Development of Advanced High Strength Cast Alloys for Heavy Duty Engines

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Caterpillar Inc.

Vehicle Technologies – Annual Merit Review
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Project ID: PM 059

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Overview

Timeline

- Project start - December 2012
- Project end - February 2017*
- Percent complete ~ 70%

Budget

- Total project funding: $5.27M
  - DOE share: $3.48M
  - Contractor share: $1.79M
- Expenditure of Gov't Funds:
  - FY2013: $524,942
  - FY2014: $816,519
  - FY2015: $717,149
  - FY2016: $288,664 through Mar.'16

Barriers

- Efficiency: material and process must achieve 214 MPa endurance limit to enable higher cylinder pressure and temperature combustion regimes.
- Power Density: achieve 25% increase in strength over A842 compacted graphite iron.
- Cost: no more than 110% of production A48 gray iron cast units

Partners

- Interactions/ collaborations
  - **QuesTek Innovations**
  - **University of Alabama at Birmingham**
  - **Argonne National Laboratory**
  - **Dr. Doru Stefanescu**
  - Northwestern University
  - Elkem
- Project lead – Caterpillar Inc.

Objectives

- New high-strength ferrous materials with at least 25% improvement in component strength relative to components made with A842 (Compacted Graphite Iron).
- Cost should not exceed 120% of the cost of components using A48 (Gray Iron).
- Material must be produced using sand or investment casting processes.
- Evaluate the performance of existing ICME codes to accelerate the development of new alloys and processing techniques.
- Develop comprehensive cost models demonstrating costs relative to established grey cast iron baselines and identifying a path to meet incremental cost targets.
- *Contractor specific requirement:* achieve 200+ MPa fatigue endurance limit.

Relevance

- Advanced materials that are lighter and/or stronger are essential for boosting the fuel economy and reducing emissions of modern vehicles while maintaining performance and safety.
  - Increased powertrain efficiency can be obtained by enabling engine components to withstand the high pressures and temperatures of high efficiency combustion regimes.
  - Offset weight penalties from advanced emissions-control equipment, safety devices, integrated electronic systems and power systems such as batteries and electric motors for hybrid, plug-in hybrid, or electric vehicles.
    - For example, using lighter and/or higher strength materials to achieve a 10% reduction in vehicle weight can result in a 6% – 8% fuel-economy improvement.
- Cost penalties need to be minimized to accelerate adoption by industry and creating consumer demand.
- ICME tools need to be developed and utilized to accelerate to the design and validation of new materials.

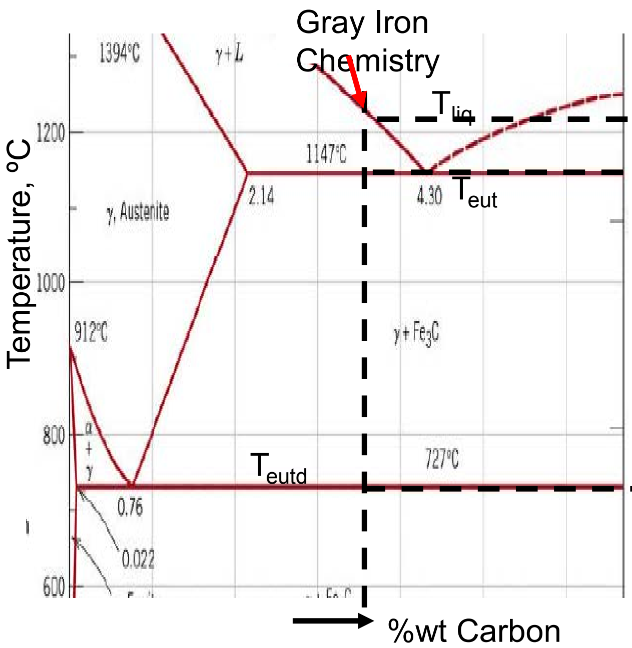
Milestones

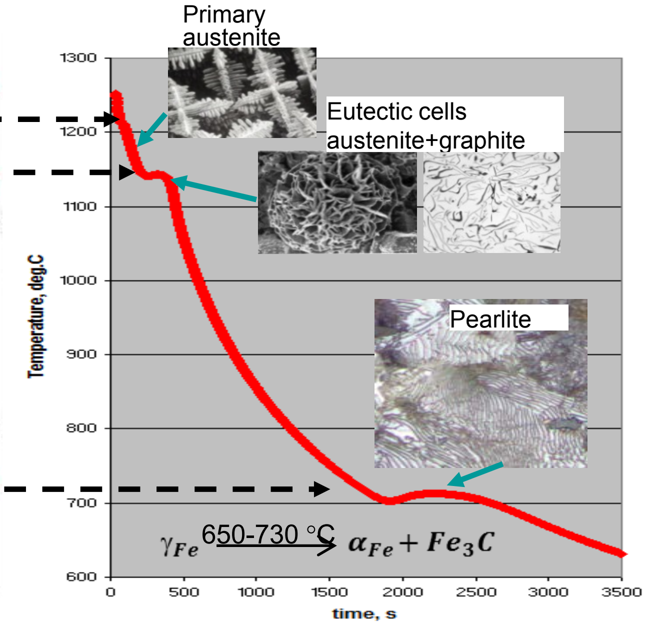
Milestone	Measure	Date	Status
Updated Project Management Plan + Reporting	Monthly + Quarterly	Ongoing	Ongoing
Definition of Alloy Requirements	Performance Requirements	Mar. '13	Complete
Generate Alloy Design Concepts	4 main areas of investigation	Aug. '13	Complete
Design Prototype Alloy Concepts	~16 prototype concepts	Apr. '14	Complete
Machinability Baseline for Current High Strength CGI	Tool wear & cutting force response surface for 450 MPa CGI, milling + drilling	Dec. '14	Complete
Design and Produce Prototype Castings	~ 16 prototype casting samples	Aug. '14	Complete
Evaluate Material Properties of Prototype Casting Alloys	> 650 Mpa	Feb. '15	Complete
Refine Design of High Potential (HP) Alloy Concepts (Iteration 2)	~4 HP alloy concepts	Aug. '15	Complete
Produce Prototype Castings for HP Alloy Concepts	~4 HP alloys	Nov. '15	Complete
Evaluate Mechanical Properties of HP Alloy Concepts	> 100 KSI tensile, > 31 KSI fatigue limit	Dec. '15	Complete
Evaluate Castability of HP Alloys	Minimize difference from HSGI, fluidity & Hot Tear	Jan. '16	Ongoing
Optimize Final Alloy Design	1 or 2 alloys	Apr. '16	Ongoing
Produce Final Alloy Test Castings	1 or 2 alloys	May '16	Ongoing
Evaluate Final Alloy Test Castings	> 125% of current CGI, 100 KSI tensile (min), excellent castability	Jun. '16	
Generate Property Datasets for FEA/Process Simulations	95% accuracy of simulations	Jun. '16	
Machinability Analysis of Final Alloy Design	Process Parameter Optimization and Cost Data	Sep. '16	
Engine Component Design/Analysis with Final Alloy	> 20% increas in power density	Sep. '16	Ongoing
Engine Component Process Design/Simulation with Final Alloy	Define Optimum Mfg. Value Stream and Process Parameters, < 120% current cost	Sep. '16	
Variation Analysis and Allowables Prediction	Define Chemistry Ranges in New Material Specification and Process Controls	Jan. '17	
Detailed Cost Model & Commercialization Plan	< 120% current cost, function of production volume	Feb. '17	

Approach

- **Utilize an Integrated Computational Materials Engineering (ICME) approach** to accelerate alloy development time by applying mechanistic materials models within a systems-engineering framework to computationally engineer new material compositions and manufacturing processes.
- **Produce prototype melts and characterize iteratively** for an alloy design approach within a stage-gate process.
- **Perform standard material testing and characterization** to validate the alloy performance against goals and provide feedback to ICME models.
- **Utilize advanced experimental capabilities,** such as the Advanced Photon Source (APS) at Argonne National Labs, to conduct innovative measurements of phase evolutions and map 3D graphite networks and identify nucleation and growth mechanisms.
- **Develop and optimized design of an engine component using an integrated modeling approach** that simulates the material, processing, and performance to demonstrate the potential benefits of the new material.
- **Develop cost models** at the material and the component/system level as a function of annual production volumes.

Introduction - Microstructure of Cast Iron





Relevant features:

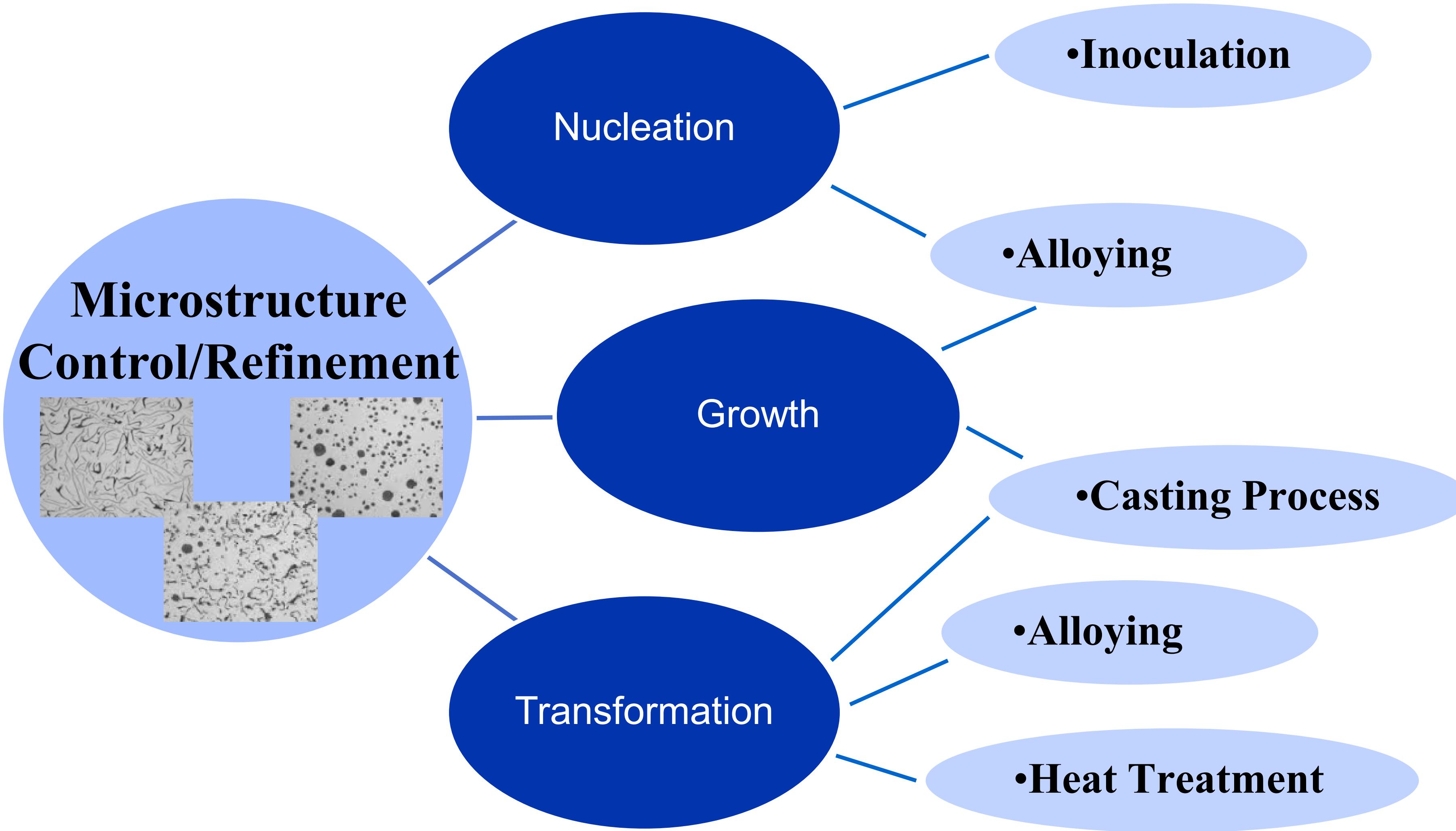
❑ **Solidification Stage:**
- ***austenite*** (primary & eutectic)
- ***graphite***

❑ **Room Temp.:**
- ***Pearlite/Bainite*** - *provides strength and hardness*
- ***graphite*** – *provides thermal conductivity, vibration dampening, decreases tensile & fatigue strength*

Possible Approaches to Improving Strength (UTS, FS) of Cast Iron:

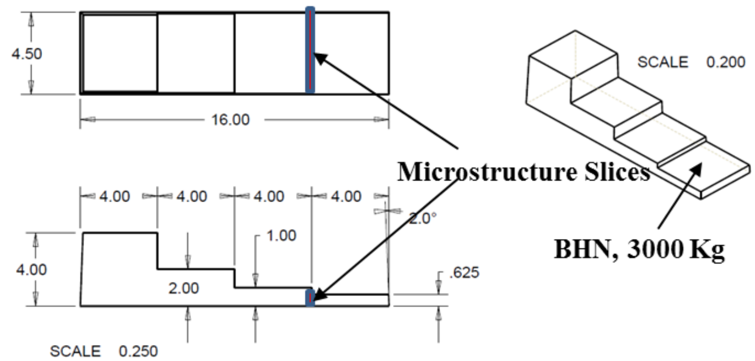
- Refining the primary austenite dendrites
- Refining the eutectic cell size:
  - ***Inoculation (find most potent inoculants)***
  - ***Solidification at the limit or outside the Eutectic Coupled Zone***
- Improve the strength of the metal matrix:
  - Pearlite refining (alloying with Cu, Mo…)
  - Ferrite strengthening (nano-precipitates)

Approach

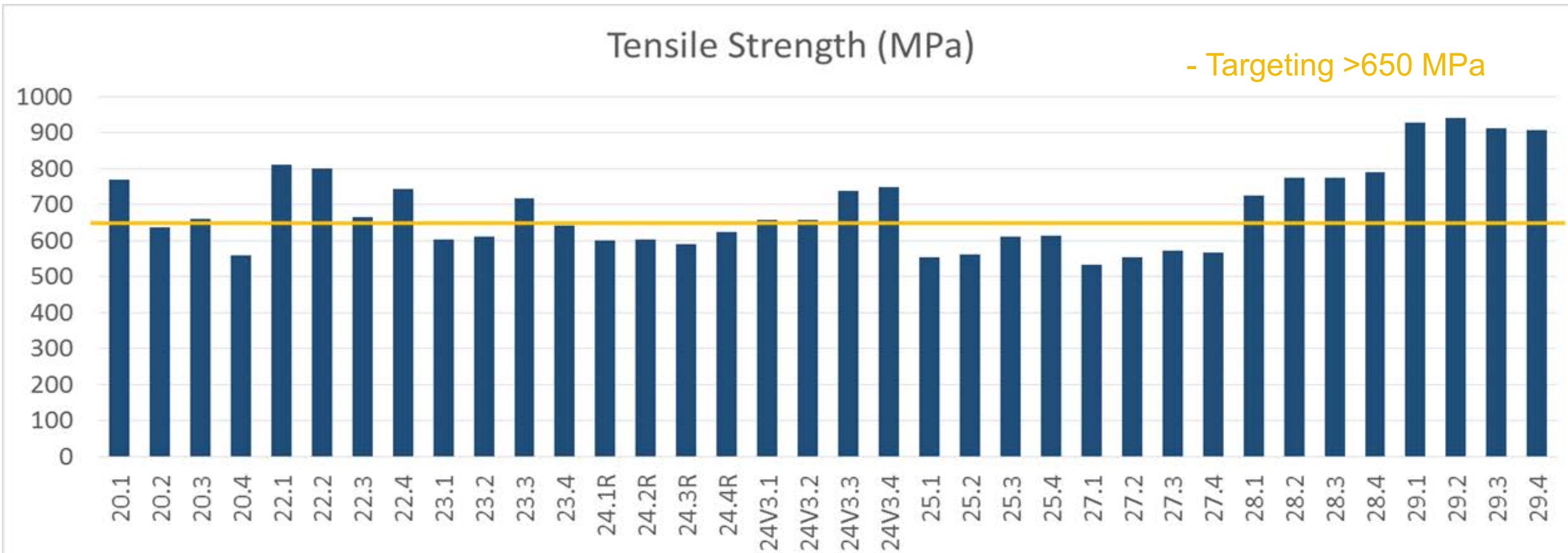

Microstructure Control/Refinement
Nucleation
Growth
Transformation
•Inoculation
•Alloying
•Casting Process
•Alloying
•Heat Treatment

Identification of High Potential Alloys

- Cast step blocks with varying sections to study effect of cooling rate
- Study various alloying elements to determine effect on structure-properties
  - C, Si, Mn, Sn, Cu, Ni, Mo, V
- Study various inoculation strategies
  - S, Ce, Bi, Zr, Ba, Al

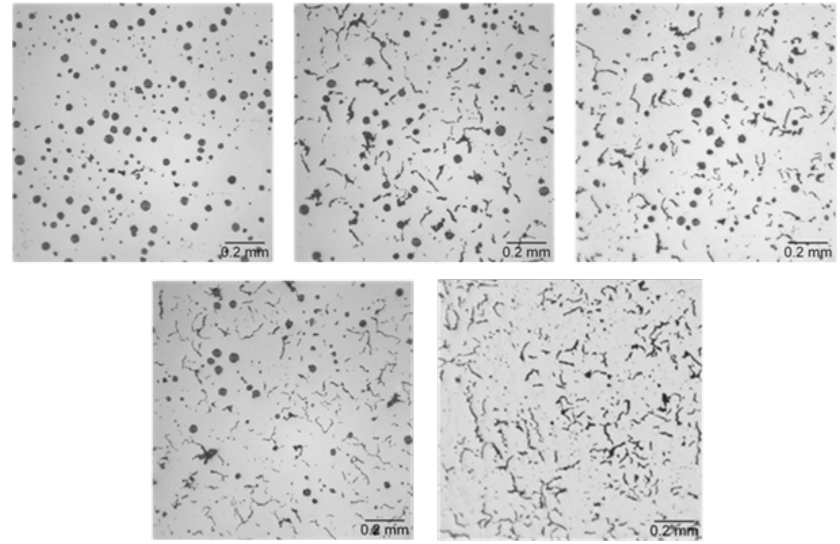


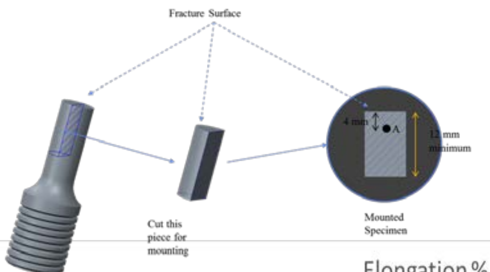
Step block castings produced at the University of Alabama at Birmingham

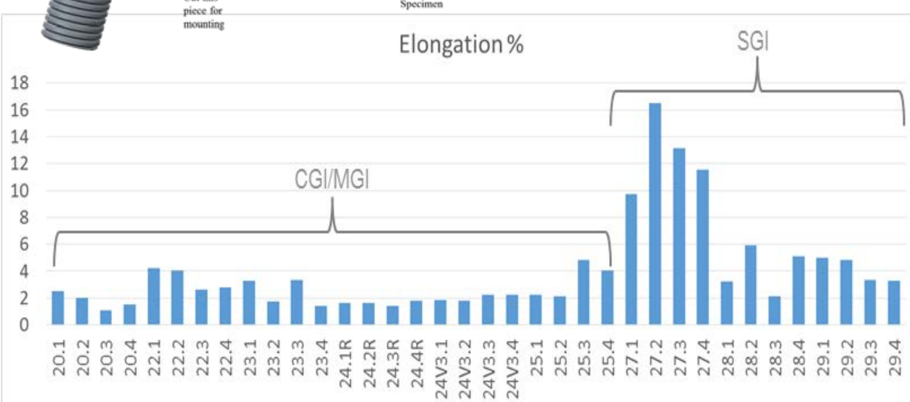


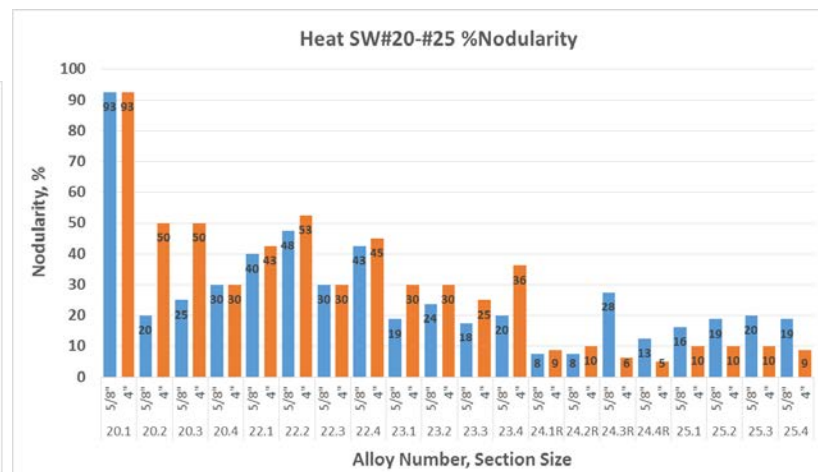
Identification of High Potential Alloys

- In-depth Structure-Property Characterization
- Graphite Characterization
  - Size, Shape, Density
- Matrix Characterization
  - Pearlite-Ferrite-Carbide phase fractions
- Property Characterization
  - Tensile, Yield, Elongation, Modulus, Hardness



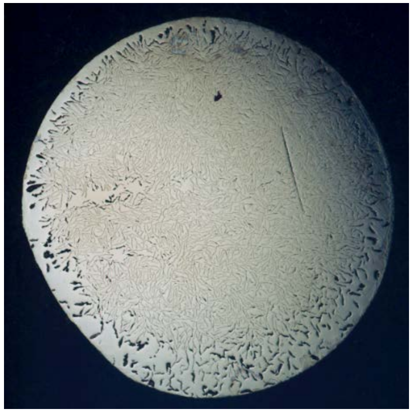




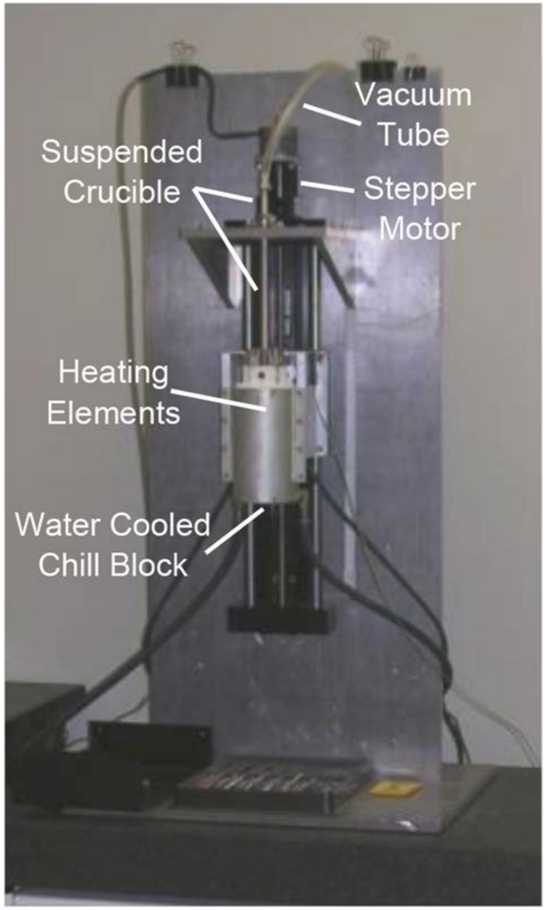


Directional Solidification Experiments

- High temp Bridgman furnace (>1300°C) with precise velocity and temperature control.
- Measure the microstructure growth in response to various thermal gradients and cooling rates.
- Ability to rapidly quench specimen to examine graphite growth at the solid-liquid interface.
- Use for validation of models and range finding for alloys studied.

2mm


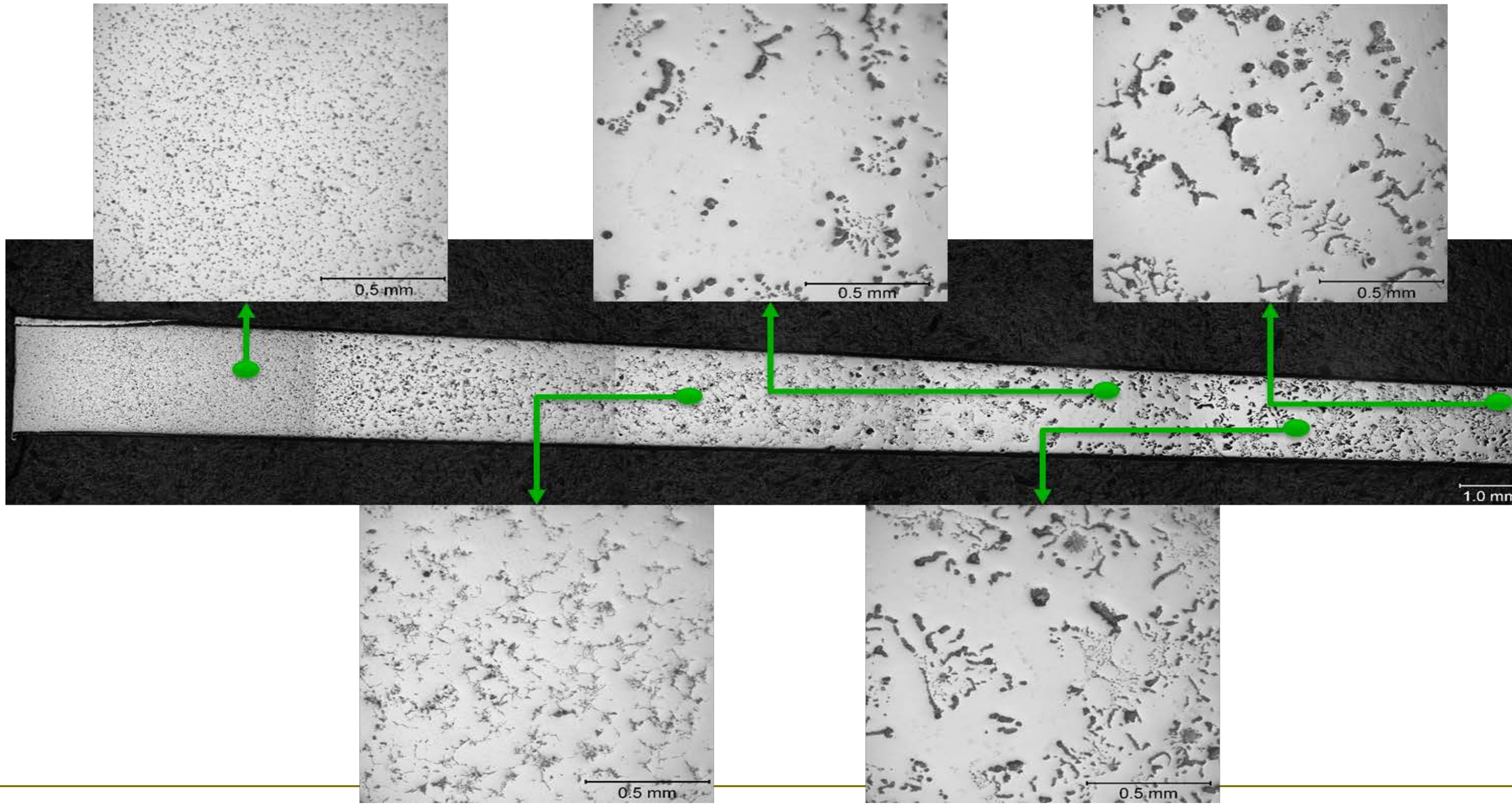
6mm



High temp. Bridgeman furnace at the University of Alabama at Birmingham (Prof. Amber Genau)

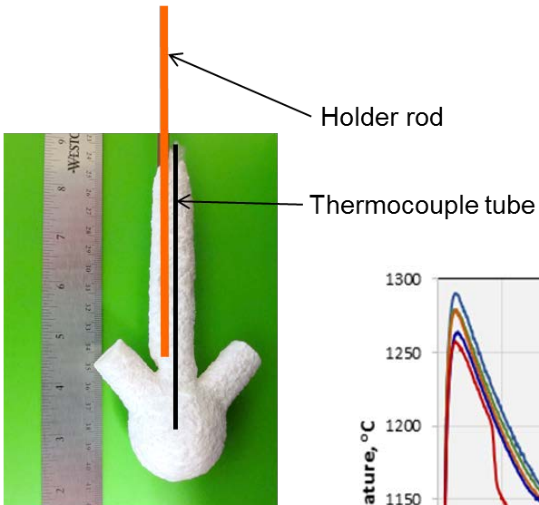
Directional Solidification Experiments

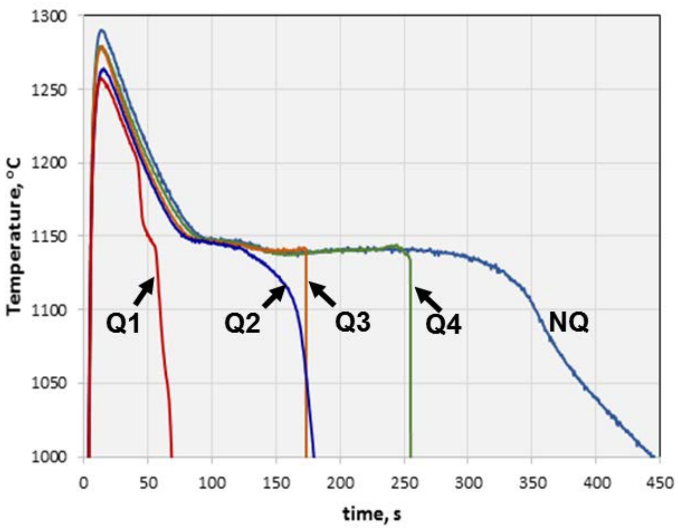
- Samples with elevated Ce and Mg processed in directional solidification furnace.
- Solidification velocity decreased incrementally as the samples was processed (left to right in image below).
- Successfully produced variations in graphite growth morphology (nodular, compacted, chunky).

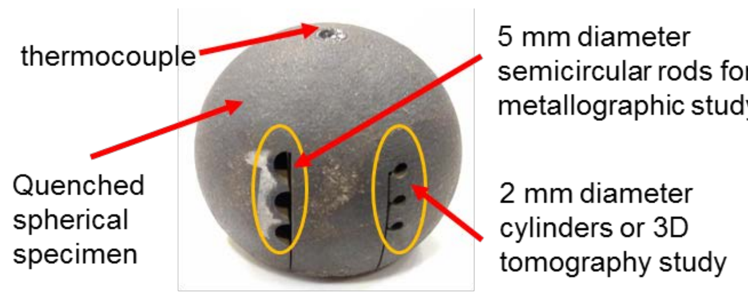


Interrupted Solidification Experiments

- Spherical samples cast from the same heat are quenched to directly form a microstructure from treated material at various stages of solidification.
- Samples taken from each casting to study the graphite growth and morphology evolution (nodular -> vermicular).







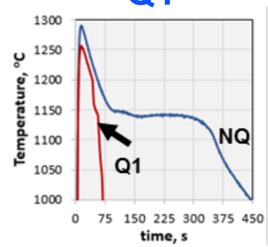
Interrupted Solidification Experiments

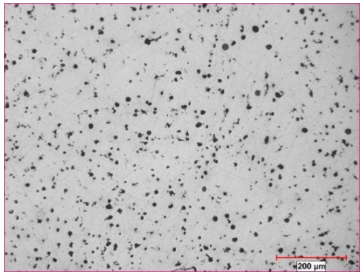
- Large number of graphite precipitates (~2000/mm2 ; ~5.5% of the surface area).
- Graphite precipitates assume both nodular and early vermicular (nodule with "tadpole" tail) shapes.
- Metallic matrix is composed of Ledeburite and Martensite+Retained Austenite.
- Graphite precipitates in contact with ledeburite indicate graphite growth from the liquid phase.
- The size of graphite indicates a fast growth.
- Some eutectic cells exhibiting vermicular graphite started developing; their size is of the order of 100-200 µm.
- The eutectic cells are surrounded by ledeburite.
- Inside the eutectic cells the metallic matrix is composed of very fine pearlite and martensite + residual austenite.
- More graphite appears as organized in eutectic cells.
- The eutectic cell size varies between 300 and 550 µm.
- Graphite tips at the periphery of eutectic cells are in contact with ledeburite, which suggests that the CGI eutectic cells grow with the graphite tips in the liquid phase

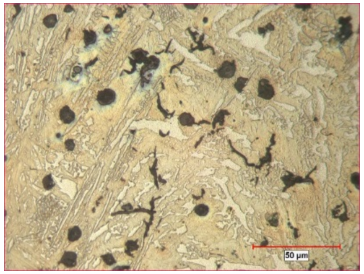
Unetched, 100X

Etched 2% Nital, 500X

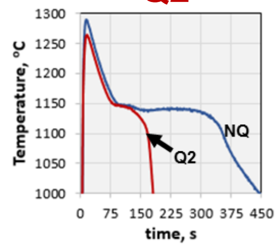
Q1

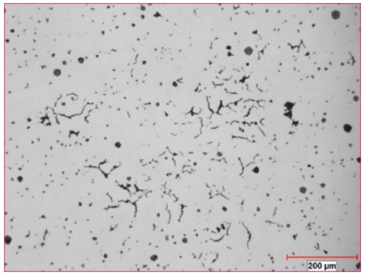


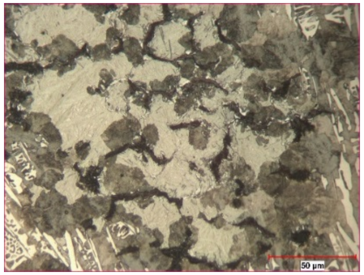




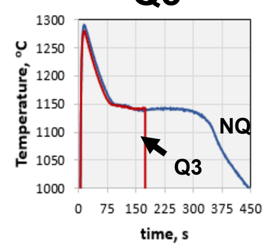
Q2

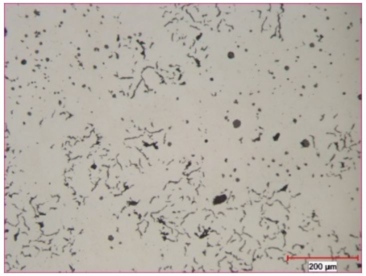


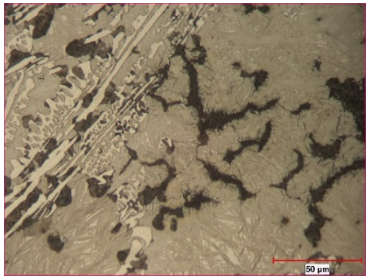




Q3





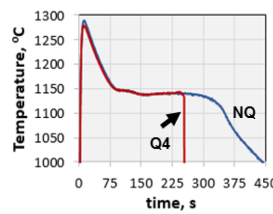


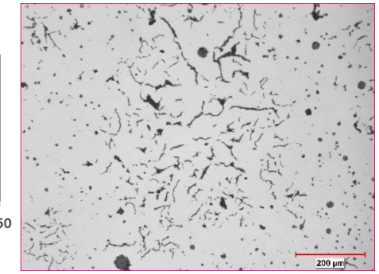
Interrupted Solidification Experiments

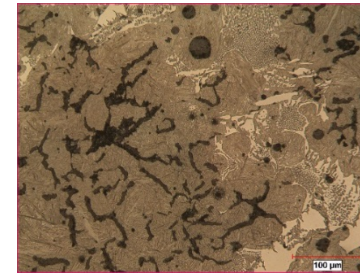
- Eutectic cells more clearly defined, with vermicular graphite somewhat thicker and longer.
- The eutectic cell size, as seen in 2D, varies between 300 and 500 µm.
- Individual graphite precipitates (vermicular and nodular) are surrounded by ledeburite, suggesting growth in the liquid at the time of quenching.
- Other nodular graphite precipitates are surrounded by martensite, which suggest a divorced eutectic growth at the time of quenching.
- Fully developed CGI microstructure, with very little nodular graphite.
- The eutectic cell size, as seen in 2D, varies between 290 and 450 µm.

Unetched, 100X | Etched 2% Nital, 500X

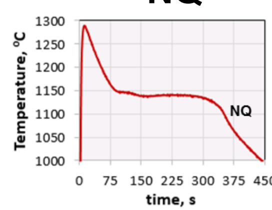
Q4

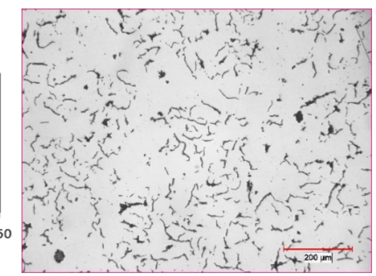


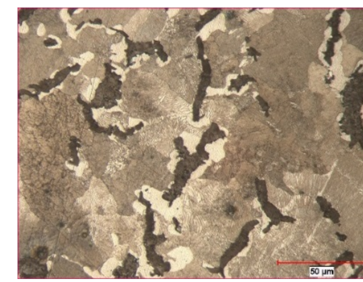




NQ



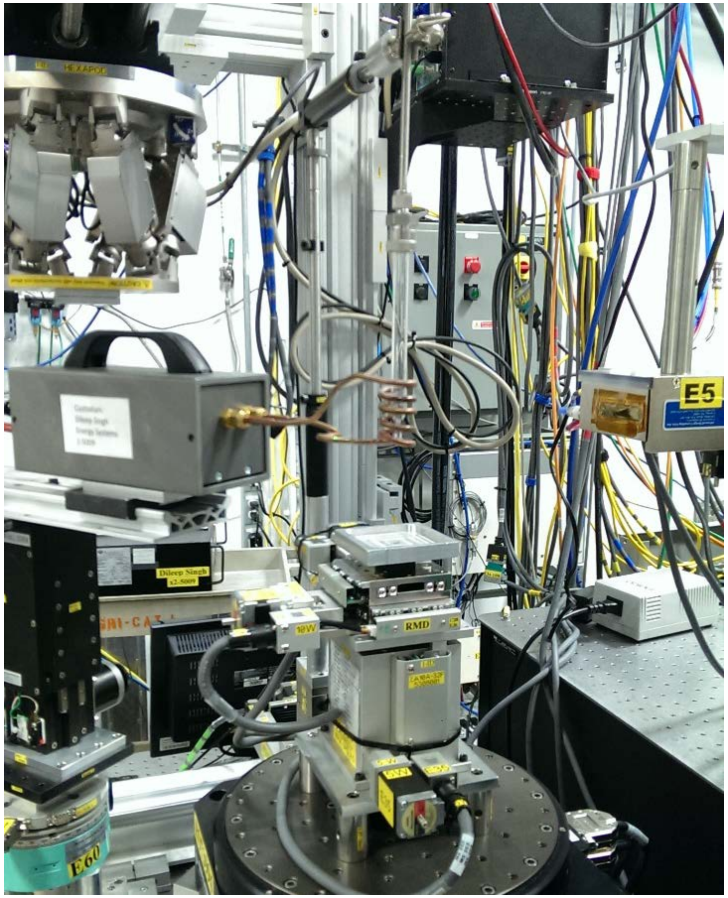




Summary

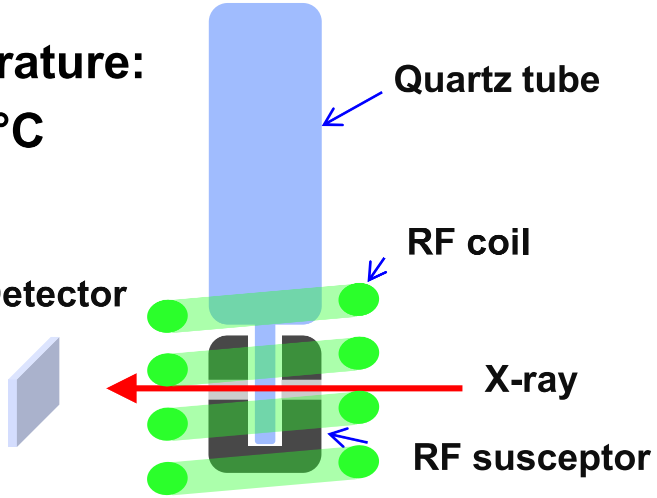
- The interrupted solidification experiment offers insight on the mechanism of microstructure evolution during solidification of CGI.
- The experiment revealed that a large number of graphite particles(~2000/mm2) nucleate.
- Even in the very incipient stage of growth, the graphite precipitates assume various shapes – from nodular to flake-like; this may be because of the fluctuations of Mg and RE concentration in the melt.
- It is apparent that the growth of vermicular graphite occurs with the tip of graphite precipitates in contact with the liquid phase

"In-Situ" Solidification Experiments

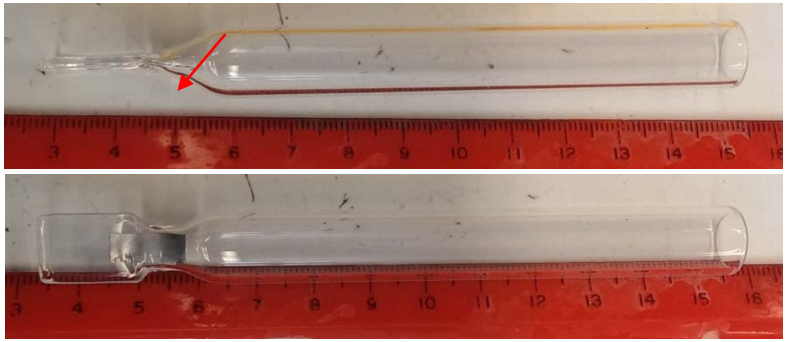


Temperature:

~1200 °C

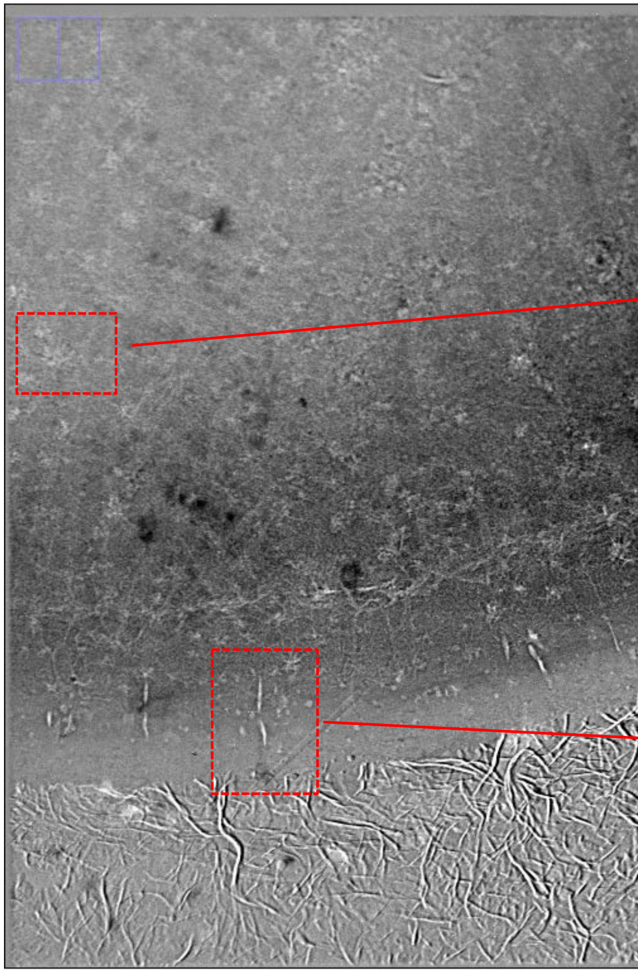


120 μm gap quartz tube

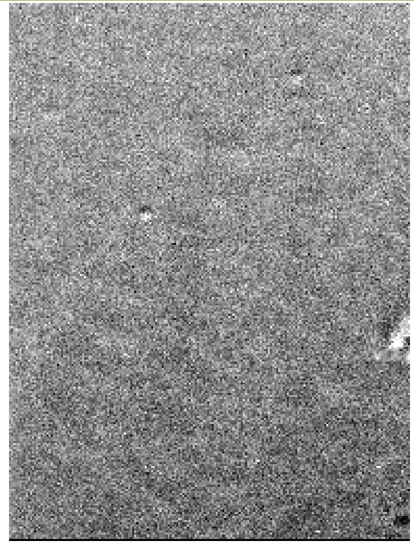


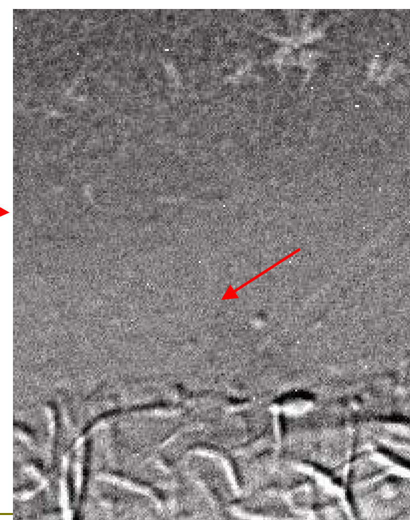
Study Phase evolution during solidification (~ 1200 °C) with WAXS and radiography imaging

“In-Situ” Solidification Experiments – 1st Cycle

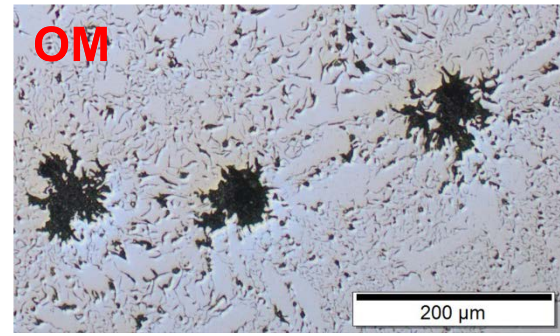


170 sec

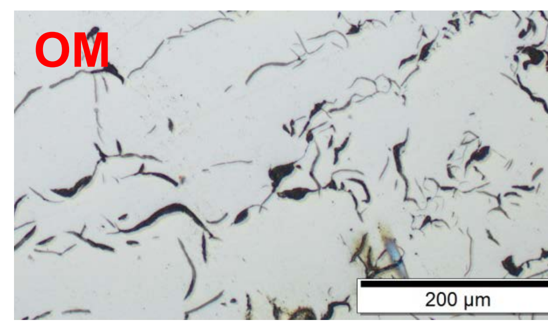




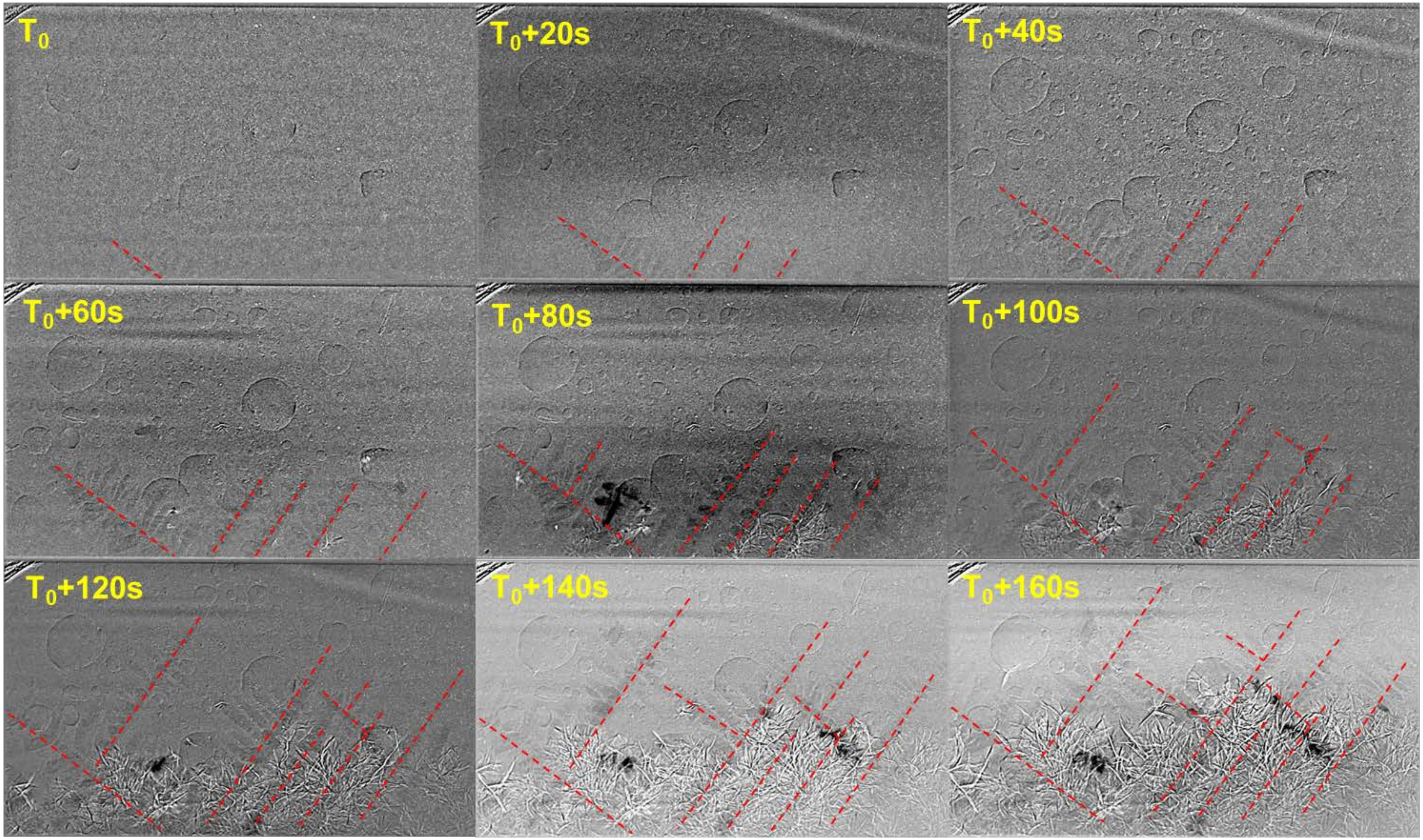
Nucleation and growth of Type-IV graphite (size ~ 70 um)



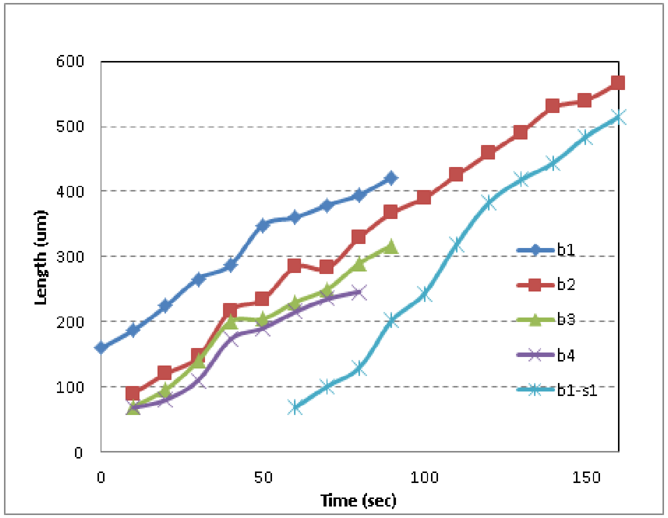
Nucleation and growth of flake graphite (size ~ 100um) and smaller NG-like particle

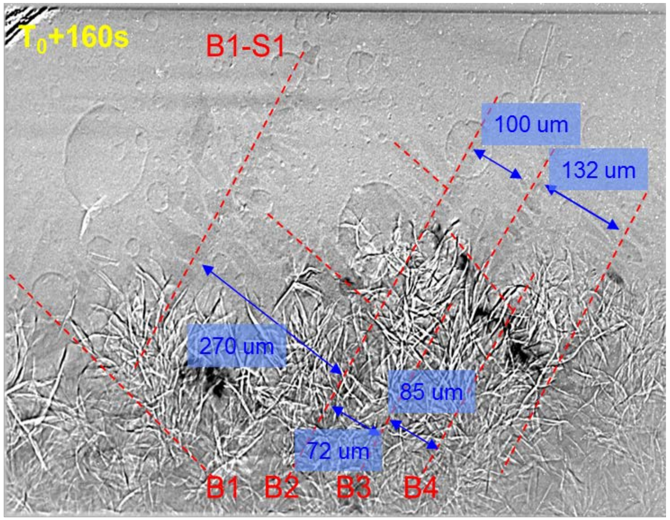


"In-Situ" Solidification Experiments – 2nd Cycle



"In-Situ" Solidification Experiments – 2nd Cycle





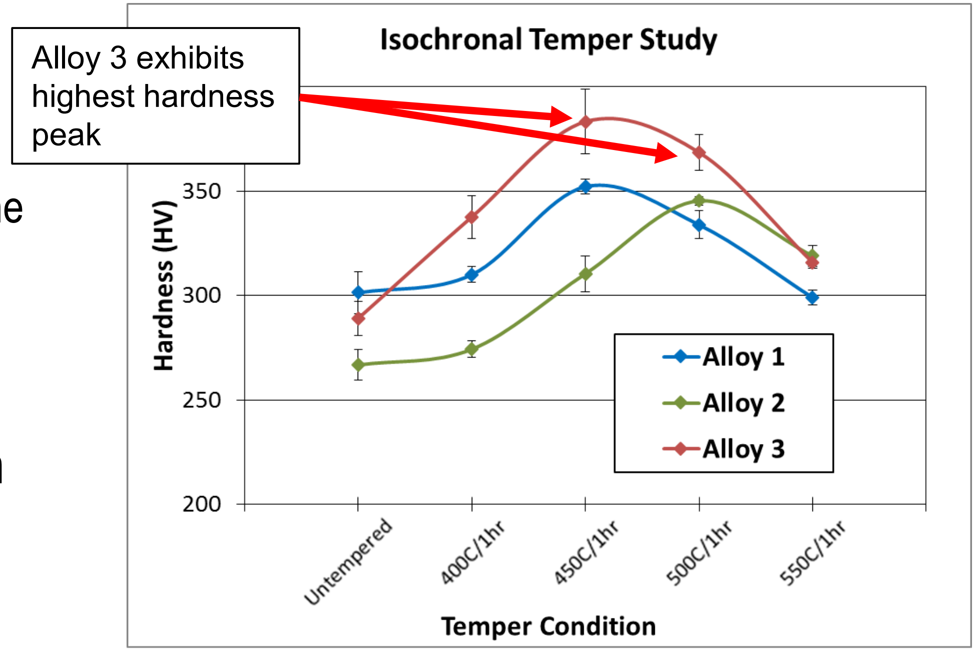
	b1	b2	b3	b4	b1-s1
velocity	2.989	3.223	3.033	2.801	4.796
angle	143	55	56	56	56

(μm/sec)

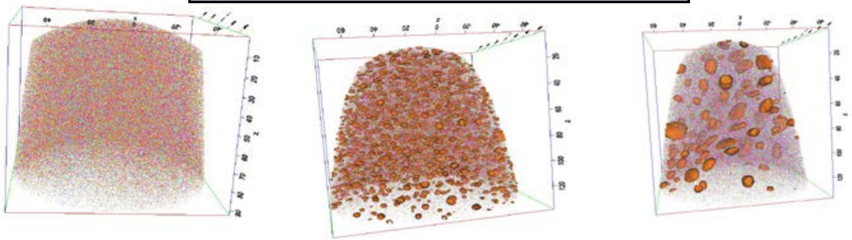
- Iron dendrite forms prior to the graphite phase, which forms near the root of dendrite, 350 ~500 um away from the front line.
- CG-like graphite can be observed in the 1st cycle, but in 2nd and 3rd cycle, only flake graphite can be seen. This indicates the fading of critical elements in the liquid.
- The nucleation of CG is civilian-like (individually nucleated) while FG nucleated at a interface and grow together.

Pearlite (Ferrite) Nano-precipitation Strengthening

- Strengthen pearlitic matrix during stress relief or cooling utilizing precipitate phases
  - Results show hardness peaks over baseline solid solution for each alloy
  - *Alloy 3* design shows highest precipitate hardening response
- LEAP (atom probe) measurements completed to determine size/composition of precipitates
  - Results used to calibrate precipitation models
- Enhanced quench suppressibility
  - Target precipitates to push peak hardness to higher temperatures
  - Avoid precipitate formation during initial cooling
- ***Must confirm precipitate formation in pearlite!***

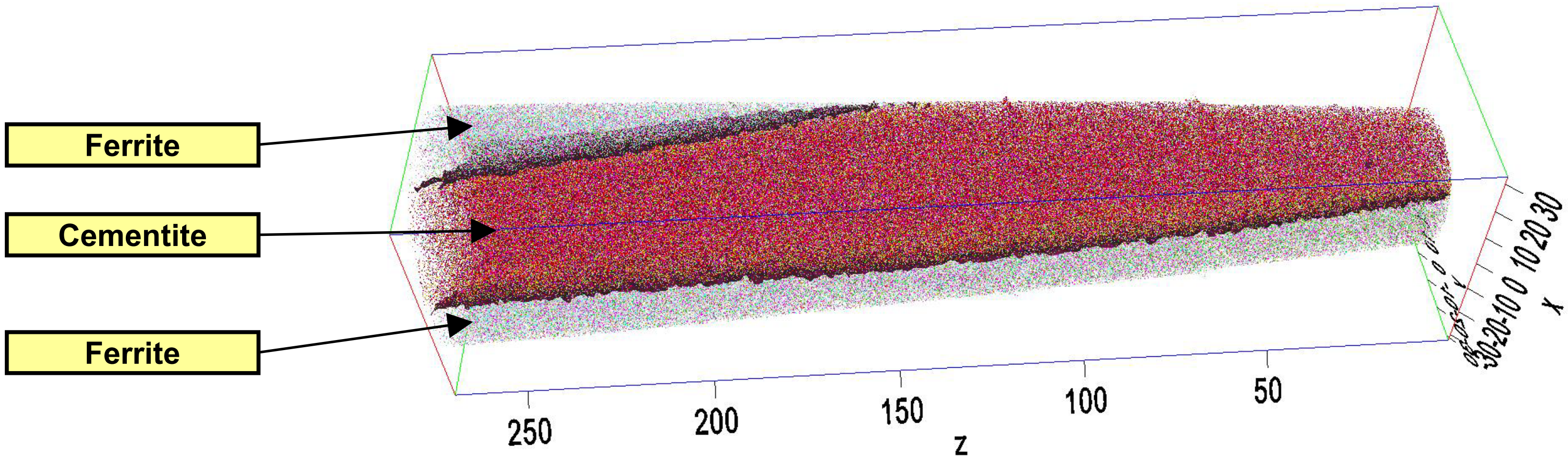


LEAP Results (Alloy 1)



As homogenized | Peak hardness | Over-aged

LEAP reconstruction of Cu-based precipitation in Pearlite: Ferrite/cementite and precipitate regions



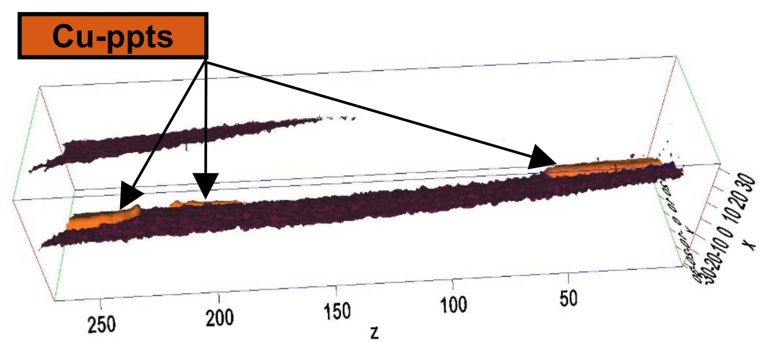
Successful FIB lift out and LEAP imaging of pearlite region (at cementite/ferrite interface)

- ~50-80 nm thick lamella
- Cementite ~100s of nm apart in current sample region

Cu-based precipitates found at cementite/ferrite interfaces

- Ni segregates to the Cu-ppts
- Small ppts (~10-40 nm)

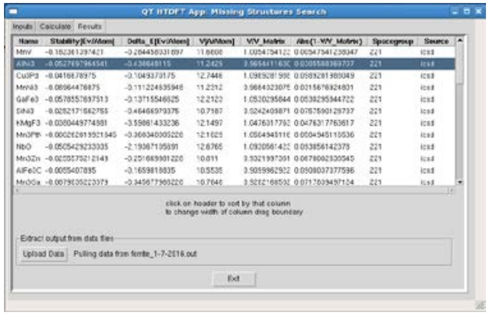
Cu precipitates located at cementite interface:

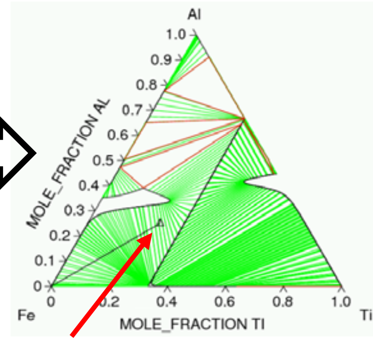


2.6 at.% Cu isosurfaces +
2.2 at.% C isosurfaces

Identification of Novel Phases for Precipitate Strengthening

QuesTek HTDFT and Phase Diagram Creation Program





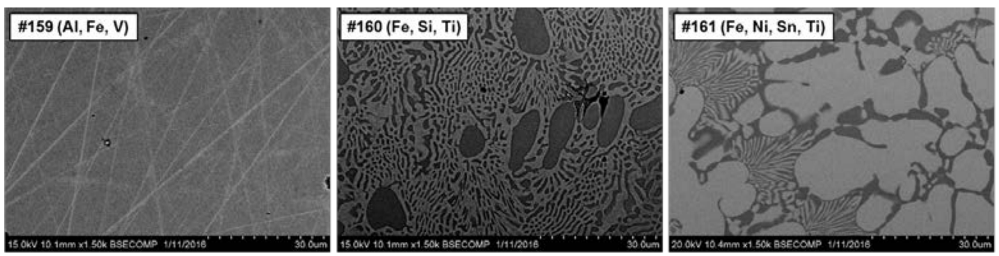
Test target phase stability with bcc iron

Target/Actual Button Chemistries

Button #	Concept Designation		Chemistry (wt%) Fe	Al	Mn	V	Ni	Ti	Si	Sn
158	Fe + MnV	Target	51.339	-	25.249	23.412	-	-	-	-
		Actual	53	-	25.2	21.9	-	-	-	-
159	Fe + Fe2AlV	Target	81.1343	6.5327	-	12.333	-	-	-	-
		Actual	81.8	6.01	-	12.2	-	-	-	-
160	Fe + Fe2TiSi	Target	81.5159	-	-	-	-	11.652	6.8321	-
		Actual	83.2	-	-	-	-	10.7	6.15	-
161	Fe + TiNiSn	Target	42.653	-	-	-	14.944	12.192	-	30.211
		Actual	44.7	-	-	-	14.8	11.5	-	29

- High-throughput DFT results used to identify lattice-matched structures
- Buttons melted with targeted 50% precipitate phase fraction to determine stability
- SEM/EDS and XRD used to confirm phase stability and lattice matching
- Future designs will confirm precipitate strengthening in ferrite with lower ppt. phase fraction
  - Peak strengthening compositions will be designed
- Scale up to cast step blocks to determine if further strengthening of final alloy design is possible.

SEM/EDS to Confirm Phase Stability



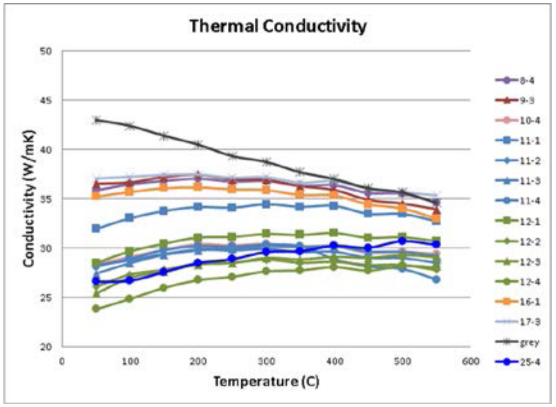
#	Alloy	Expected phases-TC	Composition (at%) Light Phase	Dark Phase	Bulk
159	Fe + Fe2AlV	Solid solution	--	--	75.3Fe-12.6Al-12.1V
160	Fe + Fe2TiSi	Laves	90.4Fe-7.3Si-2.4Ti	60.3Fe-15.5Si-24.2Ti	76.9Fe-11.1Si-12.1Ti
161	Fe + TiNiSn	austenite	28.1Fe-25.67Ni-24.2Sn-22.1Ti	91.1Fe-0Ni-3.1Sn-5.8Ti	52.11Fe-12.5Ni-18.6Sn-16.8Ti

Response to Reviewers Comments

C1. The reviewer did not fully understand how the collaboration worked nor what expertise was shared.
A1. The teams meets monthly for face-to-face fully collaborative technical working meetings. Material testing and characterization work is performed by all team members. Caterpillar, Questek and Northwestern have extensively collaborated on data and model development and execution.

C2. The focus in future is to validate the models, in this reviewer's view.
A2. The current focus is to improve the models needed to design and validate new components manufactured with a new high-strength engine material.

C3. Thermal conductivity needs more attention, in this reviewer's estimation.
A3. While a Thermal Conductivity (TC) target for the new engine alloy was not explicitly defined in the DOE FOA, the project team recognizes the importance of TC for certain component applications. The TC has been measured for several trial alloys produced. It should also be noted that heat flux through a section is a function of conductivity and distance the heat flow must travel. It is expected that section sizes can be reduced if material strength can be increased, thus reducing the impact of reduced conductivity on heat extraction rate.

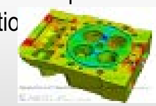


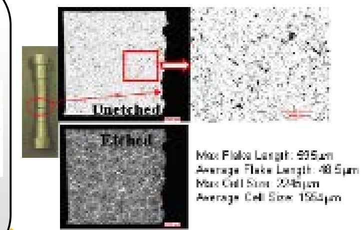
Thermal conductivity measurements of several alloy samples produced during the course of this project.

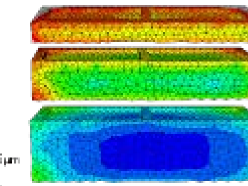
Collaboration – Project Team

Project Lead → CATERPILLAR®

- Material and Process Development
- Material Characterizatio
- Design Integration
- Integrated Simulation
- Design Optimization
- Concept Design Cost Model



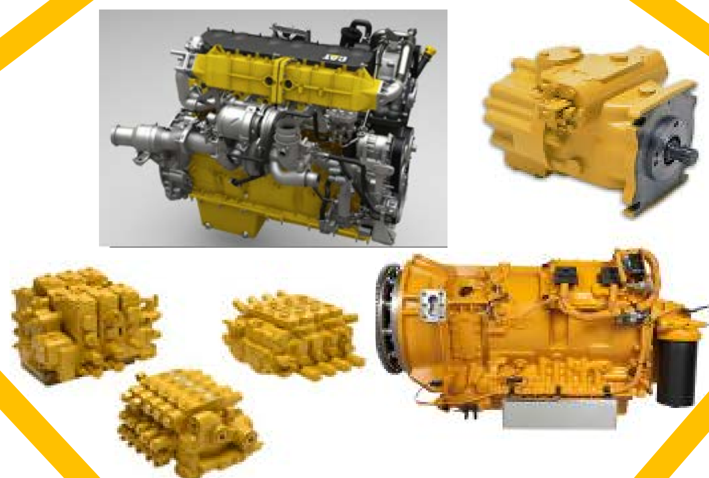




215 – 300 MPa

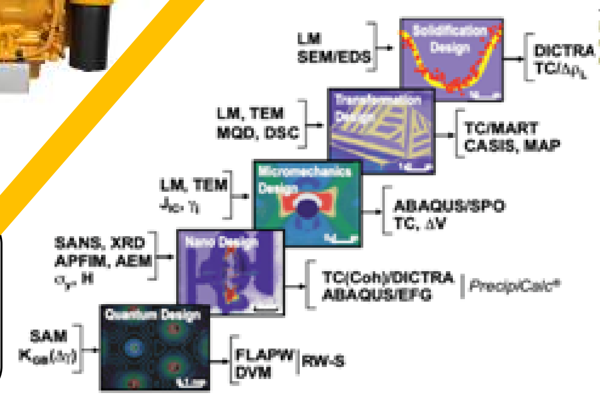
Argonne NATIONAL LABORATORY

- Material Evaluation using Advanced Photon Source (APS) X-Ray and MTS Testing Machine
- In-Situ Microstructure and Damage Measurements



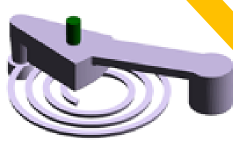
QuesTek INNOVATIONS LLC

- Computational Material Design
- Solidification Design
- Transformation Design
- Nano Design
- Material Characterization



<u>Addition Support:</u>

- Dr. Doru Stefanescu, OSU
- Northwestern University
  - Dr. P. Voorhees
  - Dr. C. Wolverton



Fluidity Spiral Test Casting

UAB THE UNIVERSITY OF ALABAMA AT BIRMINGHAM

- Experimental Casting Material Samples
- Liquid Metal Fluidity Evaluation
- Hot Tear Resistance

CATERPILLAR® | QuesTek INNOVATIONS LLC Materials By Design® | UAB THE UNIVERSITY OF ALABAMA AT BIRMINGHAM | Argonne NATIONAL LABORATORY

Remaining Challenges and Barriers

- Nucleation and growth of austenite + graphite is not completely understood for CGI.
  - It has been determined that sulfides are the primary nucleation sites for all graphite. Search for more potent inoculants has not been successful. Focus has narrowed to creating more nucleation sites for sulfides, primarily oxides, and compositions that increase the undercooling, thereby activating more nuclei.
    - Care must be taken to not increase undercooling too much to avoid graphite nucleating on particles other than sulfides to avoid undesired graphite shapes or surpassing graphite nucleation altogether.
  - Primary phase nucleation may be only refinement mechanism, extremely difficult to identify austenite nuclei.
- Material design that meets the mechanical property targets while simultaneously satisfying thermal conductivity and manufacturing cost requirements is a significant challenge.
  - MGI (Compacted+Nodular) needed for very High-Strength iron in the as-cast condition.
  - Uncertainty in Strength-Conductivity trade-off in design process requires extensive validation.
  - Uncertainly in Strength-Fatigue relationship for CGI. Fatigue testing started for selected High-Potential alloy candidates.
- Satisfactory ICME tools not available for the fundamental material modeling and design of cast irons.
- Fundamental R&D work still needed for cast iron materials. As a result, uncertainty in the ability to control the structure in high performance CGI remains, which creates a risk for production implementation.
  - Not unlike other materials systems where increasing the performance regime increases the sensitivity to variations and defects in the structure.
  - High-Performance regime largely unexplored for cast irons despite excellent strength vs. density ratio.

Future Steps

- Phase Nucleation and Growth to Optimize Final Alloy Design
  - Serial sectioning on high-potential inoculant sample to identify role in sulfide nucleation.
  - DFT calculations to identify improved primary phase nucleation strategy
  - Continue melting button samples to validate potential strengthening phases from DFT calculations.
  - *In-situ* solidification experiments using X-ray radiography to view graphite formation.
  - Directional solidification and Interrupted solidification experiments for CGI
    - Quantitative evaluation on the influence of alloying elements and solidification conditions on the formation sequence of CGI
  - Improve and validate "Divorced Eutectic" solidification model (Austenite +CG).
- Casting Trials
  - Develop new supplier to scale-up trials of final alloy designs.
    - 1000 lb. heats to be produced at Southern Cast Products and Caterpillar's Mapleton Foundry.
    - Evaluate repeatability of final alloy designs.
  - Develop experimental process for increasing the solidification rate of step block castings.
- Strength Models
  - Define process-structure-property models and strength vs. thermal conductivity trade-offs.
  - Investigate fatigue performance of the high-strength alloy concepts.
- Prototype Component Design
  - Demonstration component design has been started using an integrated modeling approach.

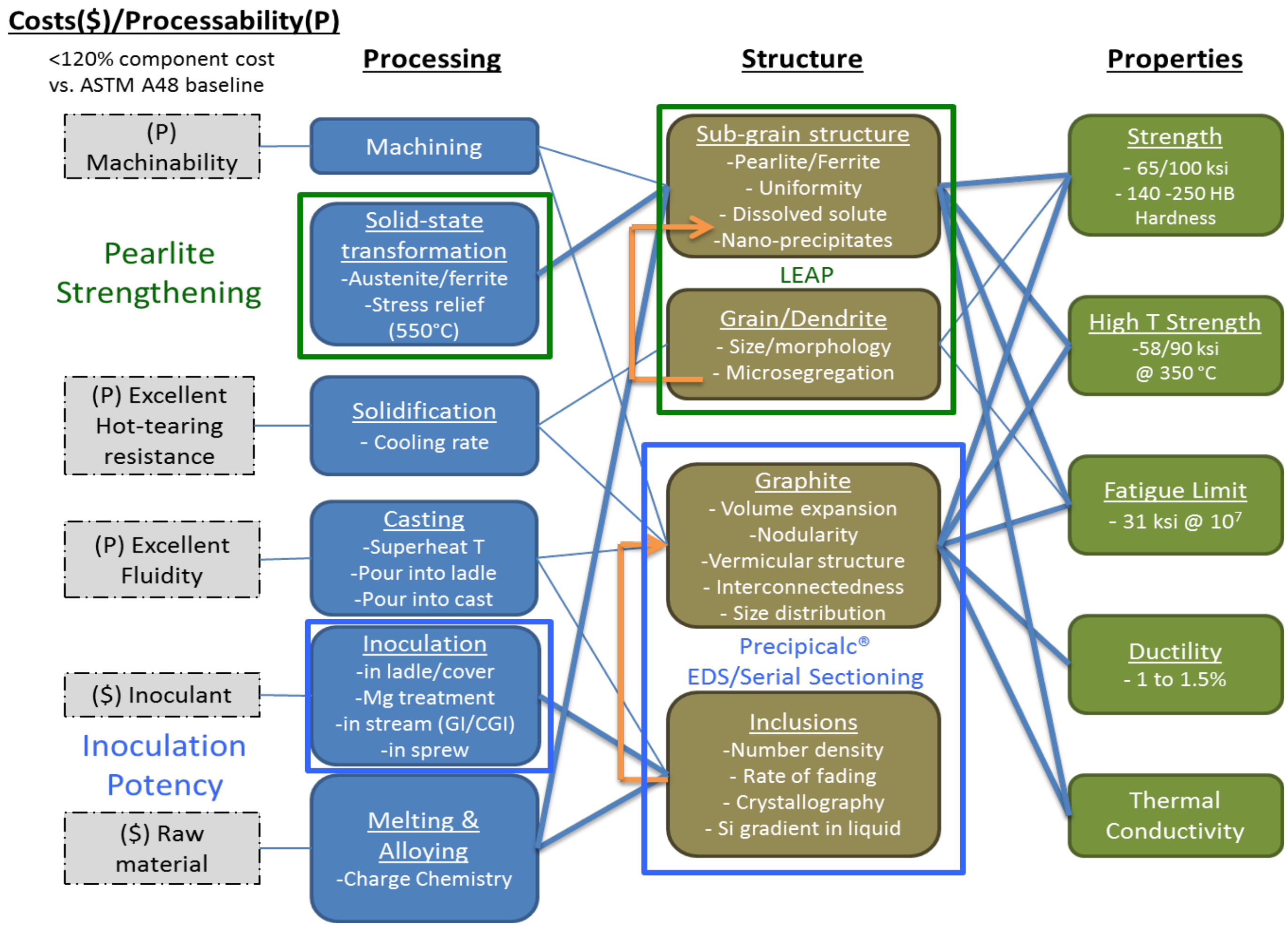
Summary

- Project is relevant to the development of high-efficiency, low-emission heavy-duty engines
  - Improved material properties are needed to enable heavy-duty engines to operate in optimal combustion regimes for both power and emissions.
  - Improved mechanical properties will allow engines with increased power densities to be developed, reducing engine displacements and thus dramatically reducing the size and weight, which will improve fuel-economy at the vehicle level.
- FY13-16: focus on identifying high-strength alloy concepts and modeling the critical mechanisms governing the microstructure development during solidification
  - Sulfide nuclei identified and characterized in several types of graphite particles.
  - X-ray methods established to reveal complex 3-D graphite networks in CGI.
  - New inoculant strategies for austenite and graphite phases and potential precipitation strengthening phases developed using high-throughput DFT calculations.
  - Several advanced experiments are in process that are helping to better understand the nucleation and growth of the phases in cast irons.
  - **Casting trials have successfully identified High-Potential alloy concepts with strengths ranging from 650 to 950 MPa tensile strengths for CG->MG->SG.**

Technical Back-up Slides

Approach

Updated systems-design chart for cast iron



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