NATIONAL ENERGY TECHNOLOGY LABORATORY

New High Temperature Iron-Base Alloys

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Coal-Fired Power Plants

Steam Condition	Conditions	Net Plant Efficiency	Net Plant Heat Rate (HHV)
Subcritical	2,400 psig (17 MPa) 1050ºF/1050ºF (566°C)	35%	9,751 Btu/kWh
Subcritical HARP Cycle	2,400 psig (17 MPa) 1080ºF/1080ºF (582°C)	37%	9,300 Btu/kWh
Supercritical	3,500 psig (24 MPa) 1050ºF/1075ºF (566°C/580°C)	38%	8,981 Btu/kWh
Advanced Supercritical	Limit of 4,710 psig (33 MPa) 1130ºF/1165ºF/1165ºF (610°C/629°C/629°C)	42%	8,126 Btu/kWh
Ultra-Supercritical	5,500 psig (38 MPa) 1300ºF main steam (704°C)	44%	7,757 Btu/kWh

Background

- Ferritic/Martensitic Cr steels form the backbone of current steam delivery systems.
- In general these alloys are less expensive to produce & can be recycled.
- CrMoV, NiCrMoV, and steels with < 5% Cr make up the majority in tonnage in steam turbine & boiler plants operated below 570°C.
- For hotter sections of the boiler & major components of the turbine, advanced 9-12% Cr steels are used.
- 620°C is the current maximum use temperature due to long-term microstructural instability.
- Currently, creep strength at 650°C for times up to, or greater than, 100,000 hours is not possible.

Background *(cont.)*

- If ferritic/martensitic steels could be developed for use at 650°C, significant improvements in efficiency would be gained at a fraction of the cost needed to build a 700°C power plant using austenitic steels & nickel-based superalloys.
- Increasing the attractiveness of coal fired power plants is done by reducing the cost of construction, by increasing the efficiency, or by both.

Past Research

- Research in improving temperature & pressure capability of ferritic/martensitic steels has been active since the 1950's.
- Acceptable oxidation resistance at 650°C while meeting the requirement of a creep life of 100,000 hours at 100 MPa, is the goal.
- Fujita developed TAF steel in 1968 [1], which nearly met today's creep lifetime requirement. High B level in base steel was major contributing factor for strength.
- However, TAF steel proved difficult to fabricate & weld.
- Major plant components such as rotors, headers, & thick section pipe, require (1) sufficient forgeability for production and (2) weldability for installation & repair.

[1] Fujita, Trans. JIM, (1968)

Objectives/Milestones

- This project is a new start for FY2010:
  - Alloy design & thermodynamic modeling to down-select alloy compositions.
  - Melt, cast, & fabricate alloys of interest.
  - Evaluate microstructure & determine baseline mechanical properties.
  - Refine alloy chemistry to optimize properties.

Technical Approach

- Design & fabricate ferritic/martensitic steels capable of use at 650°C in advanced combustion systems.
- Understand basic high temperature strengthening mechanisms and how to preserve strengthening effect through microstructural control.
- Achieve balance between the following competing effects:

Competing Microstructural Effects

- Necessary C, V, Nb, (and/or Ta) and N to generate MX (M: metal; X: C/N), thereby, slowing down dislocation movement.
- Balanced amount of Mo and W for solution & precipitation hardening by $M_{23}C_6$ and 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 Cu to nucleate Laves phase at Cu precipitates for alternative strengthening.
- Addition of B to stabilize $M_{23}C_6$ precipitates, and thus, sub-grain structure.
- Correct amount of Cr for oxidation resistance (e.g., Cr additions significantly greater than 9% reduce creep strength).
- Optimum Si level 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 and Jung, J. Mater. Pro. Technol. (2009), and Chilukuru *et al.* Mater Sci. Eng. A. (2009).

Alloy Design Concept

- Eliminate the sources of microstructural instability found in ferritic/martensitic alloys currently used in coal fired power plants.
- Ameliorate sources of microstructural instability, such as coarsening of the $M_{23}C_6$ carbides & MX precipitates during prolonged exposure, and limit or eliminate Laves & Z-phase formation.
- From 19 candidate compositions, 3 alloy chemistries were selected for further study.

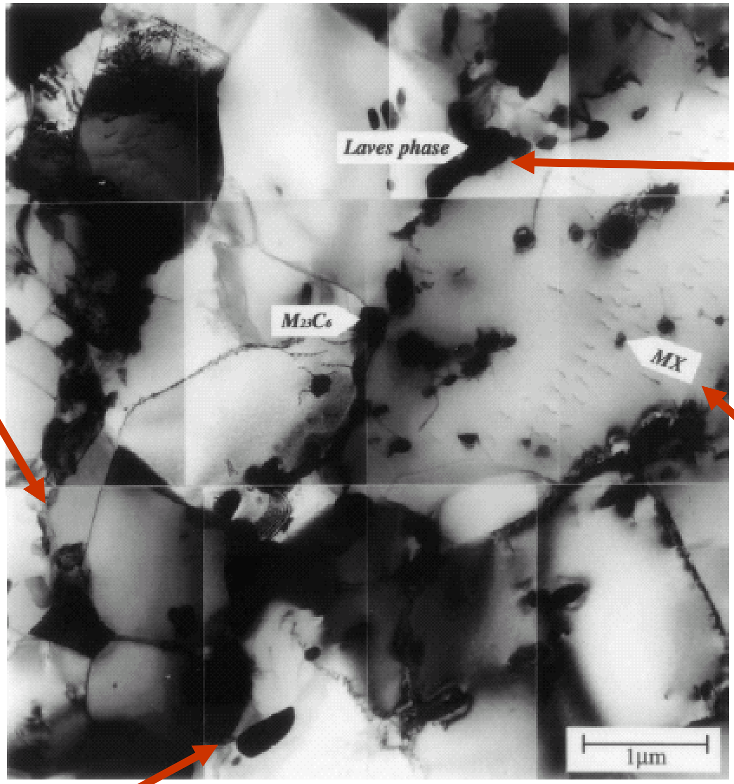
Summary of Major 9-12Cr Steels Used for Steam Turbine Rotors

Chemistry														
Material	***C***	***Mn***	***Si***	***Ni***	***Cr***	***Mo***	***V***	***Nb***	***N***	***W***	***B***	***Co***	**Fe**	**Other**
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	
TOS107	0.15	0.55	0.05	0.70	10.00	1.00	0.18	0.04	0.04	1.00			Bal	0.005 Al
TOS110	0.11	0.08	0.10	0.20	10.00	0.70	0.20	0.05	0.02	1.80	0.01	3.00	Bal	
TMK2 (TR1150)	0.13	0.50	0.05	0.70	10.20	0.40	0.17	0.06	0.05	1.80			Bal	
TR1200	0.12	0.50	0.05	0.80	11.20	0.30	0.20	0.08	0.06	1.80			Bal	
HR1200	0.10	0.55	0.06	0.50	11.00	0.23	0.22	0.07	0.02	2.70	0.020	2.70	Bal	
GE 10Cr	0.16	0.70	0.30	0.50	11.00	1.00	0.20	0.08	0.04				Bal	0.005 Al

There are many more 9-12Cr steels used as airfoils in steam turbines and as tubes, pipes, headers and super-heaters in the boiler. However, they all have the same common microstructural features.

Microstructure of Advanced 9-12Cr Steels

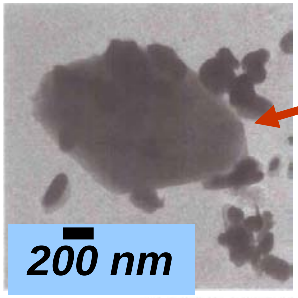
Sub-grains play an important role in strengthening.



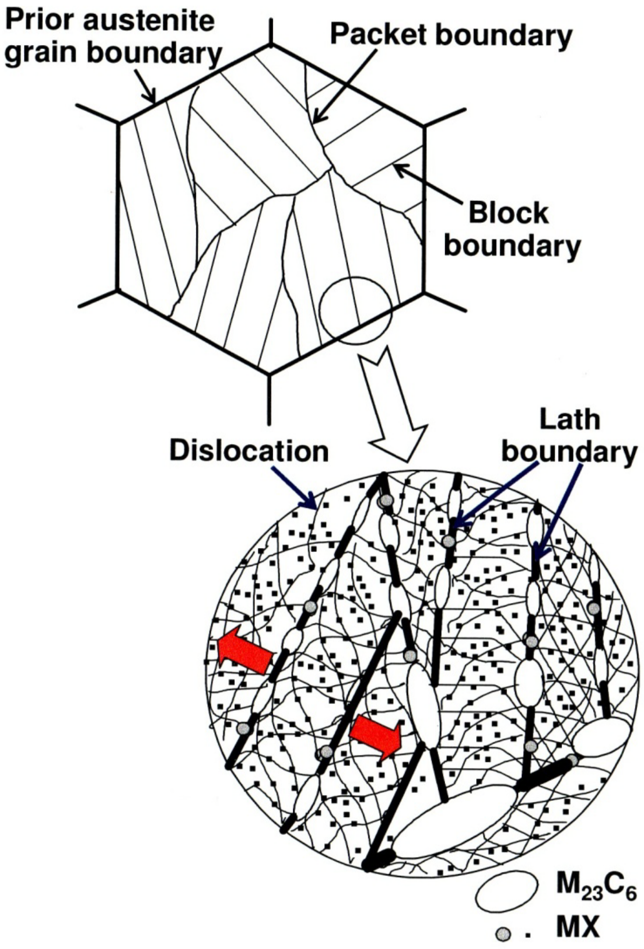
Laves phase precipitates during service and its consequences are not clearly known.

MX (VN) particles are the rate controlling obstacle.

$M_{23}C_6$ stabilizes sub-grain boundaries.



Z-phase [Cr(Nb,V)N] precipitates during service and eats up MX.



Schematic Representation of 9Cr Microstructure

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 breakdown of any of these microstructural features will destabilize the alloy and lead to increased 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.

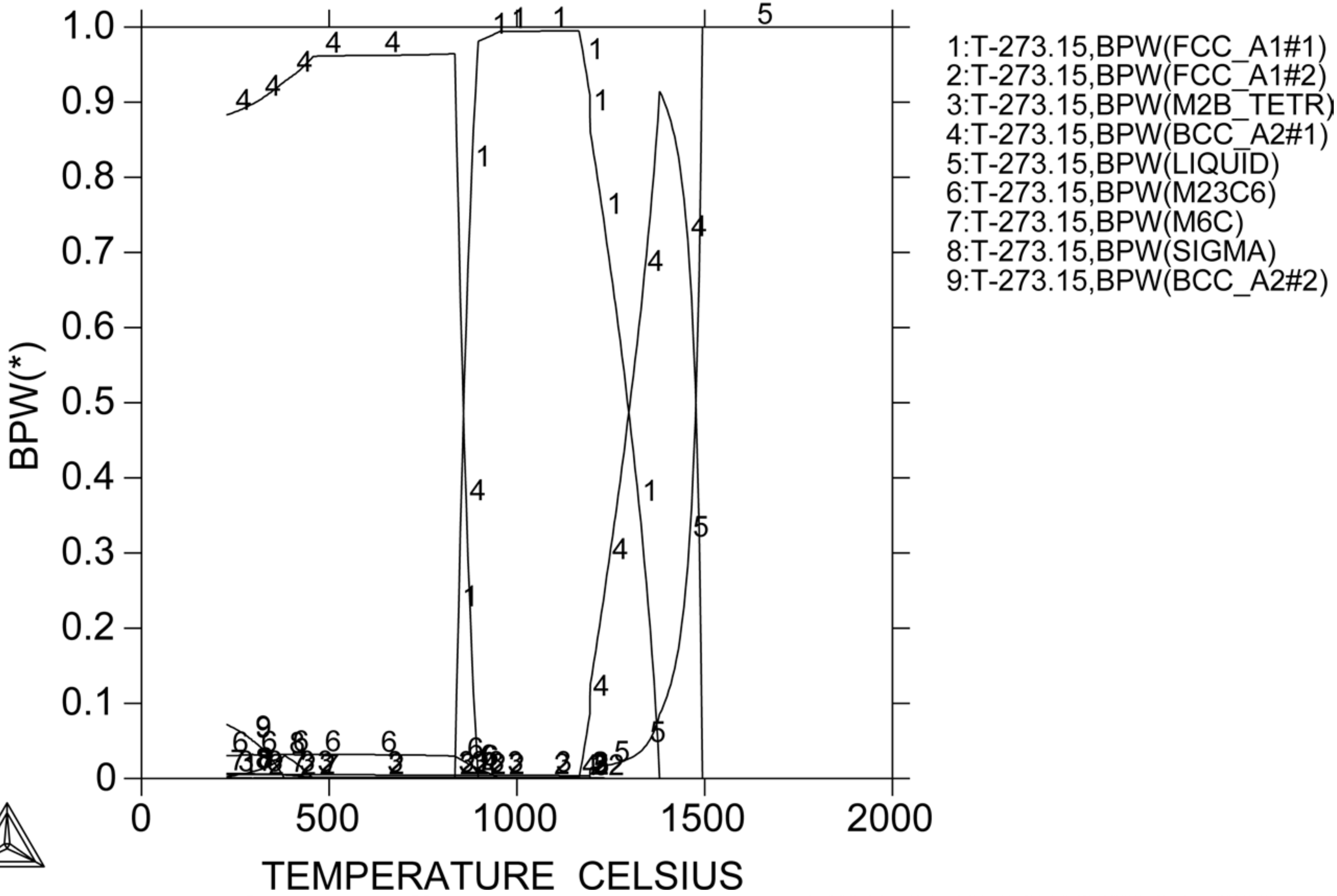
From Abe, Proceedings of the 8th Liege Conference, (2006)

Computational & Experimental Approach

- Model & design alloys using computational thermodynamics software.
- Formulate, melt, & cast heats for each composition.
- Homogenize each alloy according to computationally optimized heat treatment developed from thermodynamic & kinetic modeling.
- Fabricate alloys into plate form through hot forging & rolling operations.
- Assess as-fabricated microstructures.
- Alter microstructure through normalizing & tempering heat treatments.
- Assess creep & tensile properties against COST alloys.

ThermoCalc Modeling: TAF Alloy

10.5Cr-1.5Mo-0.2V-0.15Nb-0.5Mn-0.3Si-0.18C-0.03B



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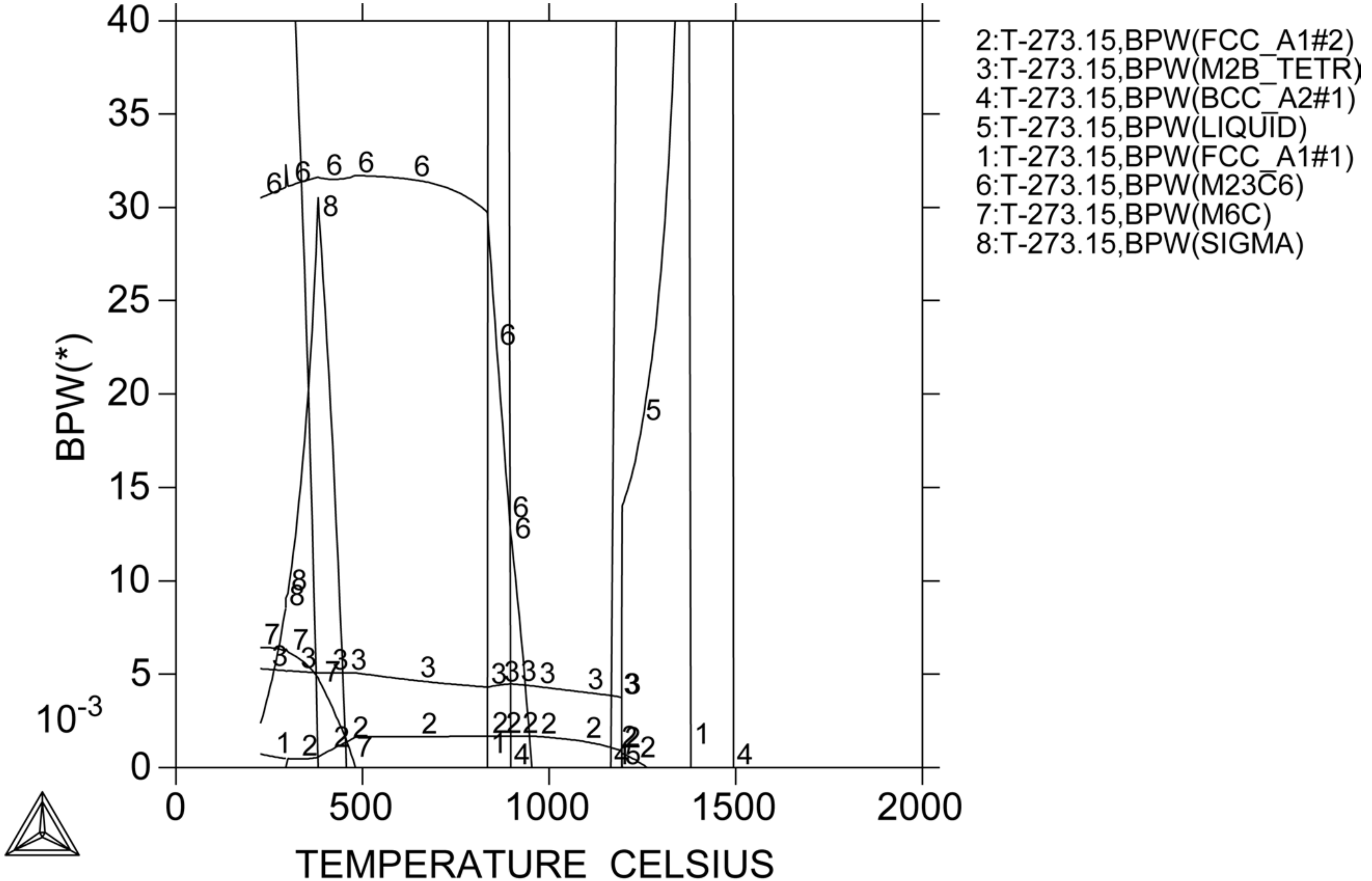
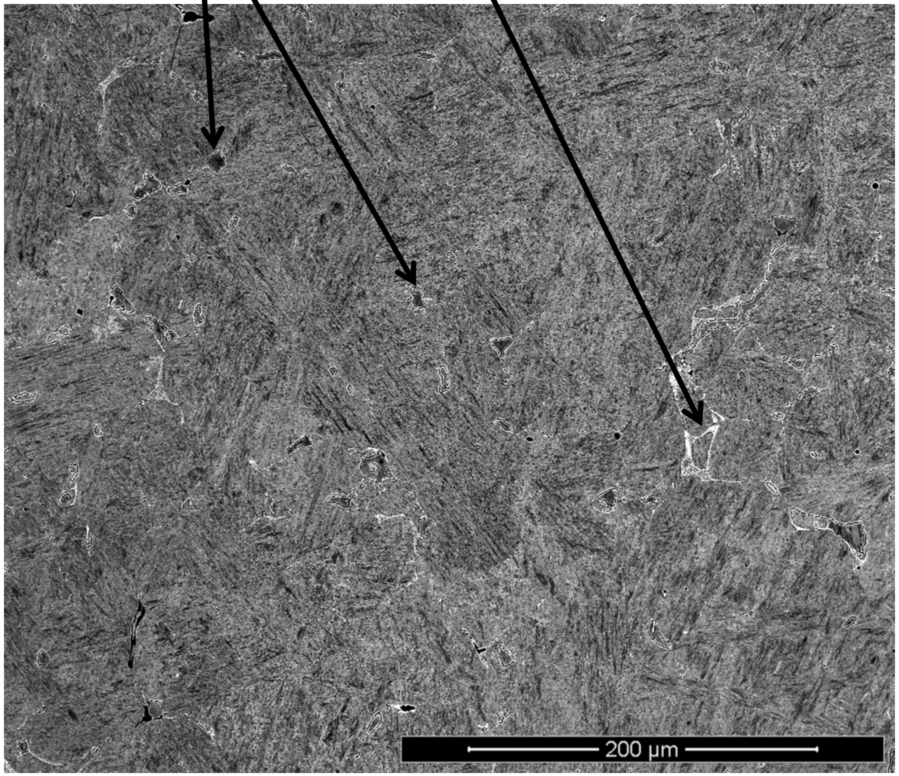
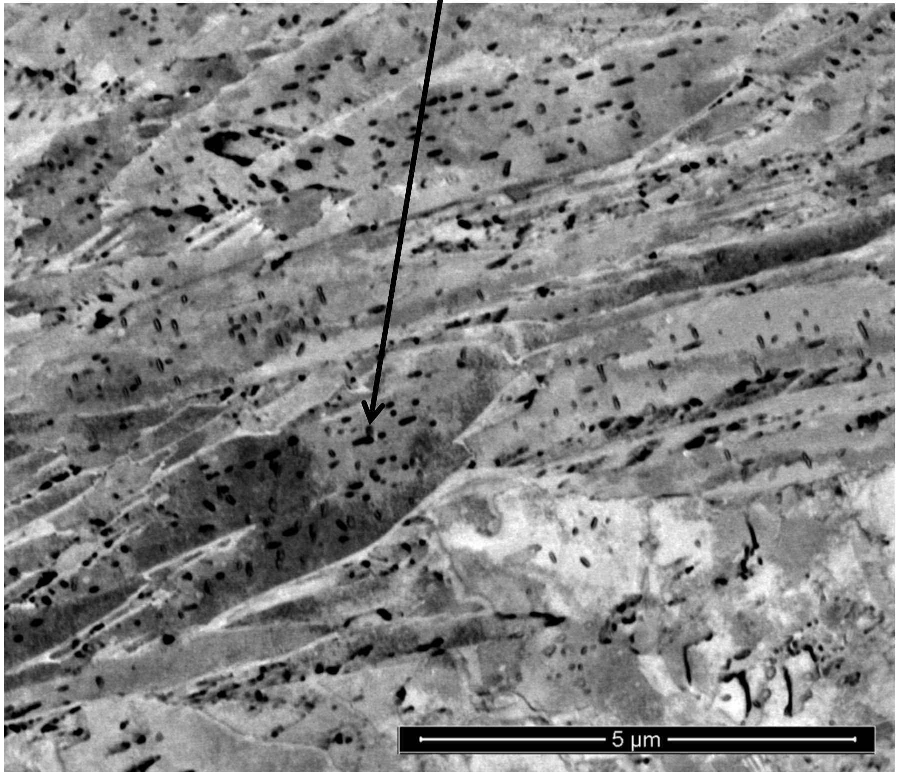


As-Cast Microstructure: TAF Alloy

Some ferrite and Mo-rich interdendritic regions



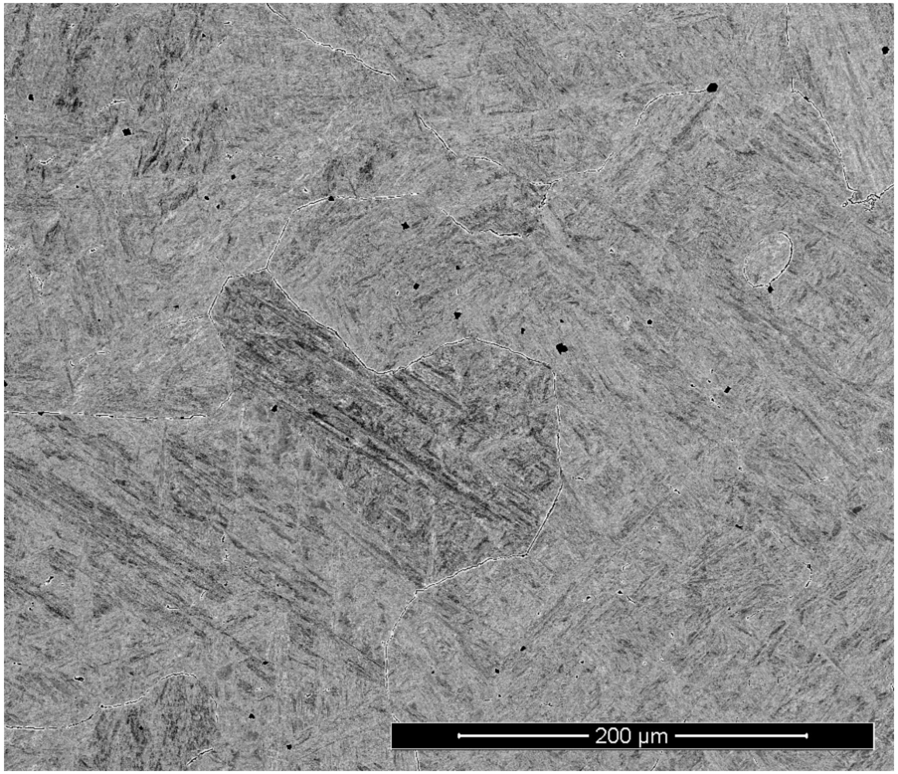
M_2B precipitates within the martensite



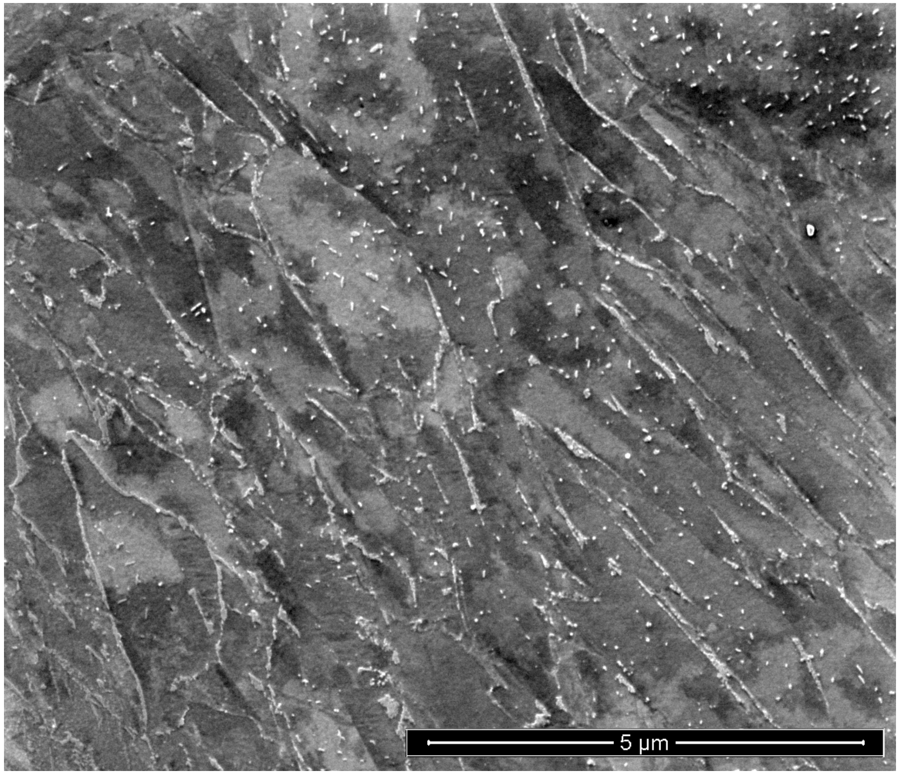
10.5Cr-1.5Mo-0.2V-0.15Nb-0.5Mn-0.3Si-0.18C-0.03B

As-Cast Microstructure: Alloy 1

Fully Martensitic cast structure

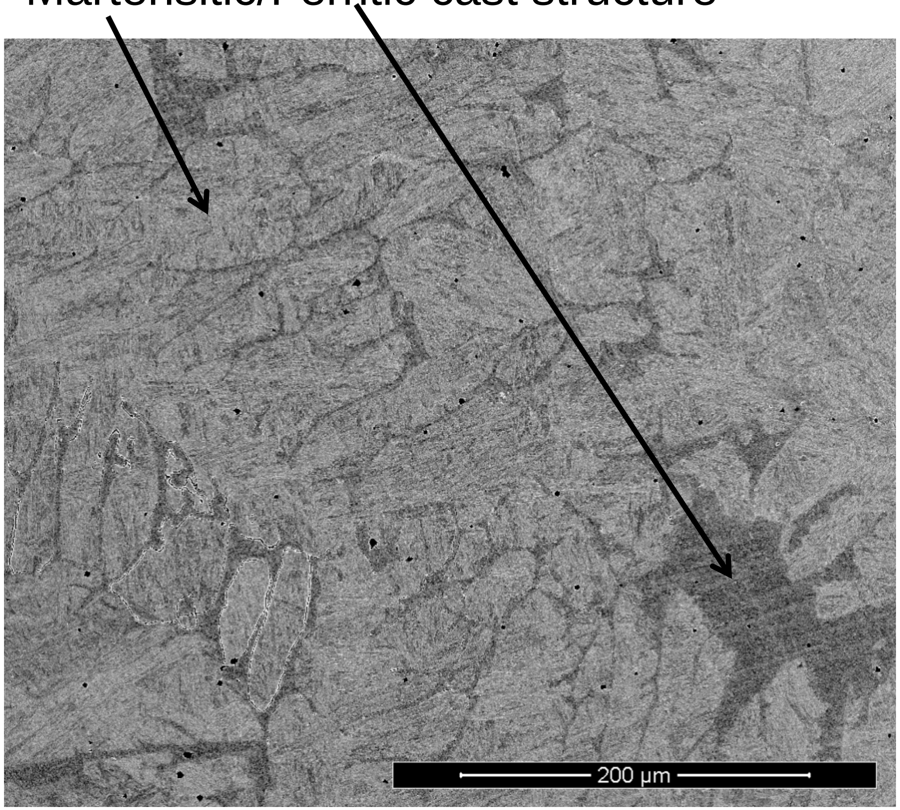


Fine lath spacing and precipitates

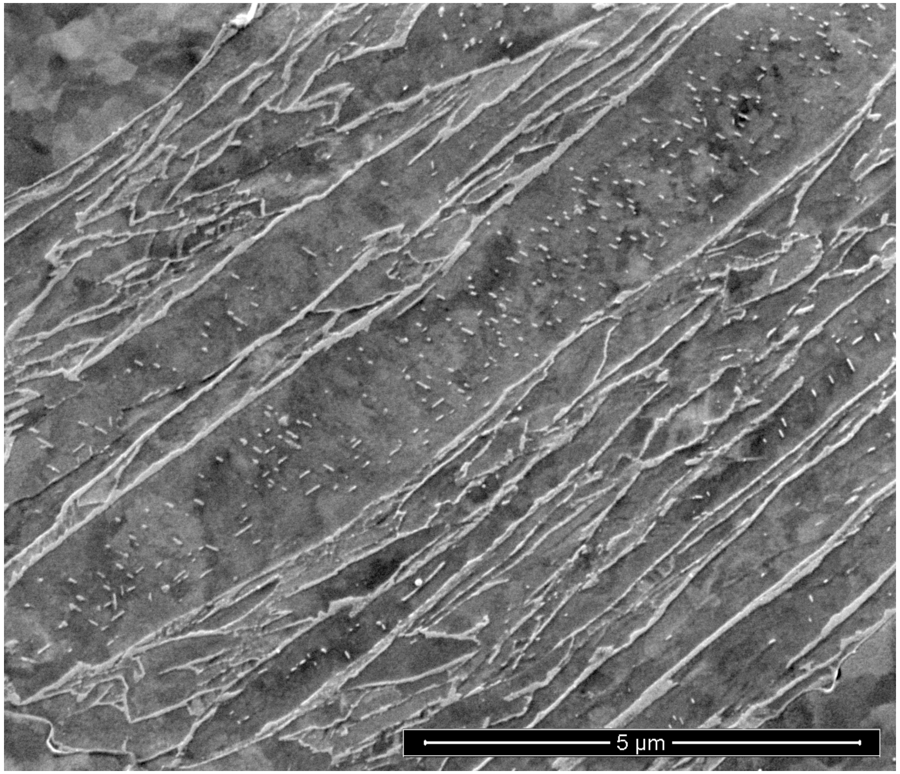


As-Cast Microstructure: Alloy 2

Martensitic/Ferritic cast structure

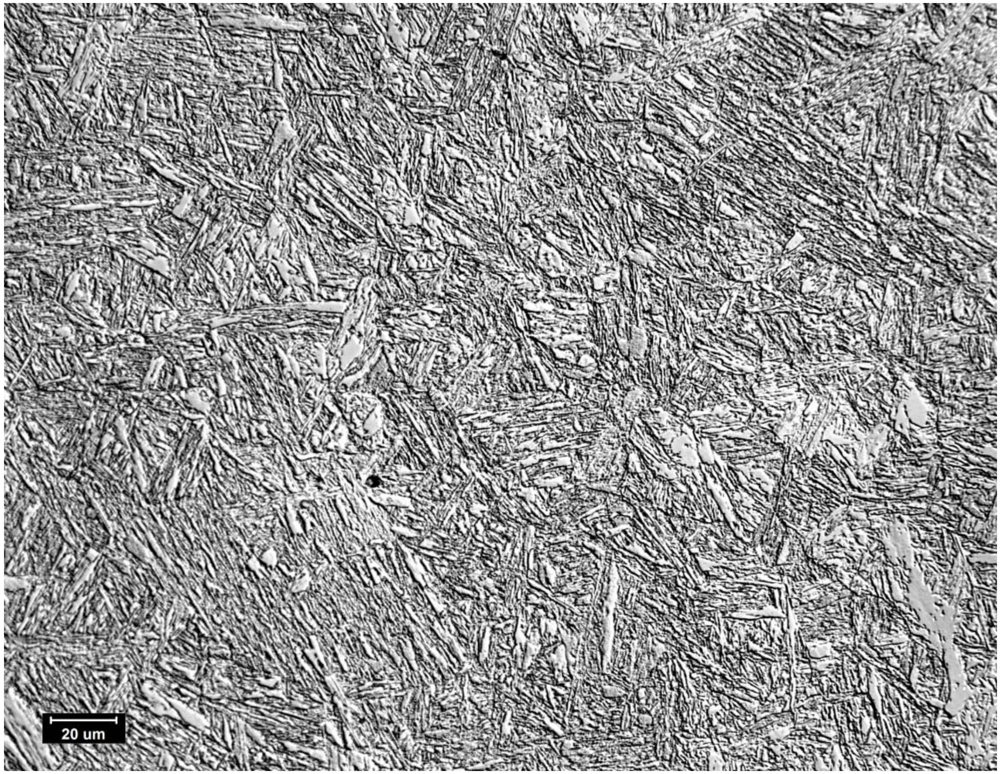


Fine lath spacing and precipitates

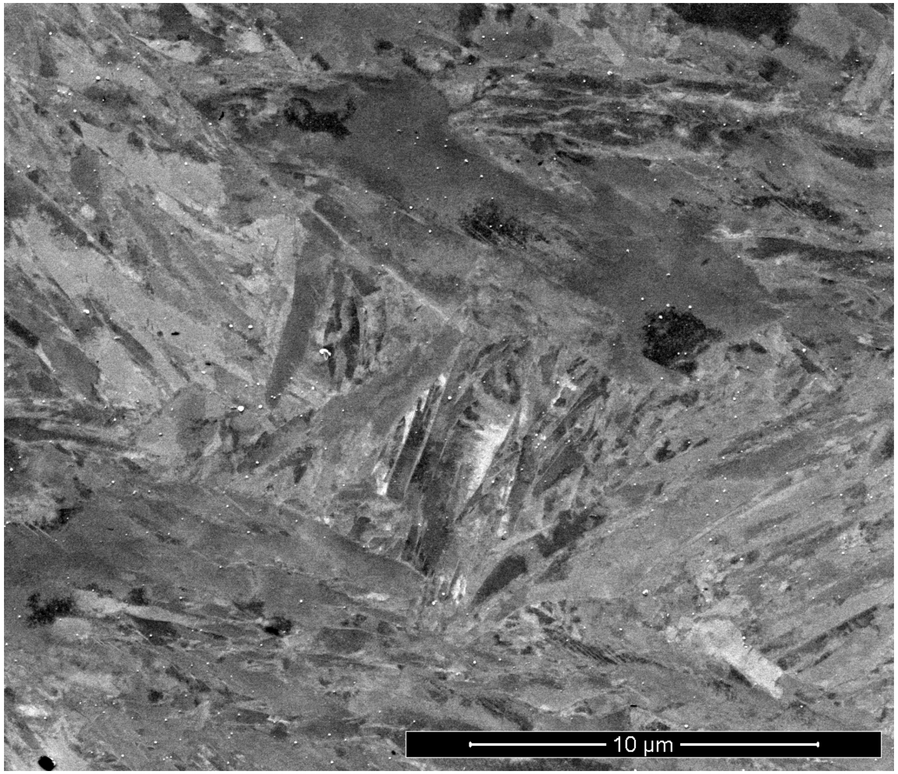


As-Fabricated Microstructure: Alloy 1

Fully martensitic wrought structure

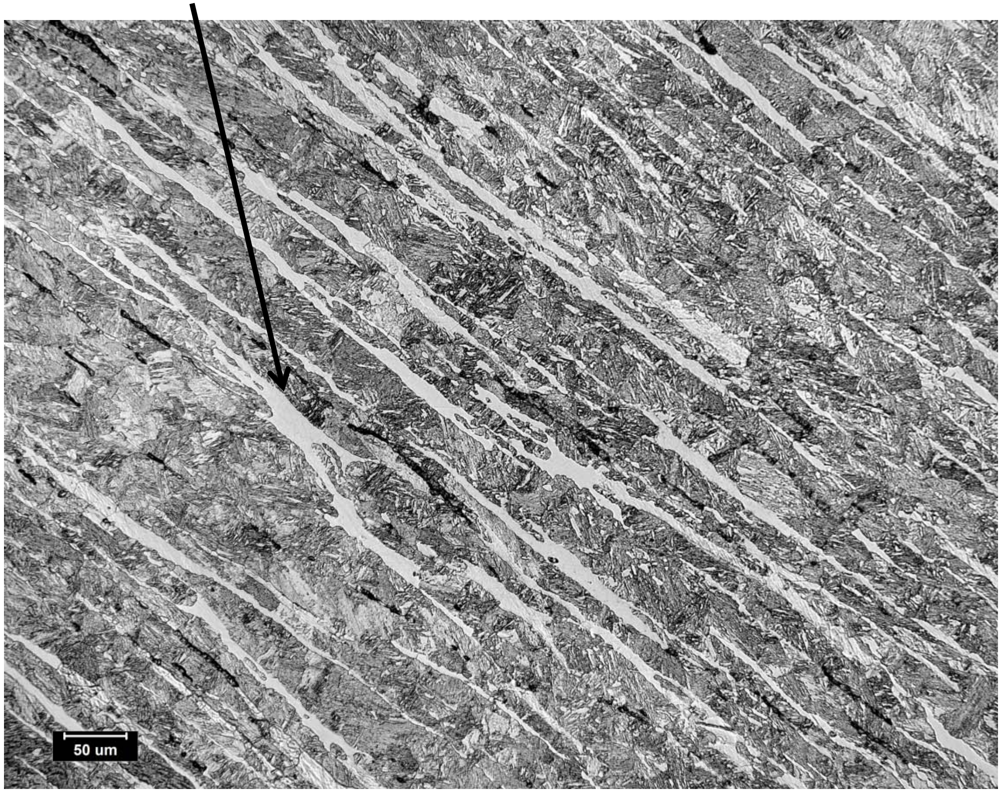


Fine precipitates

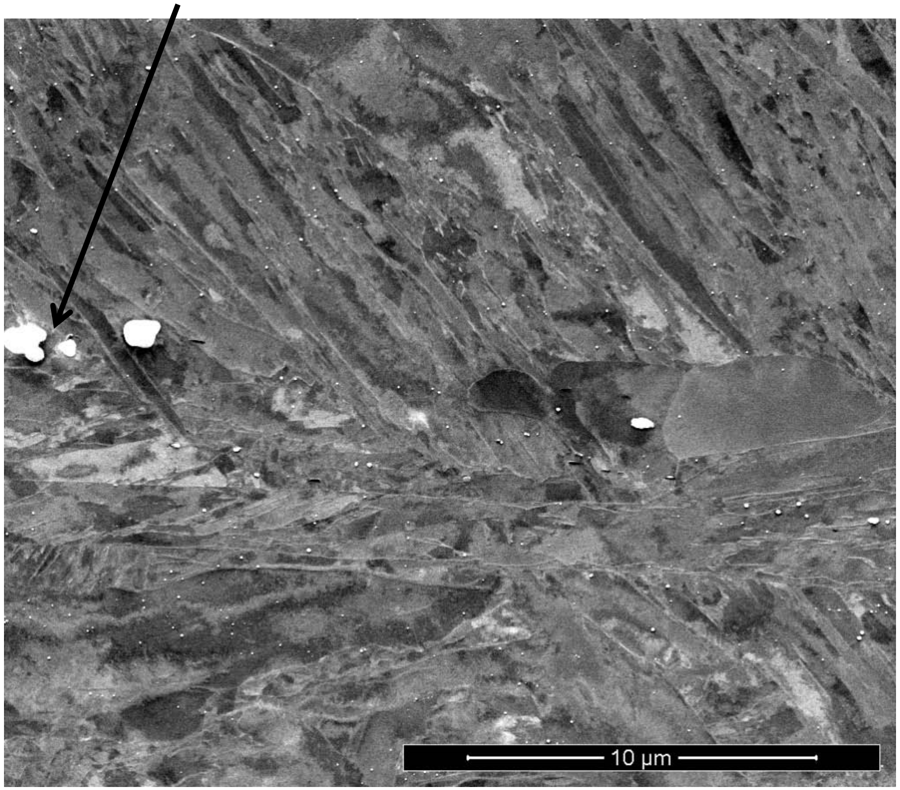


As-Fabricated Microstructure: Alloy 2

Ferrite banding in the rolling direction

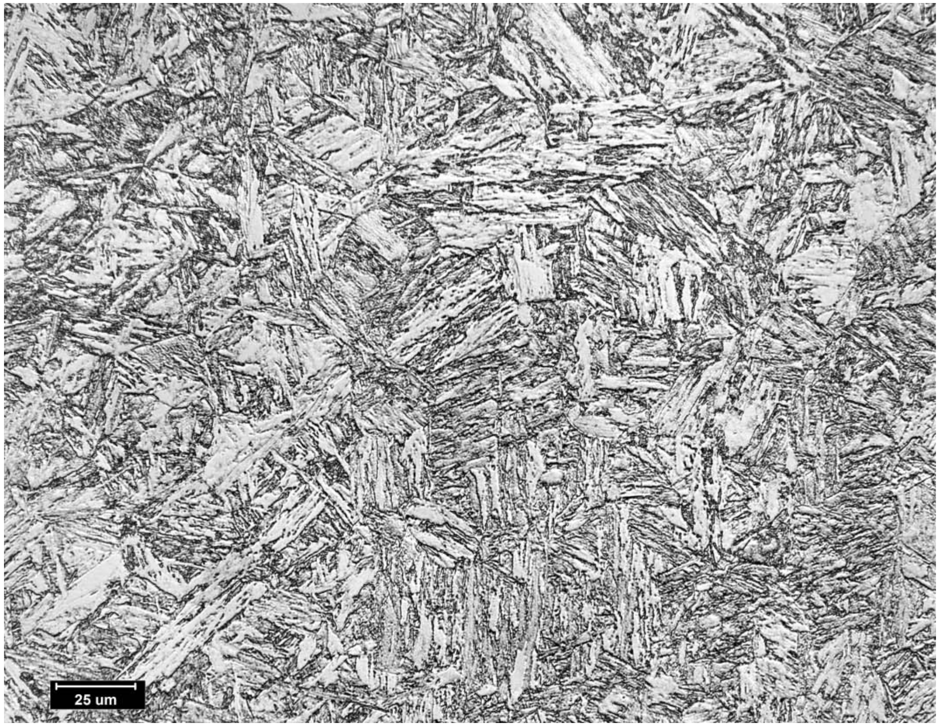


Larger precipitates



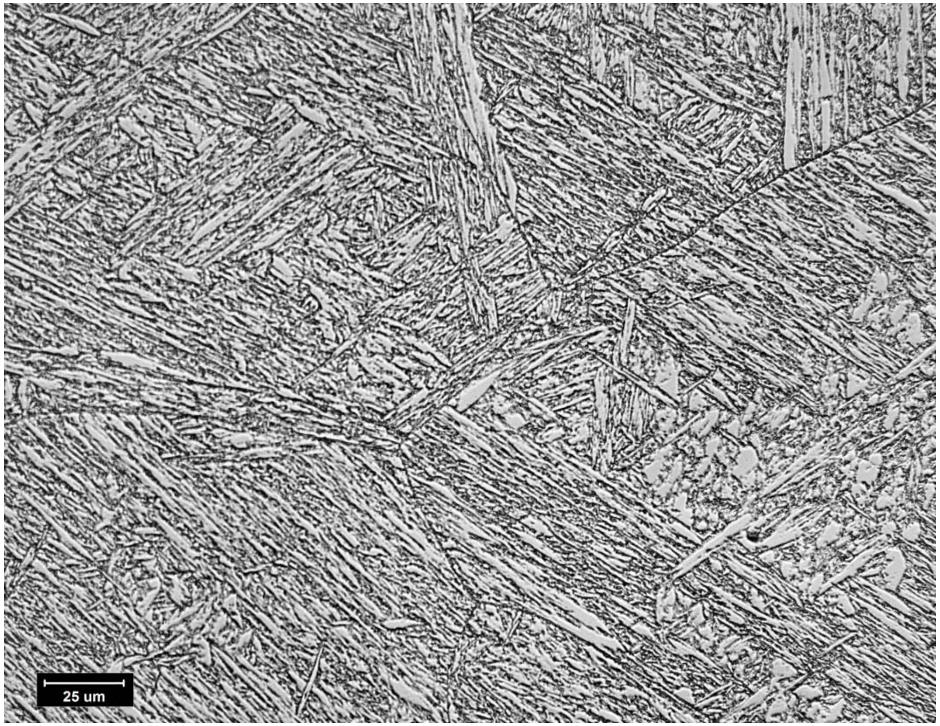
COST E & COST B2 Microstructures

COST E



10Cr-1.5Mo-0.6Ni-0.2V-0.05Nb-0.05N-0.1C

COST B2



9Cr-1.5Mo-0.1Ni-0.2V-0.05Nb-0.02N-0.2C-0.01B

These are normalized and tempered microstructures from an industrial scale rotor forging produced by Doosan Heavy Industries

Next Steps and Future Work

- Normalize and temper to develop microstructures consistent with those to be used in service.
- Determine tensile properties at RT and temperatures between 600 & 700°C.
- Conduct initial creep screening tests at 650°C to assess performance relative to COST alloys.
- Based upon mechanical behavior & microstructural characteristics after creep testing:
  – Reanalyze thermodynamic models
  – Alter chemistries to achieve desired structures

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