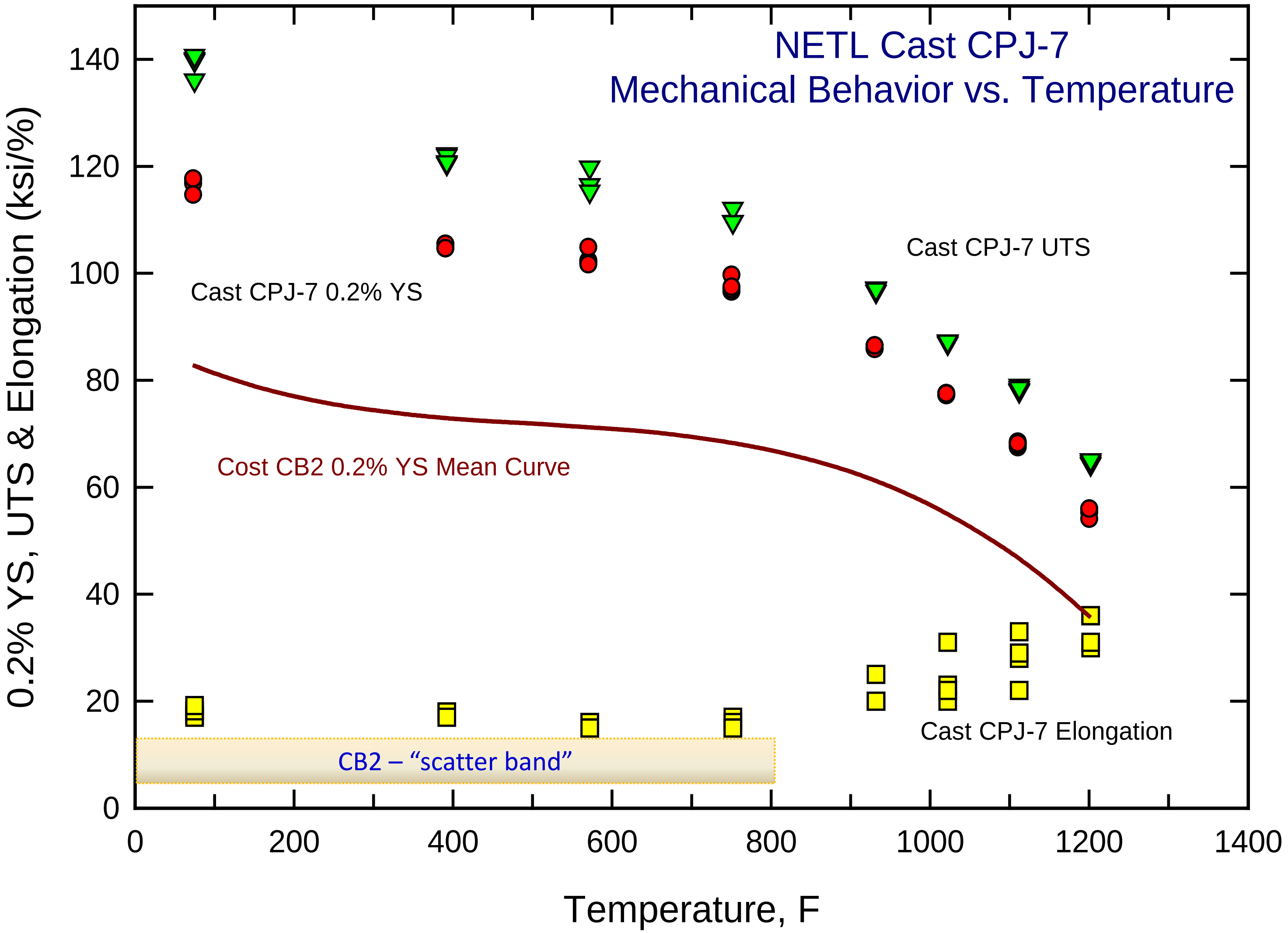
Tensile Mechanical Behavior Cast CPJ7 Steel

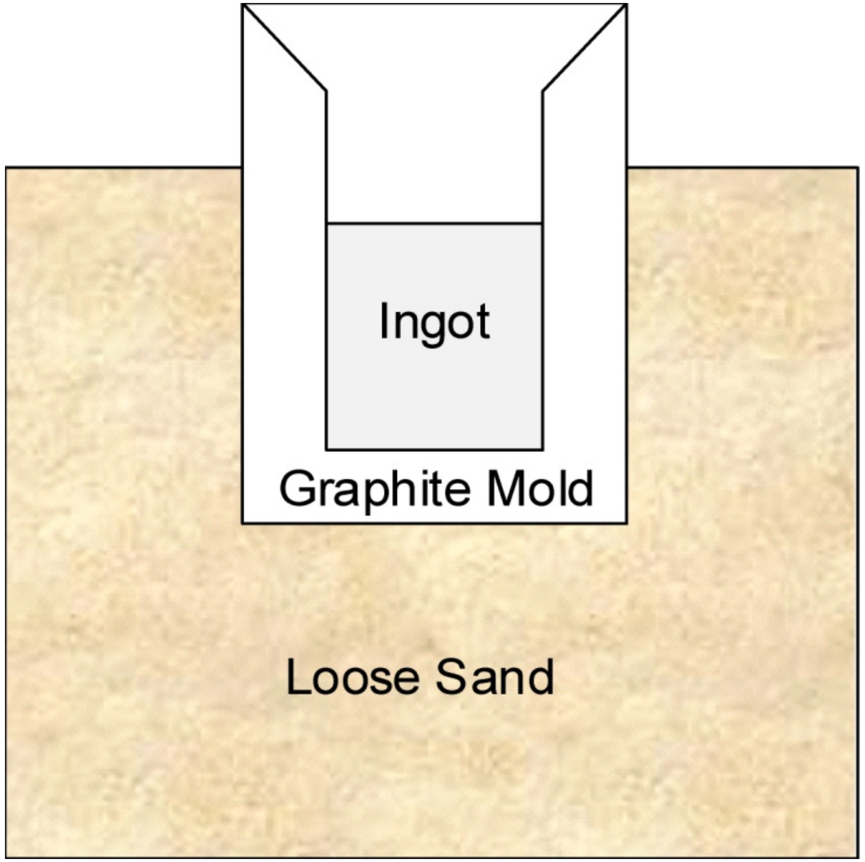


Alloy	Heat Treatment	Test Conditions (°C)	Yield Stress (MPs)	Tensile Strength (MPa)	Elongation (%)	Reduction in Area (%)
CPJ 7A Columnar	HTS⁺	RT	808	966	17	48
			803	964	17	42
		600	463	539	28	74
			470	545	33	76
		650	379	446	30	81
			384	449	36	80
CPJ 7A Equiaxed	HTS⁺	RT	809	970	18	39
			789	938	19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

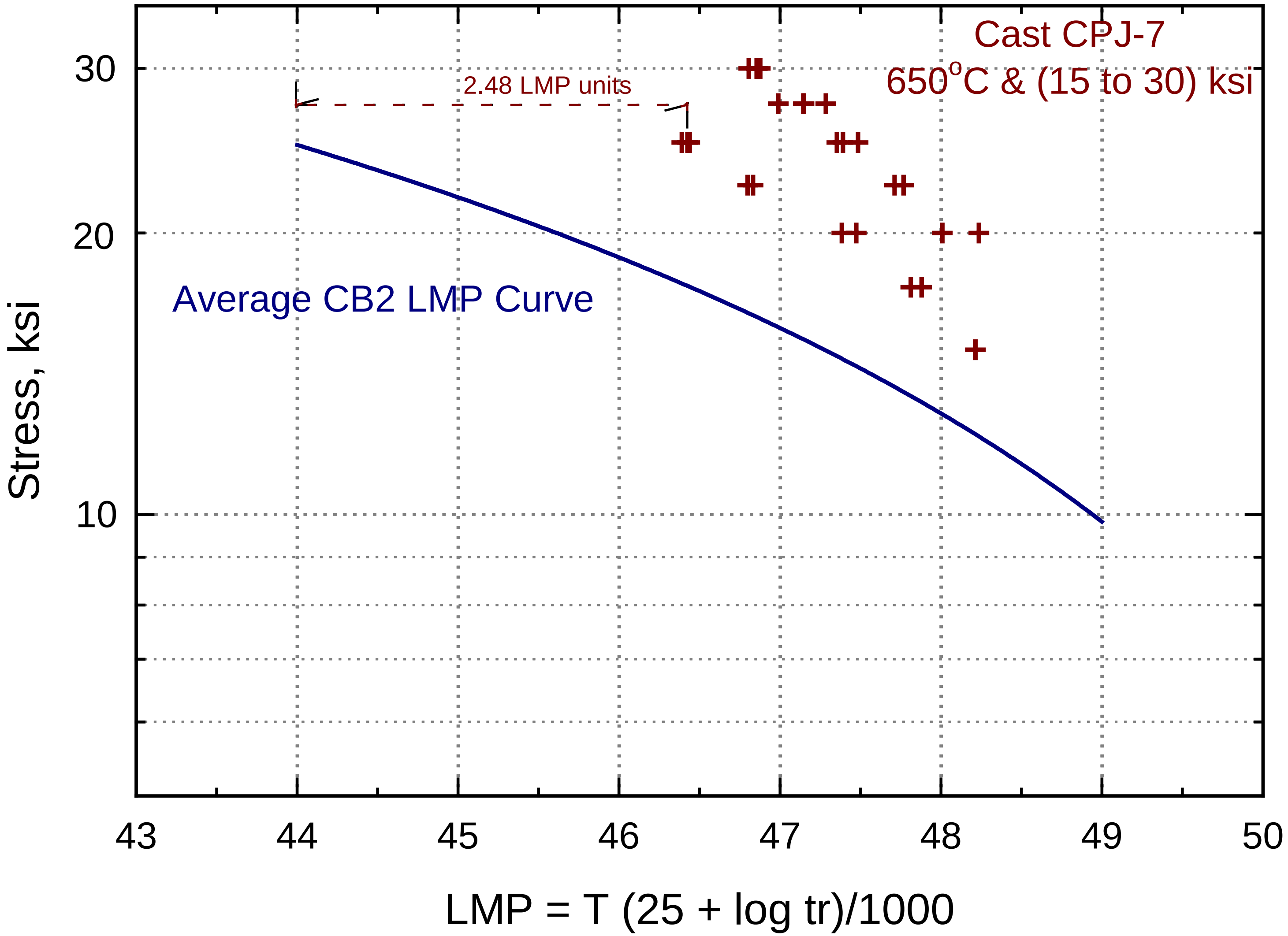
Defects more likely to be found in equiaxed region – last bit of molten metal to solidify.

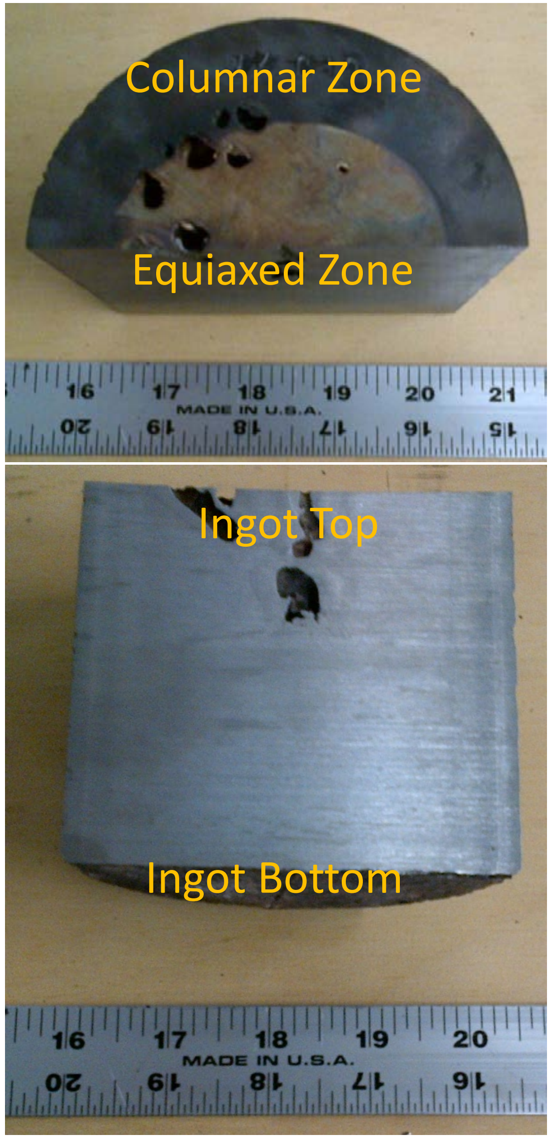
Cast CPJ7 Tensile Behavior Compared to CB2



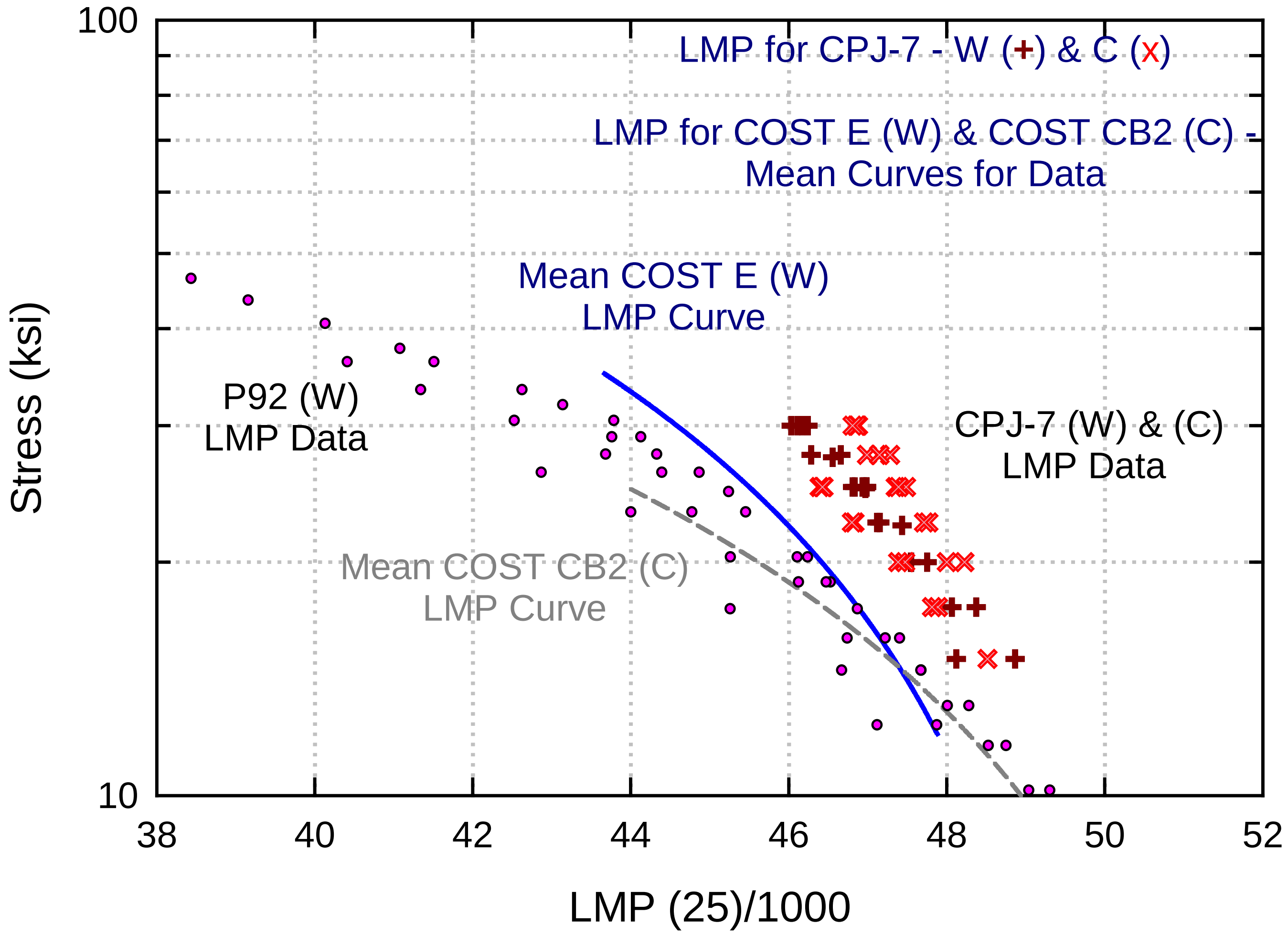


Cast CPJ7 vs. COST CB2





Creep Behavior Cast vs. Wrought CPJ7 Steel



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.

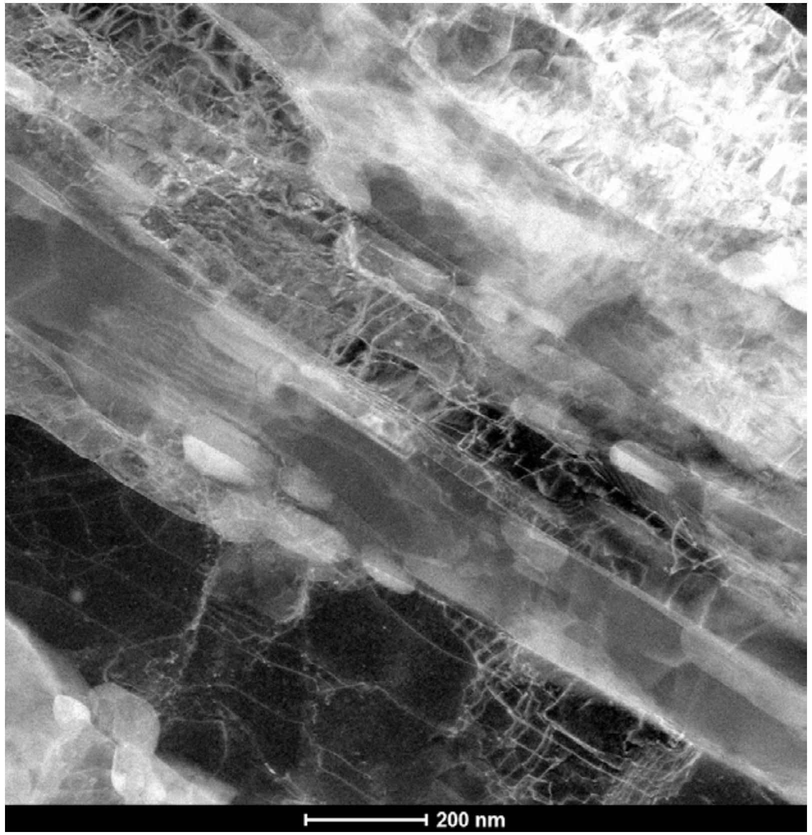
Summary & Planned Next Steps Cast CPJ7

- 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 CPJ7).
- Consider making large CPJ7 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 CPJ7 (wrought first, then castings).

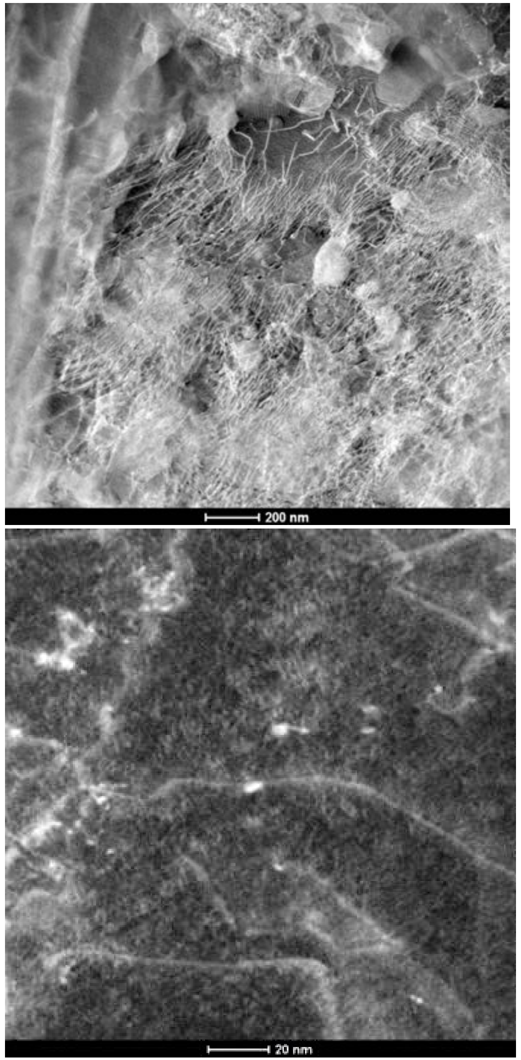
Hawk, Jablonski & Cowen, *Creep Resistant High Temperature Martensitic Steel*, US 9,556,503 B1, January 31, 2017.

What’s Next?

- ❑ Can improvements still be had for the 9% Cr family of ferritic-martensitic steels?
- ❑ If so, what?



Murayama et al., VaTech, as part of the NETL-RUA Innovative Process Technologies, 2011-2012.



COST B2 Martensitic Steel
(Creep gauge section: 650°C for 655 hours, 172 MPa)

Mo vs. W as Matrix Strengthening Element

- ☐ Two approaches were taken to develop 9% Cr family of ferritic-martensitic steels.
- ☐ COST effort looked at Mo as a matrix strengthening element.
- ☐ NIMS effort looked at W as a matrix strengthening element.
- ☐ Both elements are hard to diffuse in the ferritic-martensitic matrix. Both have attractive features if done well.
- ☐ Benefit of Mo is the Mo equivalent: where Mo = ½ W. To achieve same atomic level of W in alloys requires 2x atoms. Additional mass required as result.
- ☐ W additions can lead to Laves.

Is one approach better than the other?

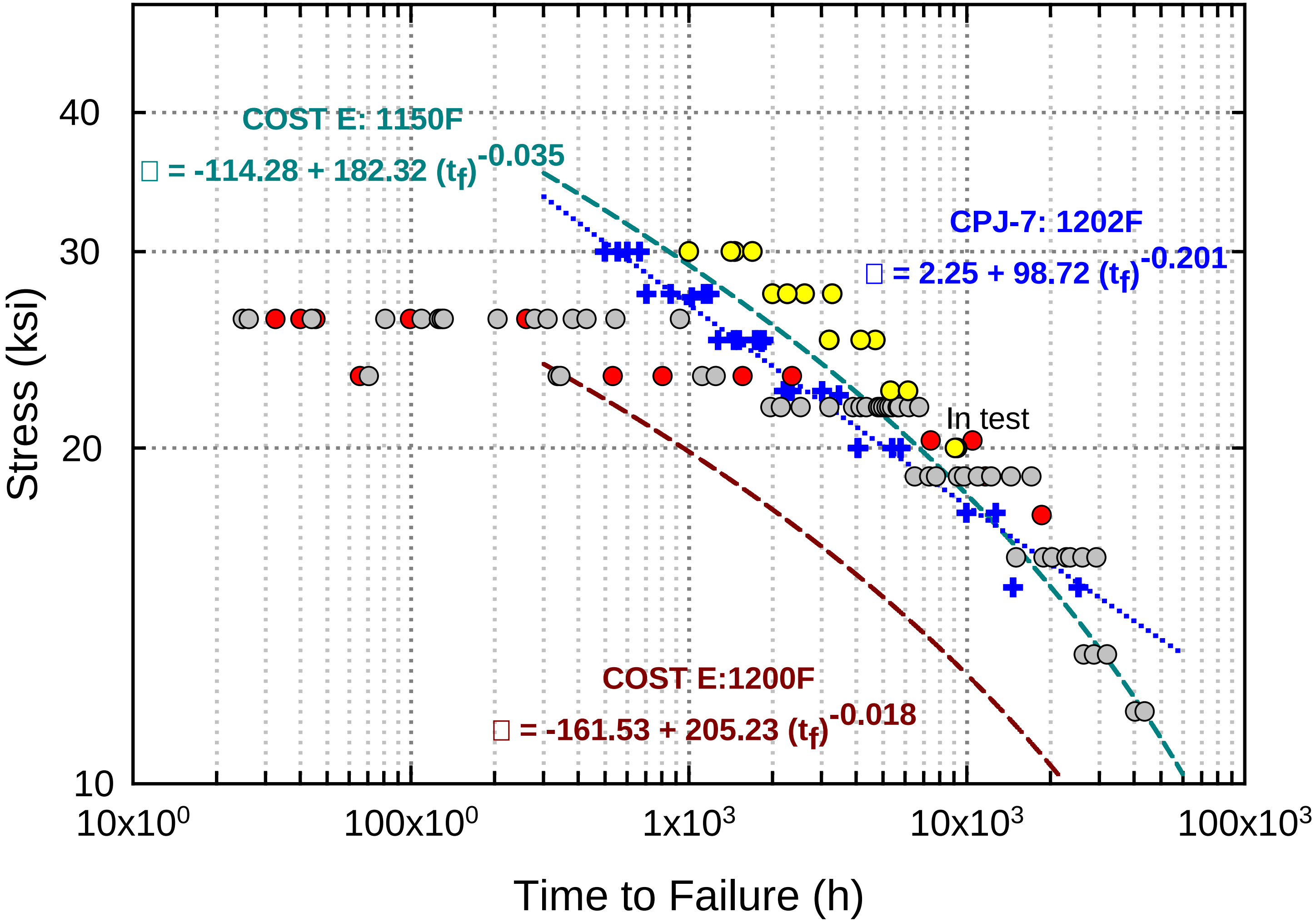
How is this manifested?

Mo vs. W as Matrix Strengthening Element

- ☐ Developed a W-based ferritic-martensitic steel based on MARBN approach by Abe but manufactured exactly like CPJ7, i.e., homogenization step plus same forging, hot rolling, normalization & tempering conditions.
- ☐ Chemistry was simplified with respect to trace element additions, except B & N, where NETL looked at low B (≤ 100 ppm) & moderate N (~250 ppm).
- ☐ Cr levels of 9%, 9.5%, 10% and 10.5% were examined as well as some minor changes to Co content & W-Mo ratio (for cost considerations).
- ☐ Comparison of creep behavior made against Abe's MARBN and commercial SAVE12.

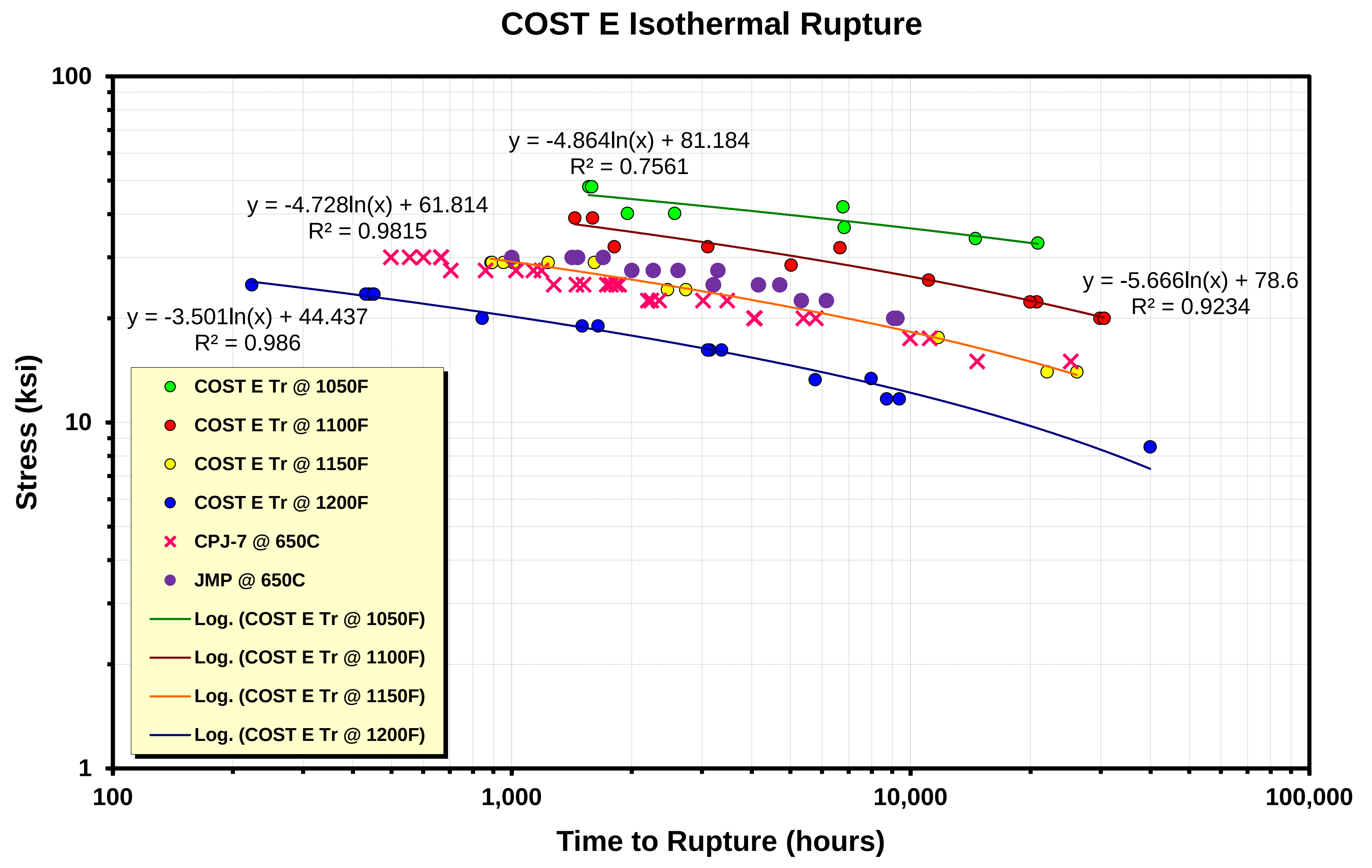
Higher levels of Cr in CPJ7 were not detrimental for creep life. Wanted to systematically assess for a MARBN-type steel.

Ferritic-Martensitic MARBN-Type Steels

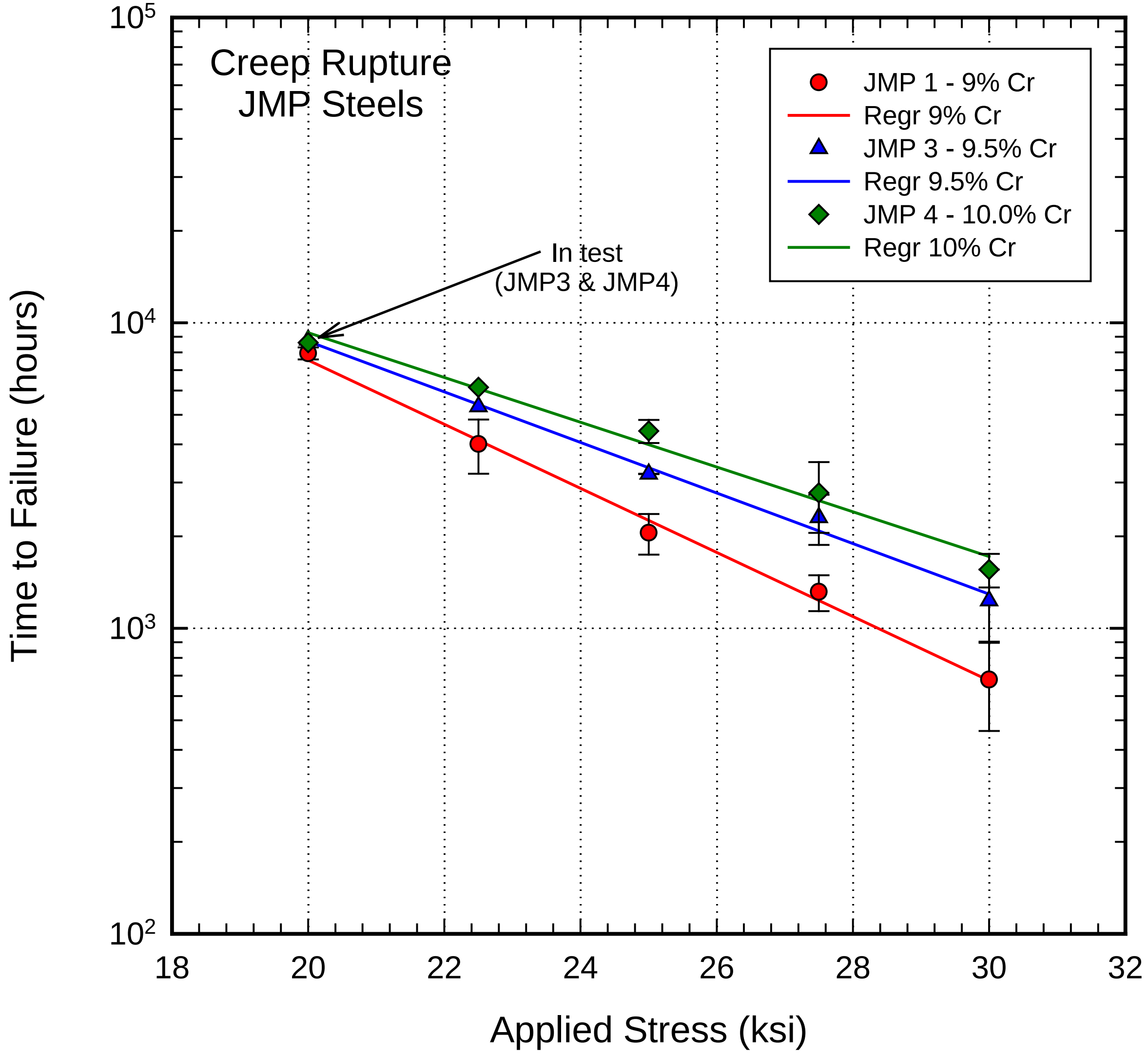


There are a number of takeaways!

Isothermal Creep Parameter Comparison

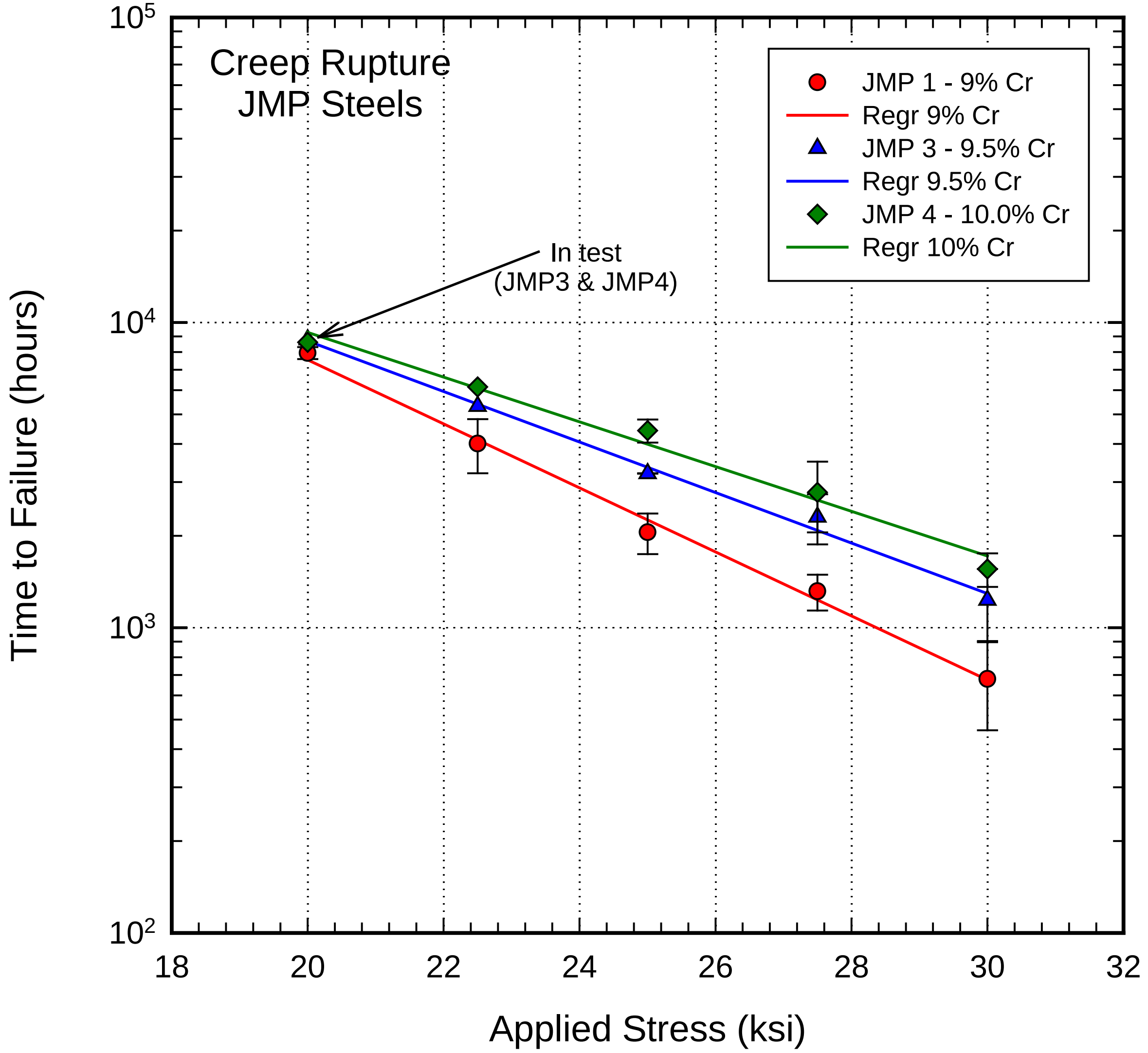


Ferritic-Martensitic MARBN-Type Steels



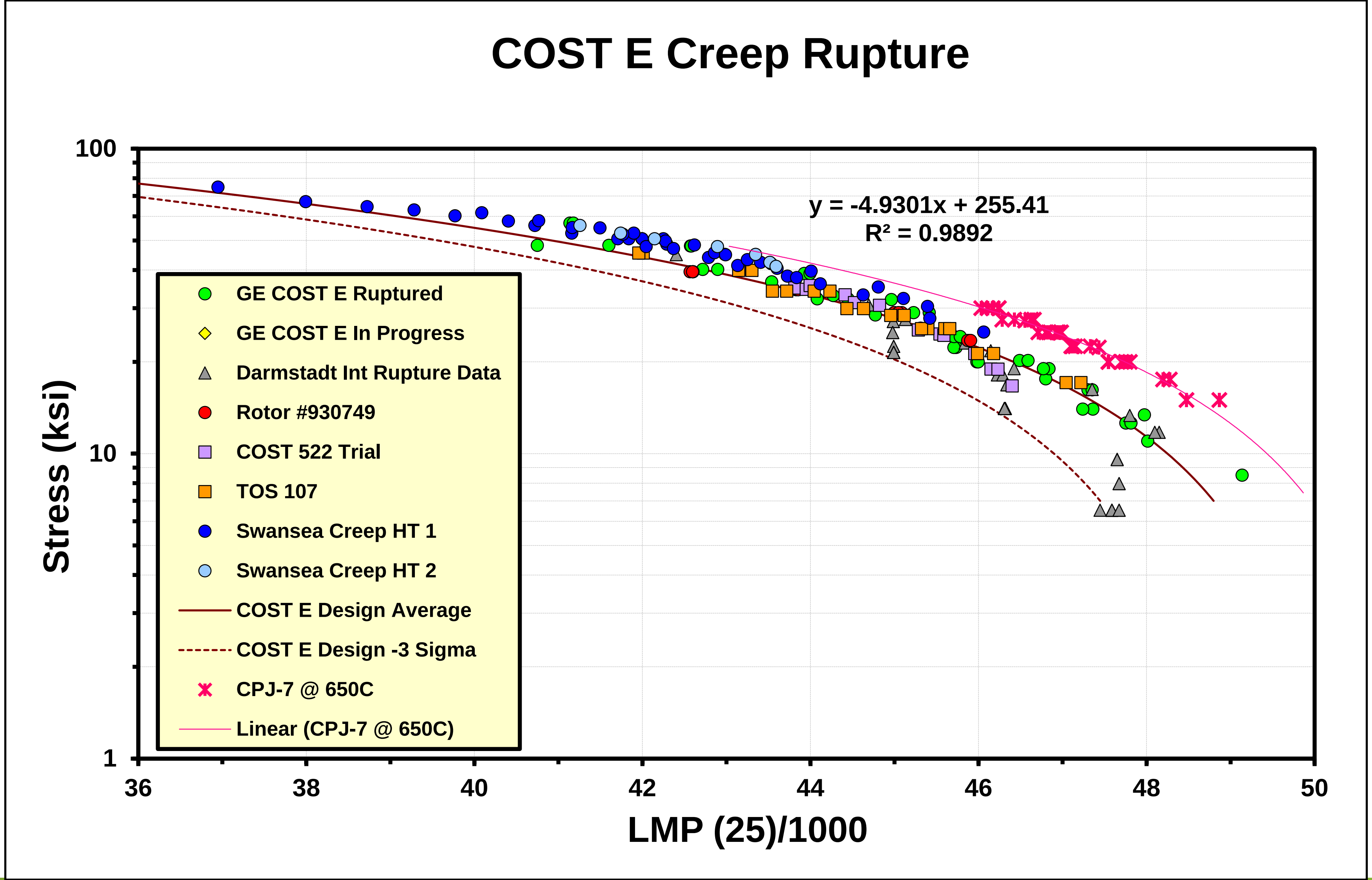
Stress	Alloy ID	Mean Life	StDev	COV
30	JMP1	678.5	217.1	32.0%
	JMP3	1231.0	326.7	26.5%
	JMP4	1556.0	196.6	12.6%
27.5	JMP1	1315.0	176.8	13.4%
	JMP3	2305.5	432.0	18.7%
	JMP4	2775.2	722.5	26.0%
25	JMP1	2054.0	312.5	15.2%
	JMP3	3201.5	4.9	0.2%
	JMP4	4425.6	383.8	8.7%
22.5	JMP1	4015.0	808.9	20.1%
	JMP3	5320	---	---
	JMP4	6150	---	---
20	JMP1	7947.4	358.4	4.5%
	JMP3	9240	---	---
	JMP4	9072	---	---

Ferritic-Martensitic MARBN-Type Steels

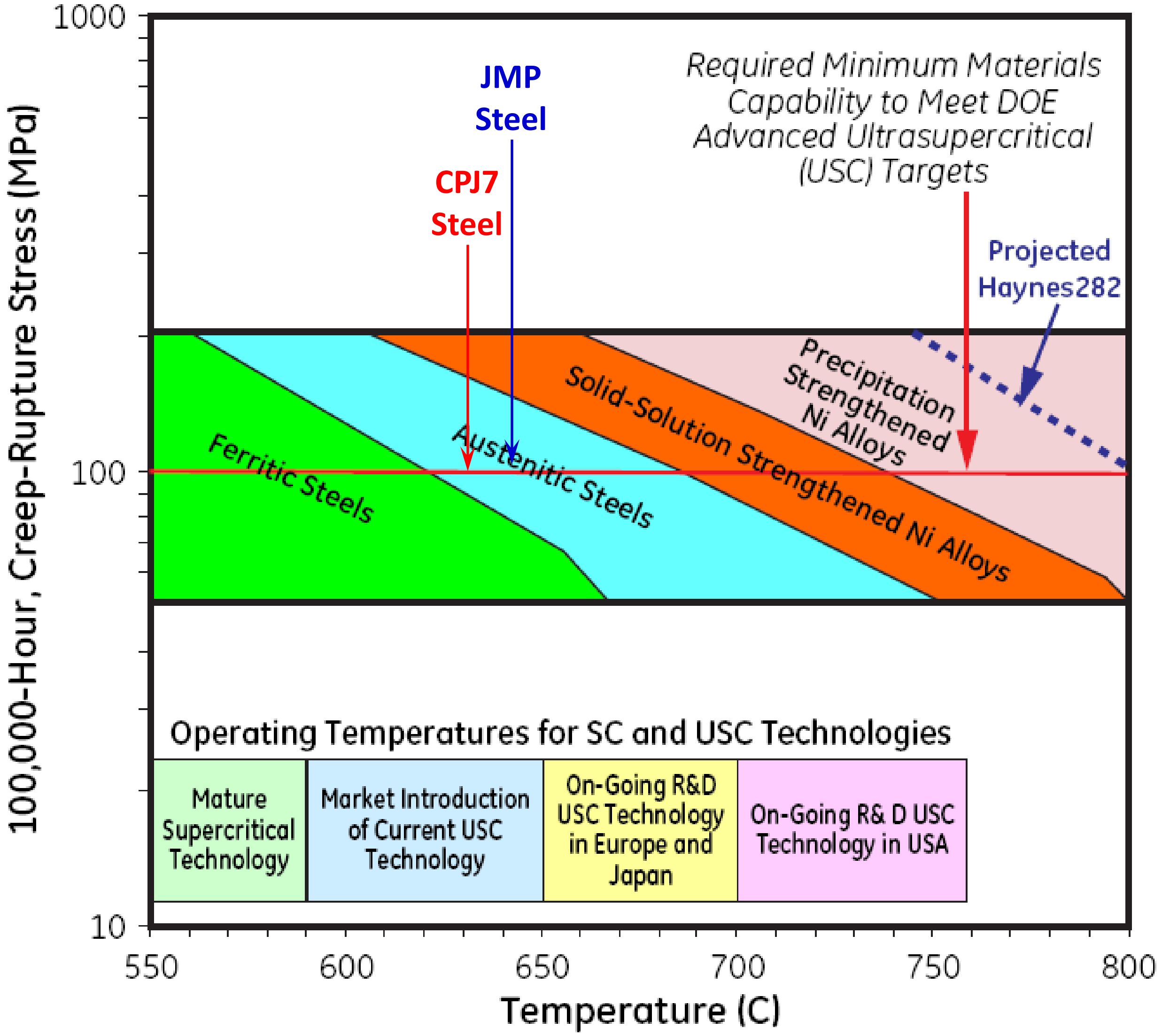


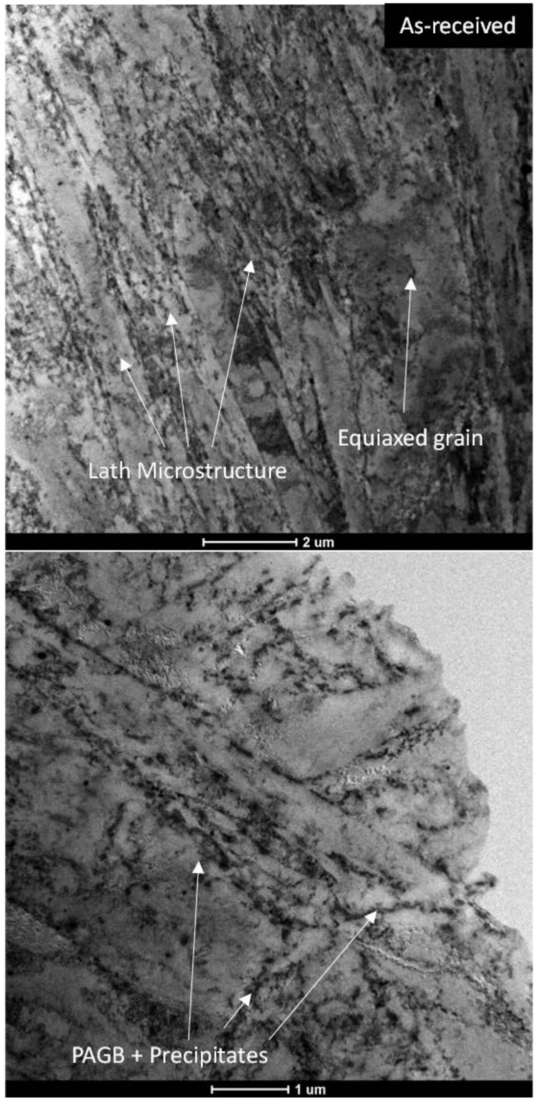
Selected tests have been completed – enough to show the trend for the JMP steel with respect to increased percent Cr in the matrix. Two tests are ongoing for the JMP3 & JMP4 steels which will establish final slope (time to failure as function of stress at 650℃) and the relative life improvement of the alloy. Tests have started for 10.5% Cr level.

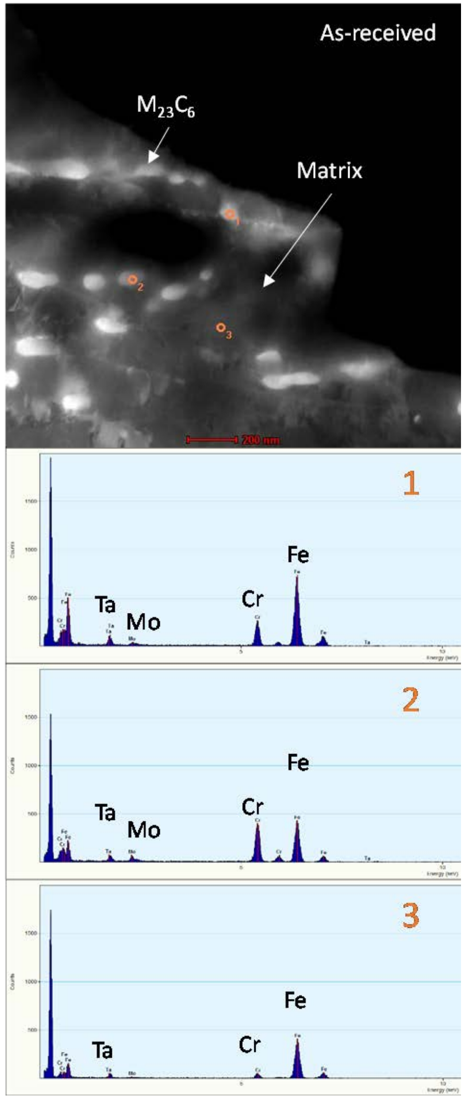
Larson-Miller Parameter Comparison



Ferritic-Martensitic 9% Cr CPJ 7 Steel







Accomplishments & Future Work

☐ Continue data generation activities for XMAT & AAD for ferritic-martensitic steels.

☐ Optimize casting process to reduce porosity & produce larger castings (i.e., use of gating system, risers, filters, etc.). Focus some effort on cast JMP steels.

☐ Continue to scale up ingot size. Produce wrought plate & cast blocks suitable for welding studies. Most significant improvements may be with 9% Cr ferritic-martensitic castings.

☐ Consider making large CPJ7 & JMP castings via air induction melting process with inert gas cover. Assess limitations of approach relative to baseline data.

☐ Assess toughness, fracture energy & dynamic response (i.e., selected fatigue screening tests at room temperature for CPJ7 & JMP steels - wrought first, then castings).

☐ Explore tempering heat treatment capability of CPJ7 and JMP steel compositions relative to yield stress, DBTT and grain size. Quantify property envelope with respect to normalization/tempering.

☐ Explore IP potential for JMP steels.

Thank you

Questions?

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