Development of Advanced High Strength Cast Alloys for Heavy Duty Engines

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Caterpillar Inc.
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Vehicle Technologies – Annual Merit Review

Project ID: PM 059

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start - December 2012
- Project end - December 2016
- Percent complete ~ 25%

Budget

- Total project funding: $5.08M
  - DOE share: $3.48M
  - Contractor share: $1.6M
- Expenditure of Gov't Funds:
  - FY2013: $524,952
  - FY2014: $378,374 thru March

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
  - Northwestern University
  - Jonkoping 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 fatigue endurance limit of 214 MPa.

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

- FY13 and FY14

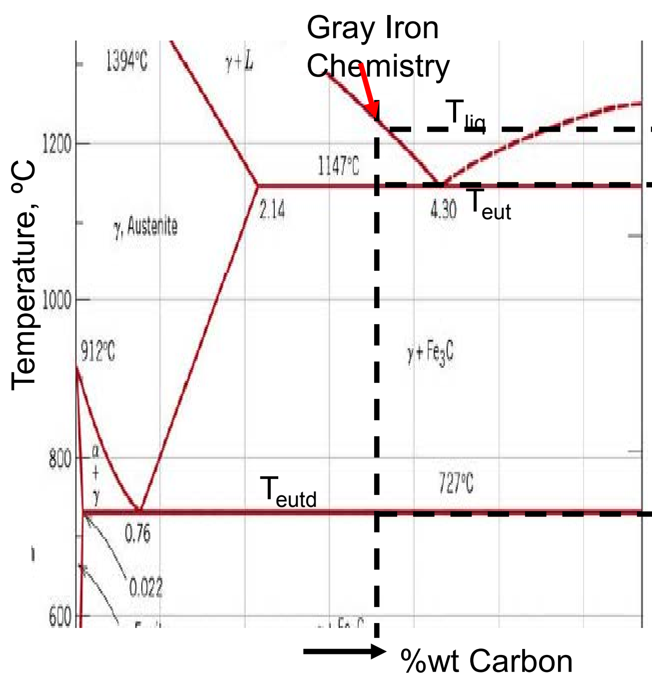
Milestone	Measure	Date	Status
Updated Project Management Plan + Reporting	Monthly + Quarterly	Ongoing	Ongoing
Definition of Alloy Requirements	Performance Requirements	Mar. ‘13	Complete
Generate Alloy Design Concepts	4 main areas of investigation	Aug. ‘13	Complete
Design Prototype Alloy Concepts	~16 prototype concepts	Dec. ‘13	Complete
Machinability Baseline for Current High Strength CGI	Tool wear & cutting force response surface for 450 MPa CGI, milling + drilling	Dec. ‘13	Ongoing
Design and Produce Prototype Castings	~ 16 prototype casting samples	Apr. ‘14	Ongoing
Evaluate Material Properties of Prototype Casting Alloys	> 100 KSI tensile, 140 – 245 HB	May ‘14	Ongoing
Refine Design of High Potential (HP) Alloy Concepts (Iteration 2)	~4 HP alloy concepts	Aug. ‘14	

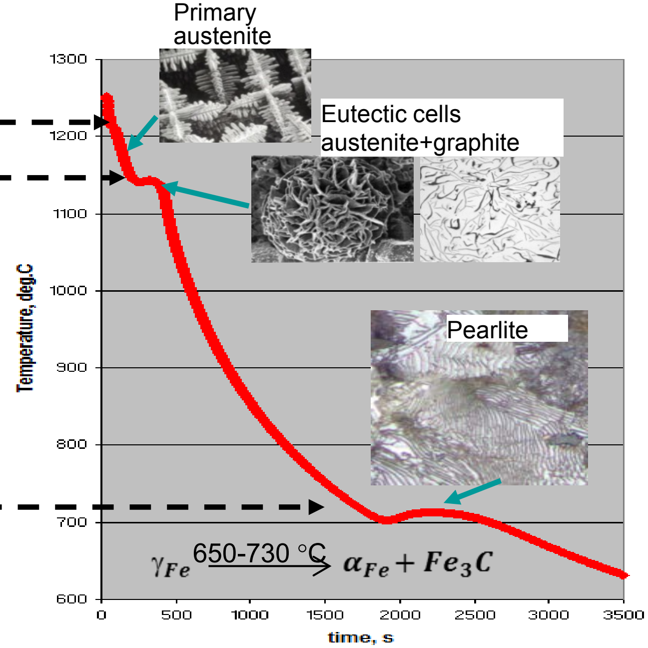
- FY15 – produce and evaluate HP alloys, down-select and optimize final alloy design
- FY16 – validate final alloy design, demo component design, cost model

Approach

- Utilize an Integrated Computational Materials Engineering (ICME) approach that has been proven to accelerate alloy development time by applying mechanistic materials models within a systems-engineering framework to computationally engineer new material compositions and manufacturing processes.
- Prototype melts will be produced and characterized iteratively for an alloy design within a stage-gate process.
- Standard characterization and material testing will be done to validate the alloy performance against goals and provide feedback to ICME models.
- Utilize the Advanced Photon Source (APS) at Argonne National Labs to conduct innovative measurements to map 3D graphite networks and identify nucleation sites. In-situ measurements of phase evolutions and damage during heating and cooling under various loading conditions is also planned.
- Utilize an integrated modeling approach that simulates the material, processing, and performance to optimize the design of a concept engine component to demonstrate the potential benefits of the new material.
- Cost models analyzed 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***

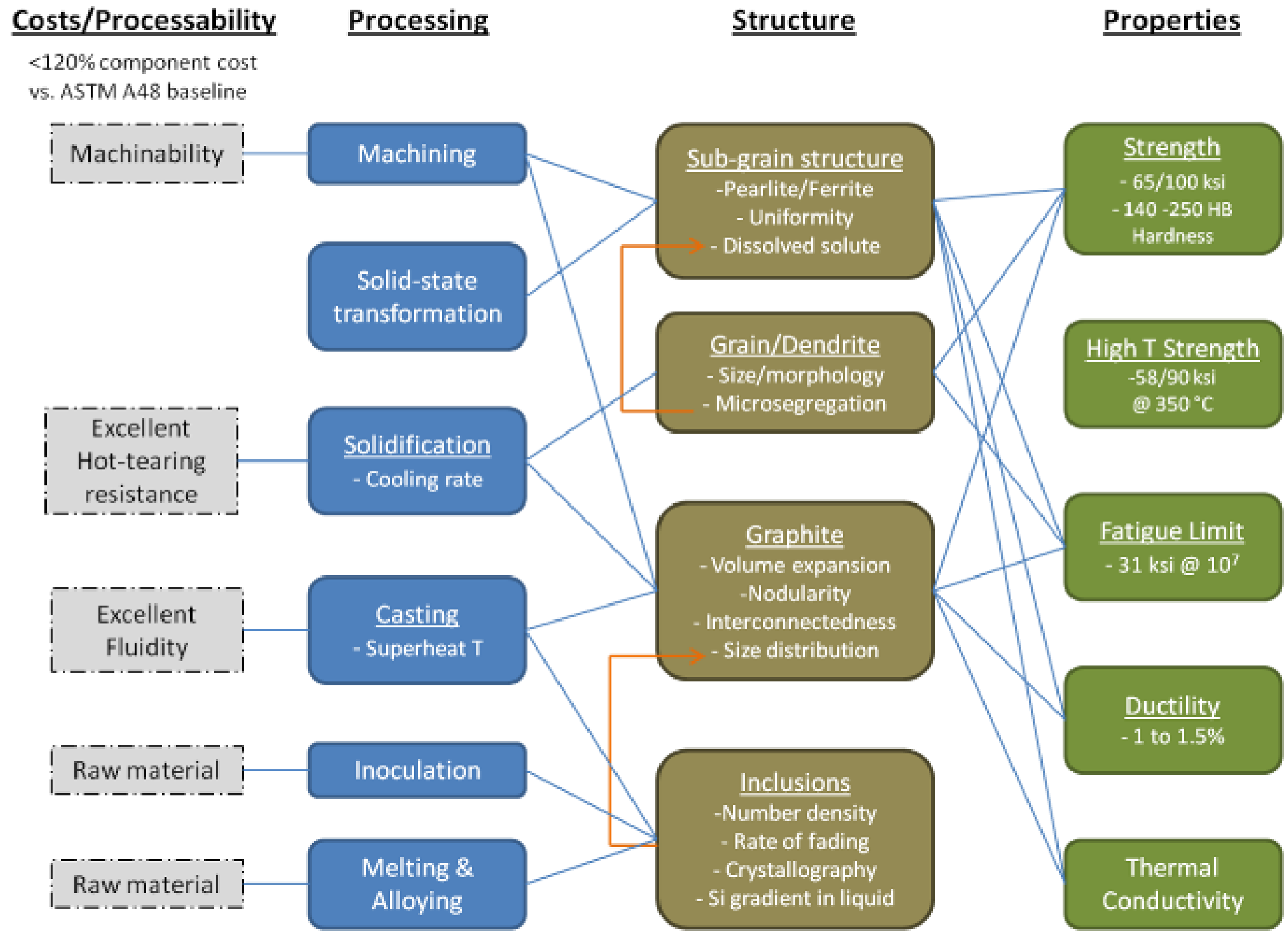
- **Room Temp.:**
  - ***pearlite*** - *provides strength and hardness*
  - ***graphite*** – *provides thermal conductivity, vibration dampening, decreases tensile & fatigue strength*

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 strength of metal matrix:
  - Pearlite refining (alloying with Cu, Mo…)
  - Ferrite strengthening (nano-precipitates)

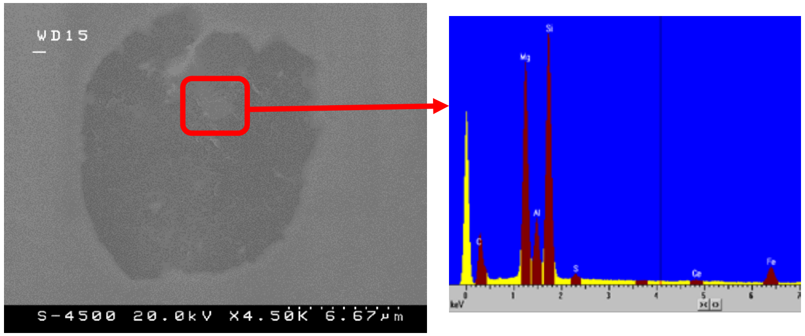
Approach

Preliminary systems-design chart for cast iron

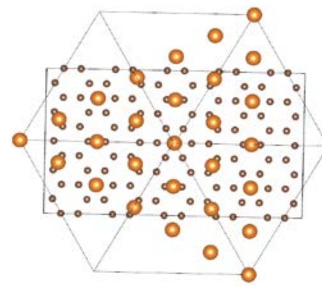


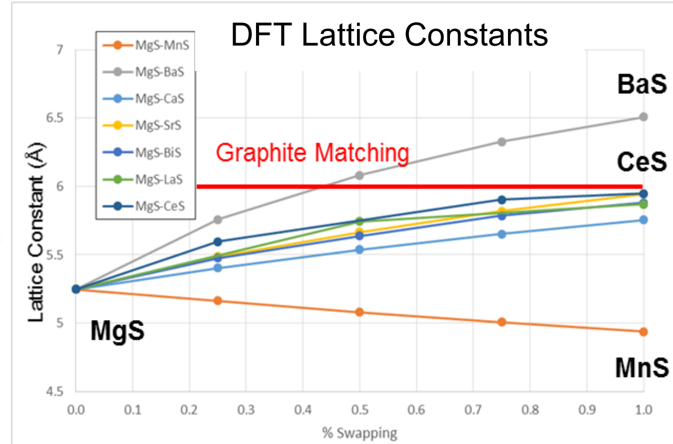
Inoculation Mechanism Determination

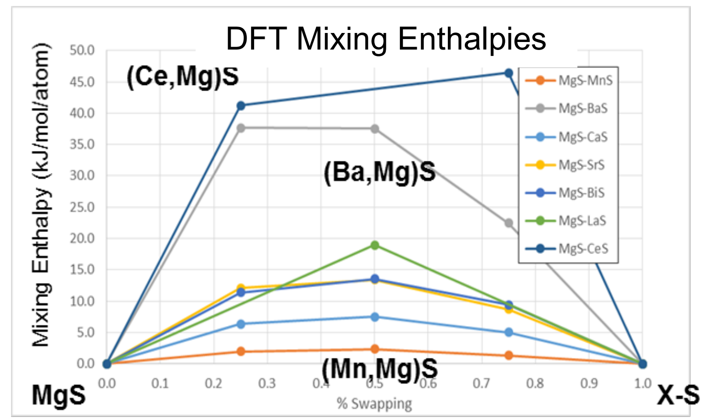
SEM/EDX Nucleant Identification



MgS / Graphite matching



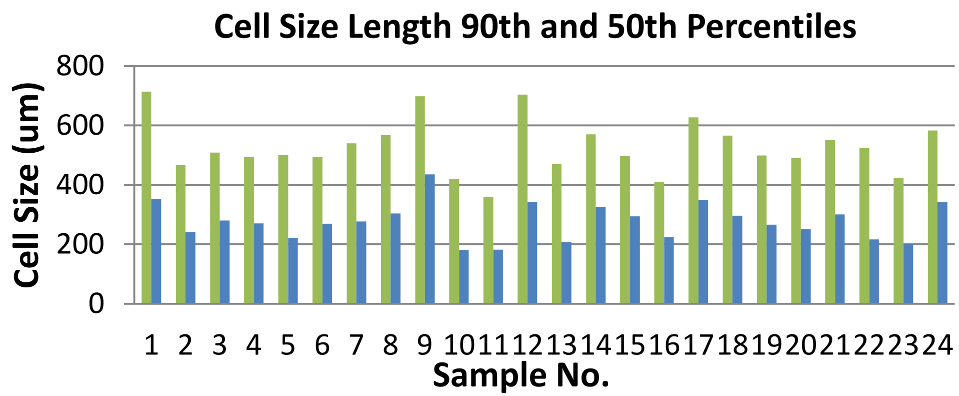


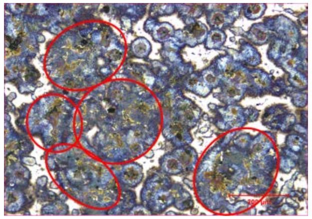


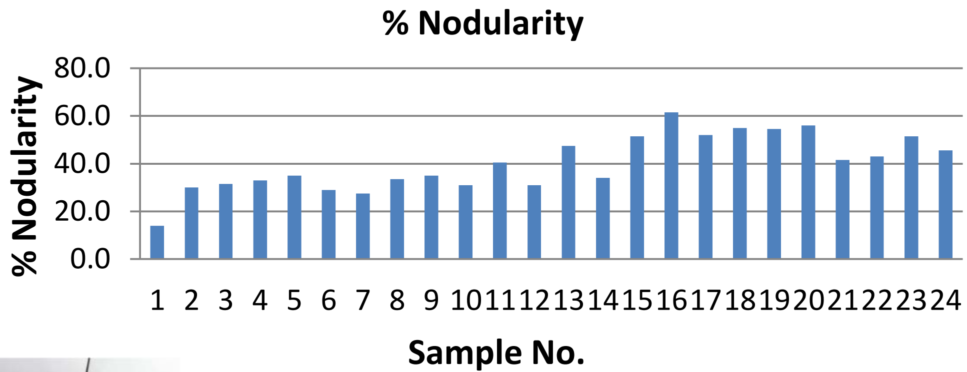
- Evidence (EDX) of sulfides as nuclei of nodules
  - No oxygen peak; Sulfur peak found (with Mg, Si, Al)
- Semi-coherent matching established (B1/Graphite)
  - Sr and rare earth elements (La, Ce) lower mismatch
- DFT calculations of mixed sulfide lattices
  - Mixing enthalpies positive: Sulfide mixing discouraged
  - CeS has best matching using DFT lattice constants
  - Rare earth sulfides lower mismatch

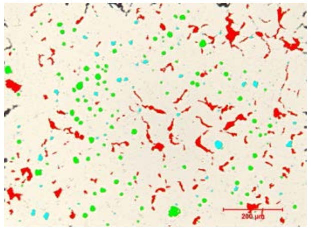
Quick Cup Inoculation DOE

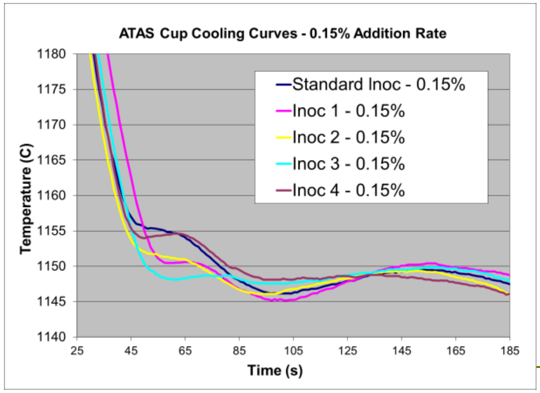
Sample #	ATAS Sample	ATAS Stand #	Ladle #	In-Stream Inoc	Rate %
1	1	1	13	Control Standard	0
				Standard Inoc	0.05
2	1	3	13	Standard Inoc	0.1
3	1	5	13	Standard Inoc	0.15
4	1	7	13	Standard Inoc	0.2
5	2	1	2	Inoc 1	0.05
6	2	3	2	Inoc 1	0.1
7	2	5	2	Inoc 1	0.15
8	2	7	2	Inoc 1	0.2
9	3	1	3	Inoc 2	0.05
10	3	3	3	Inoc 2	0.1
11	3	5	3	Inoc 2	0.15
12	3	7	3	Inoc 2	0.2
13	4	1	5	Inoc 3	0.05
14	4	3	5	Inoc 3	0.1
15	4	5	5	Inoc 3	0.15
16	4	7	5	Inoc 3	0.2
17	5	1	7	Inoc 4	0.05
18	5	3	7	Inoc 4	0.1
19	5	5	7	Inoc 4	0.15
20	5	7	7	Inoc 4	0.2
21	6	1	9	Inoc 1	0.1
22	6	3	9	Inoc 2	0.1
23	6	5	9	Inoc 3	0.1
24	6	7	9	Inoc 4	0.1

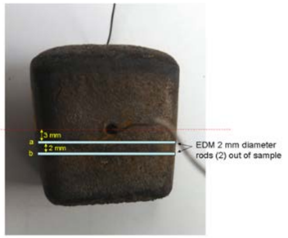






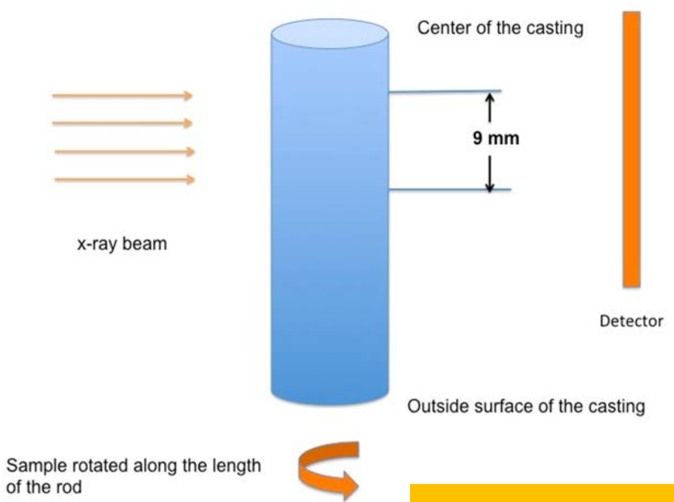


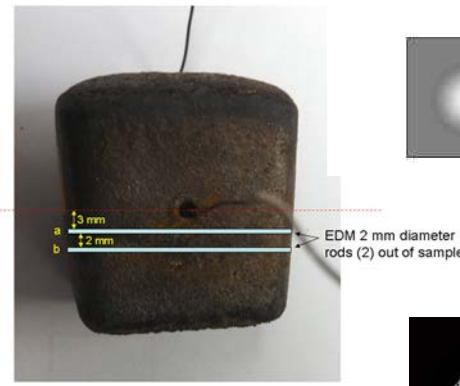


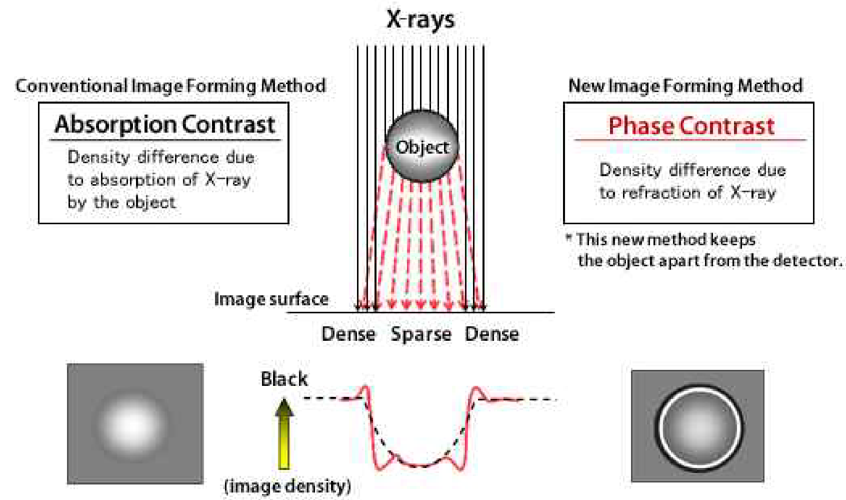


3D X-ray Tomography

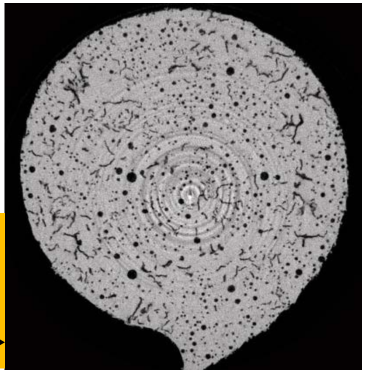
- Absorption or phase tomography
  - Full field 2D image (mm^2) of direct beam
  - Absorption contrast (near) to phase contrast (far) by changing sample-detector
  - Take image and rotate M times (M images)
  - Reconstruct ->3D volume with resolution ~ 1 µm

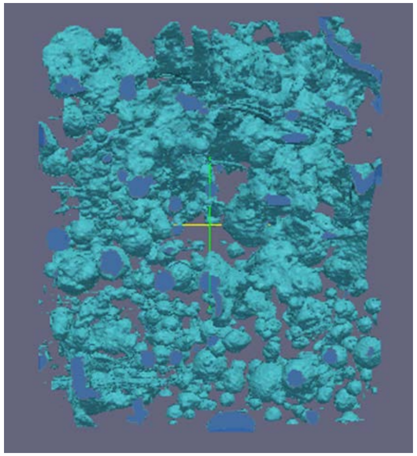




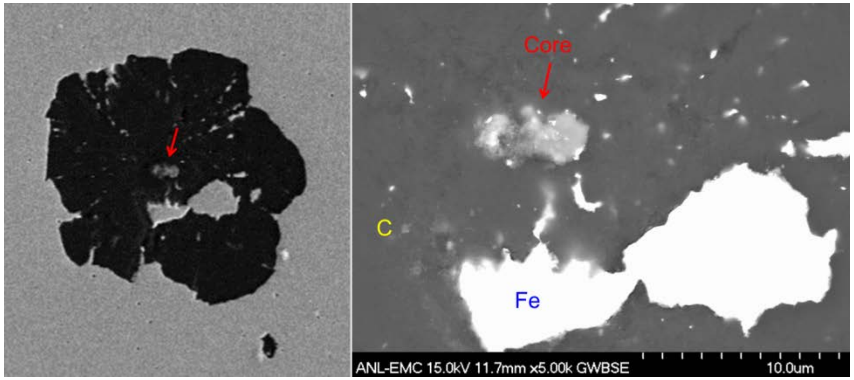


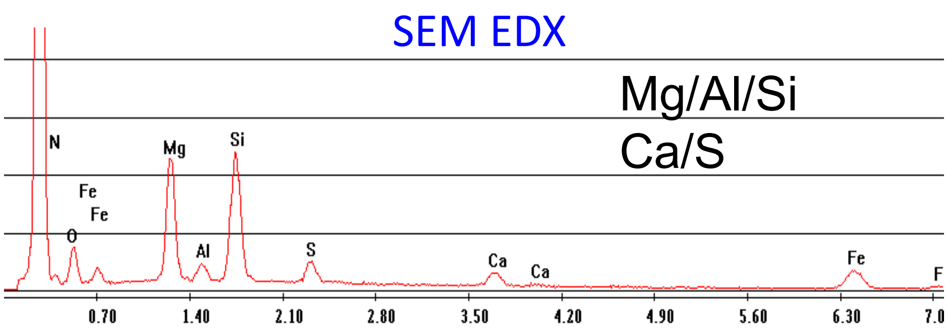
- ➢ *X-ray tomography proved capable of identifying graphite structure in iron matrix* →

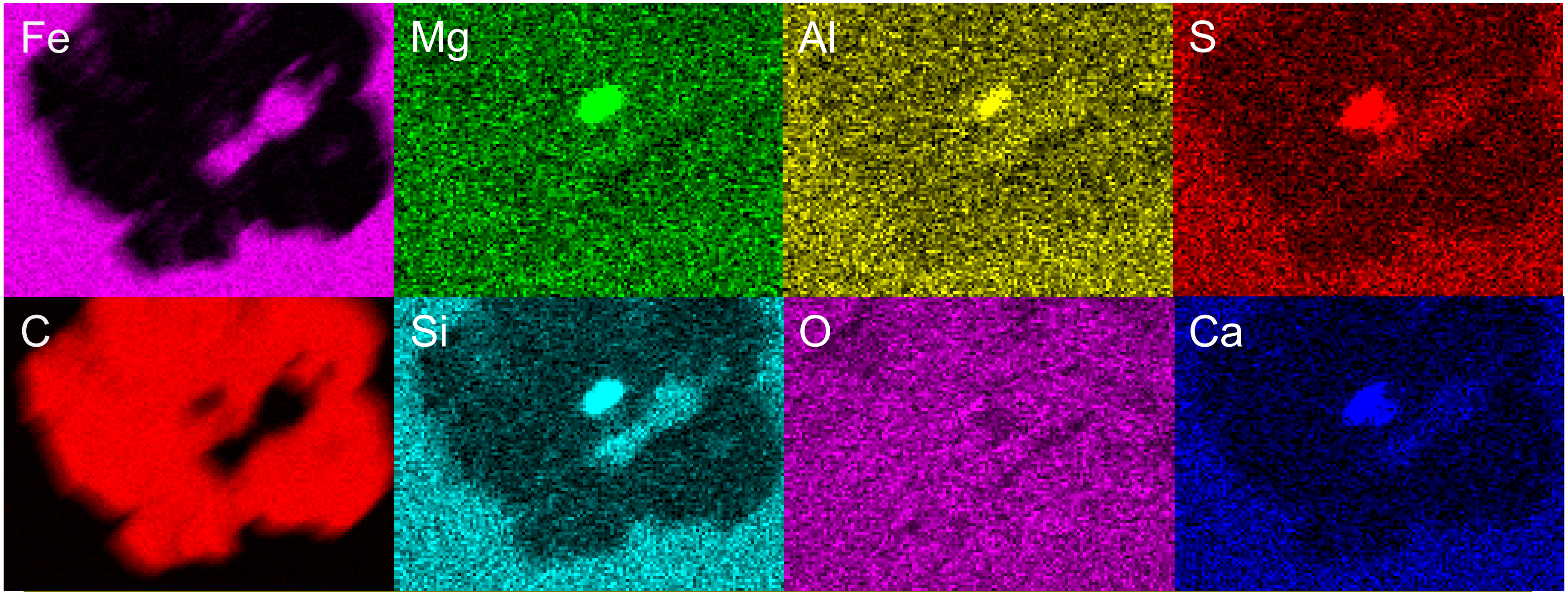




Graphite Core Chemical Analysis – SEM/EDX

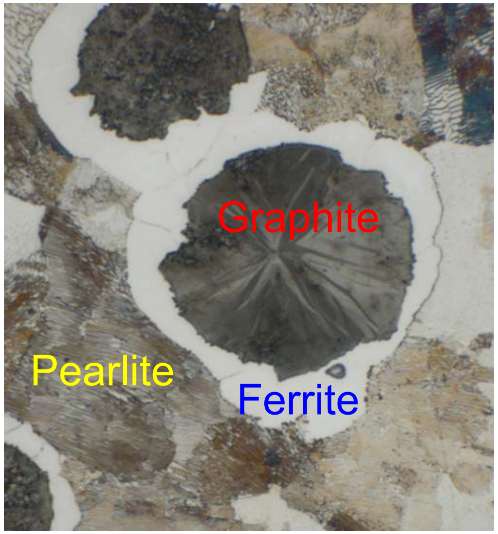




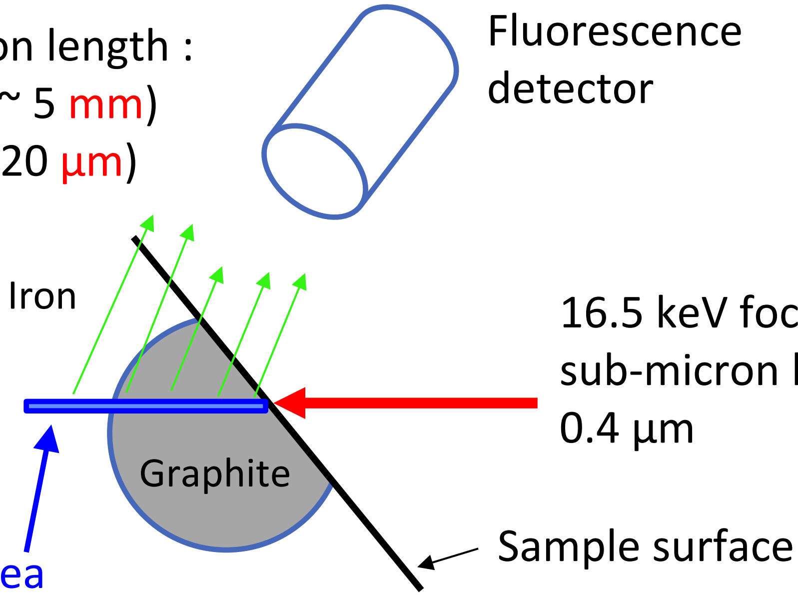


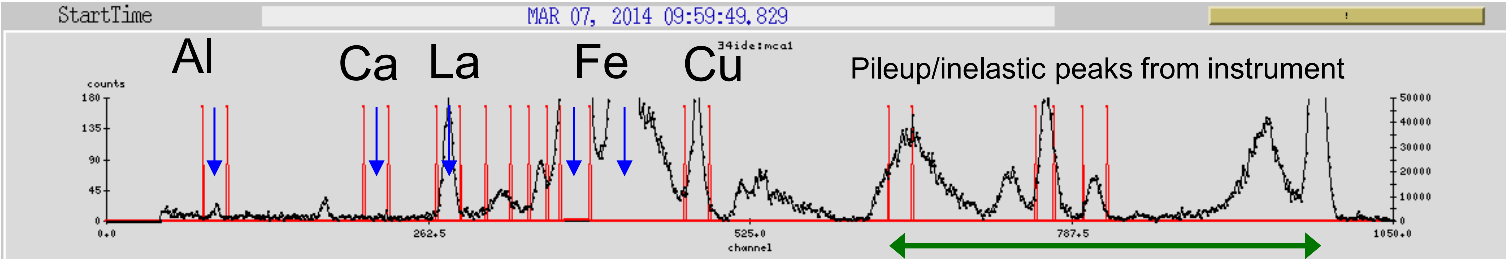
X-ray Micro-beam Fluorescence Analysis

Fluorescence analysis provide chemical information

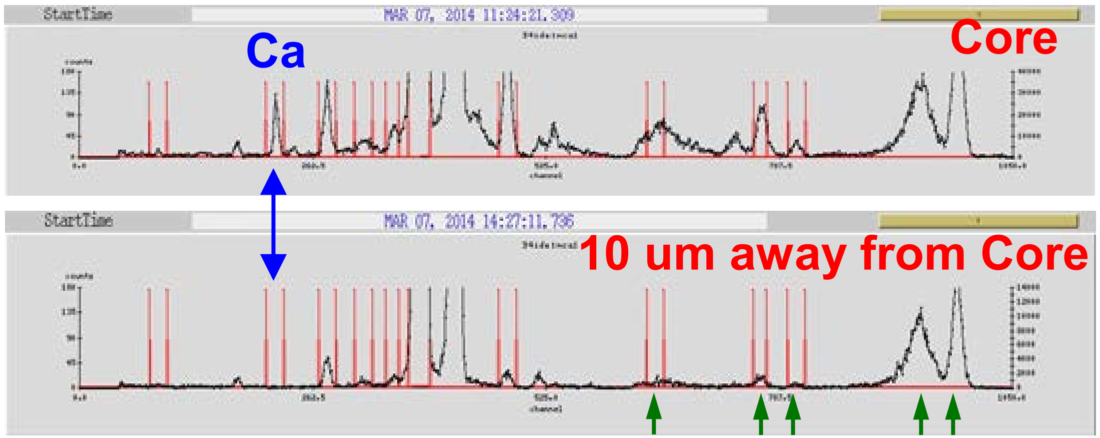


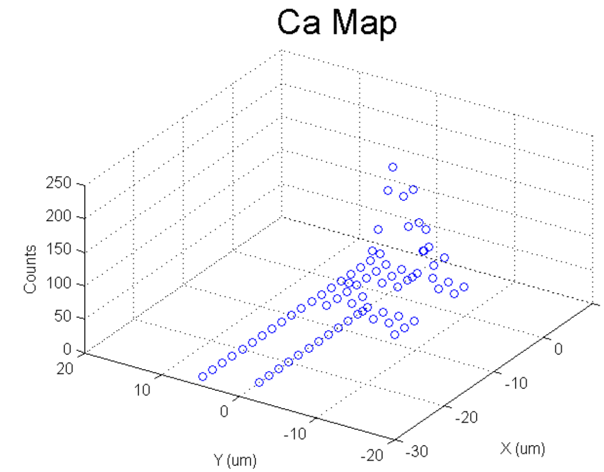
Attenuation length :
Graphite (~ 5 mm)
Iron (15 ~ 20 µm)

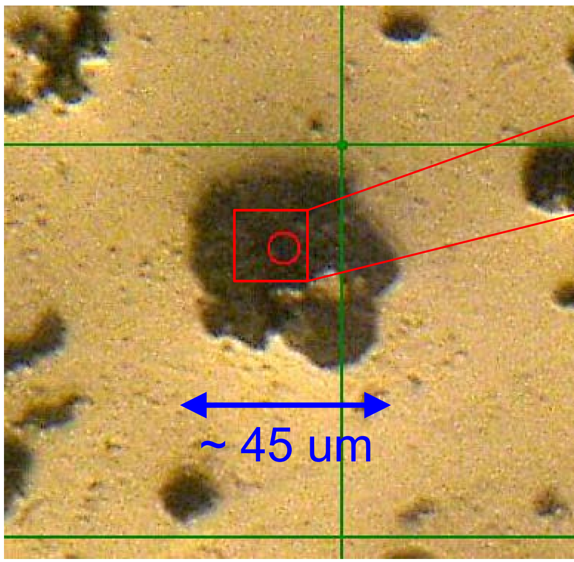


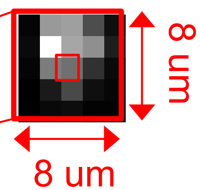


Micro-Beam Study of Graphite in Cast-Iron





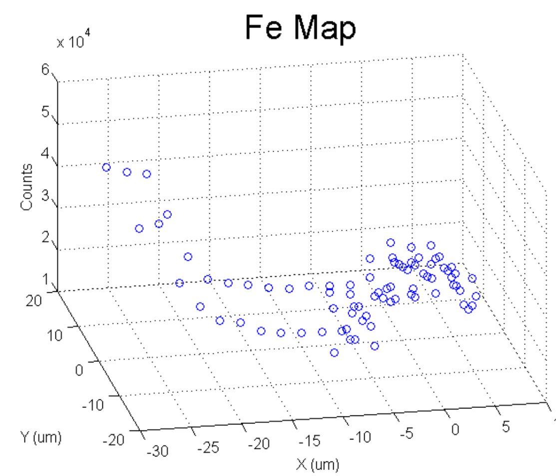




Energy:
16.5 keV

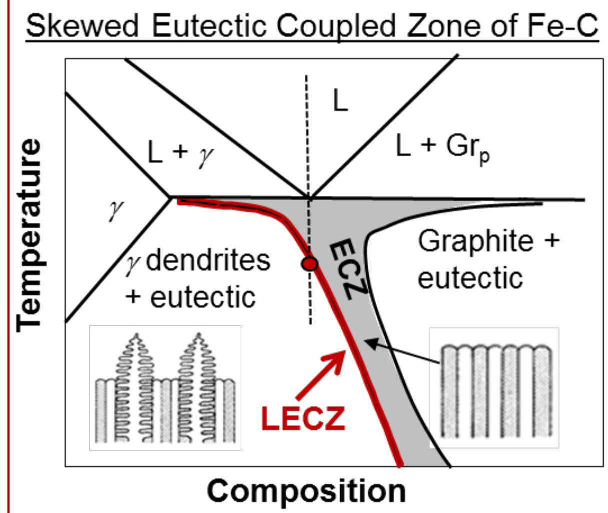
Beam size:
0.3 x 0.4 µm

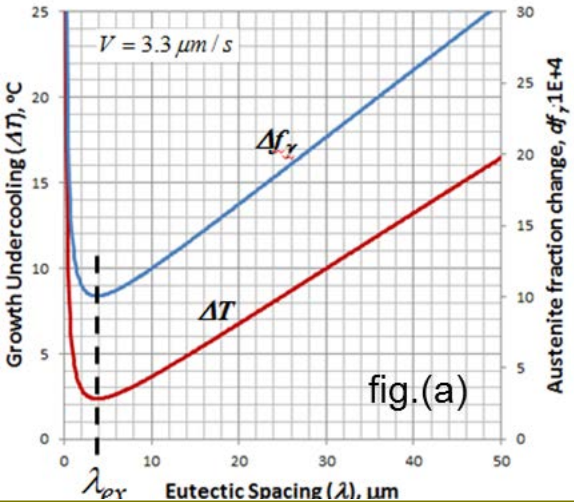
A calcium-rich core, 3 ~ 4 µm in diameter, was found at the center of a nodular graphite (~ 45 µm in diameter)

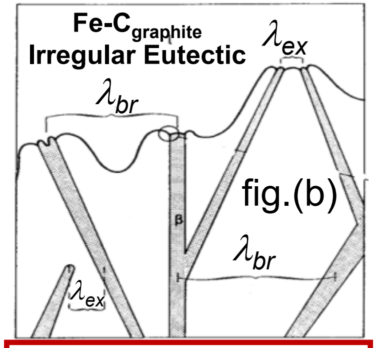


Eutectic Coupled Zone (ECZ) Solidification

- Inside the ECZ graphite and austenite grow in a cooperative manner as alternating lamellae; the graphite flake (lamella) size is comparable to that of eutectic cell size.
- Solidification outside the ECZ leads to refining of graphite flakes and increased tensile and fatigue strength of the material.
- *Developed improved theoretical model for solidification of eutectic alloys.*
- For binary Fe-$C_{graphite}$ system the model was validated against published experimental data; it was found:
  - the minimum eutectic spacing corresponds to the minimum growth undercooling (λ_{ex} in fig.(a))
  - the average growth undercooling and average lamellar spacing depend on the fraction of faceted phase (graphite) in the microstructure – fig.(b) and fig.(c)

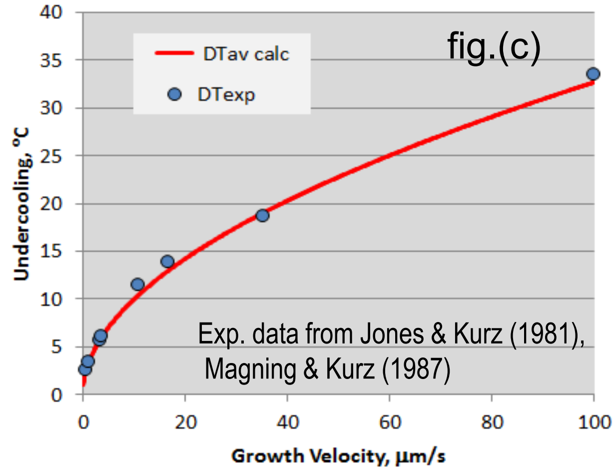






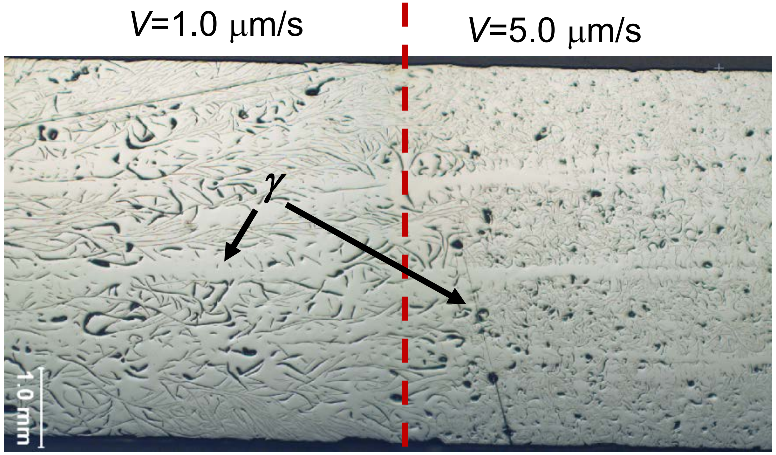
$$\lambda_{av} = \lambda_{ex} / \sqrt{f_{vol.graphite}}$$

$$\lambda_{br} = e \cdot \lambda_{av}$$



Limit of the ECZ in Fe-C Based Alloys

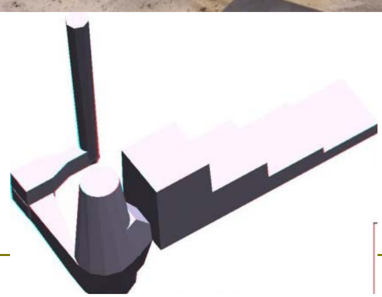
- LECZ was theoretically determined by using the *developed eutectic growth model* and the dendritic growth model available in literature (Lipton *et al*, 1984), extended to multicomponent alloys.
- For binary Fe-$C_{graphite}$ system the theoretical calculations agree well with the point of slope change of graphite lamellar spacing *vs* solidification undercooling (V_{LECZ} = 6.5 μm/s).
- Ternary Fe-3.78 wt%C-1.67wt%Si alloy (*i.e.*, slightly hypereutectic) alloy:
  - *Directional solidification experiments at solidification velocities of 1.0 μm/s and 5.0 μm/s were performed at UAB, revealing that* $V_{LECZ} < 1.0$ *μm/s.*
  - Theoretical calculations showed V_{LECZ} = 0.85 μm/s and 1.03 μm/s for values of carbon diffusion coefficient in liquid of $1.0 \cdot 10^{-9}$ m^2/s and $1.25 \cdot 10^{-9}$ m^2/s, respectively. This reveals the need for improved knowledge on the diffusion coefficients of alloying elements in liquid iron.
- Current findings:
  - Si lowers V_{LECZ} and increases the eutectic lamellar spacing as compared to binary Fe-C eutectic.
  - For the same undercooling, the solidification velocity of eutectic alloy with 1.67wt%Si is 21% higher as compared to that of binary Fe-C eutectic.
  - At solidification velocities $V > V_{LECZ}$ austenite dendrites appear in the microstructure of an alloy of eutectic or hypereutectic composition, leading to refinement of graphite lamellae. Improved mechanical properties are expected for a material exhibiting more austenite dendrites and finer graphite in the microstructure.

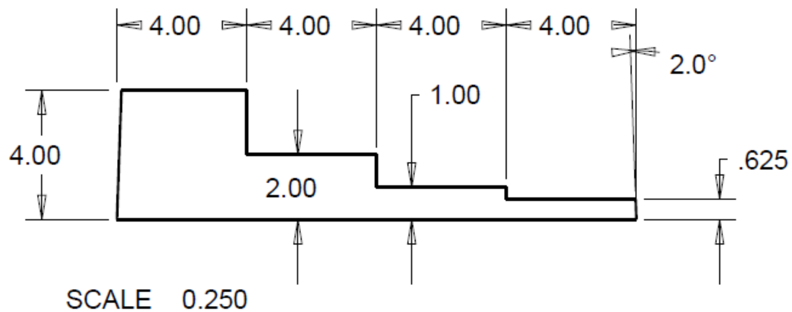


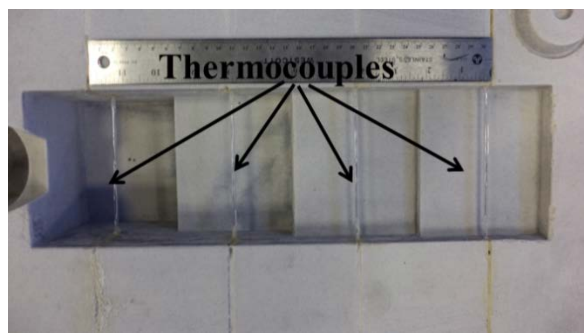
Austenite dendrites (γ) in Fe-C-Si alloy of hypereutectic composition solidified at $V > V_{LECZ}$

Casting Trials

- Scaled up casting trials being performed at UAB's experimental foundry
  - Step block geometry chosen for test casting to provide a range of solidification rates



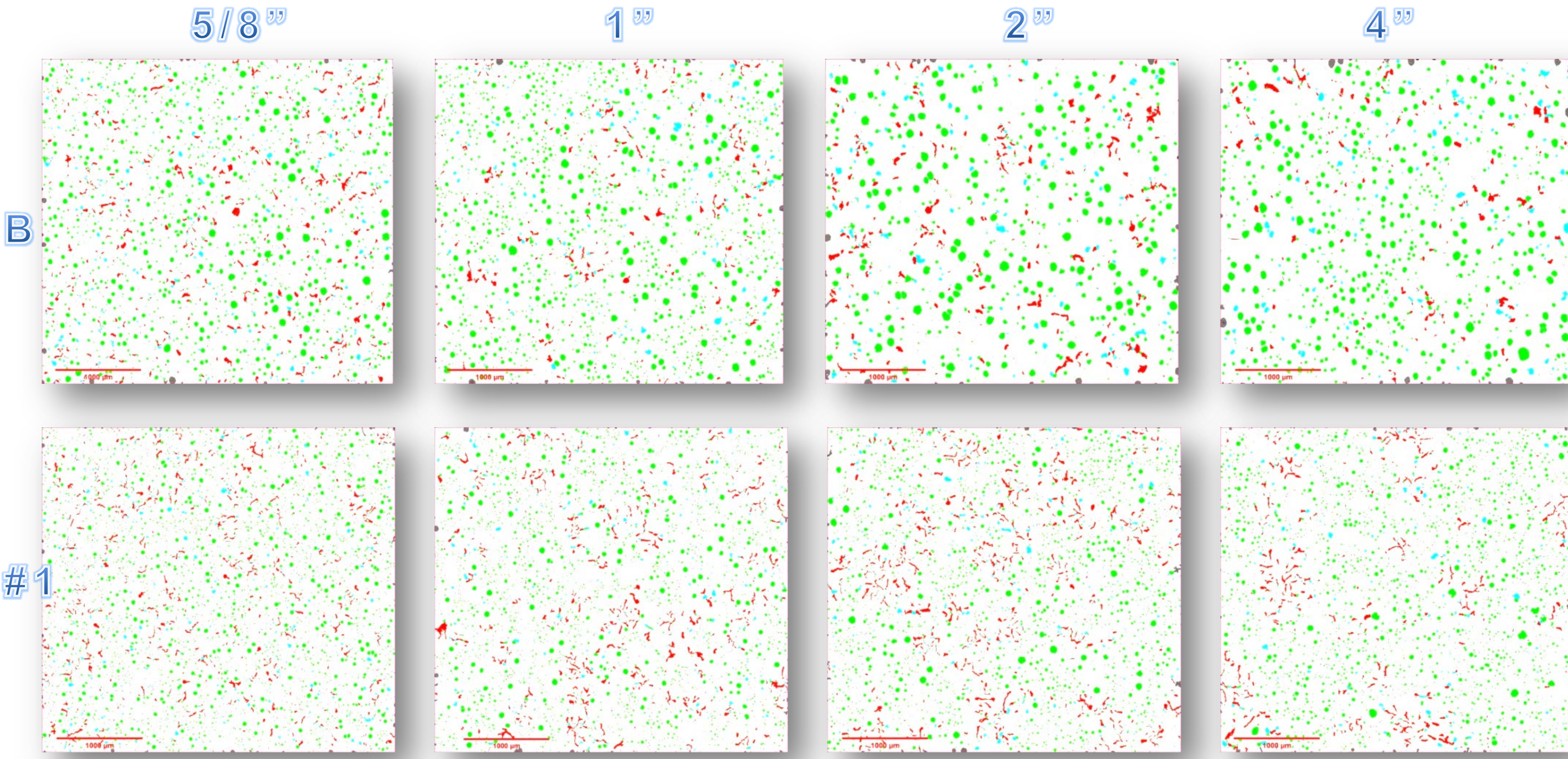




Thermocouples placed within a glass tube inside the mold

Set up for in-stream post inoculant addition

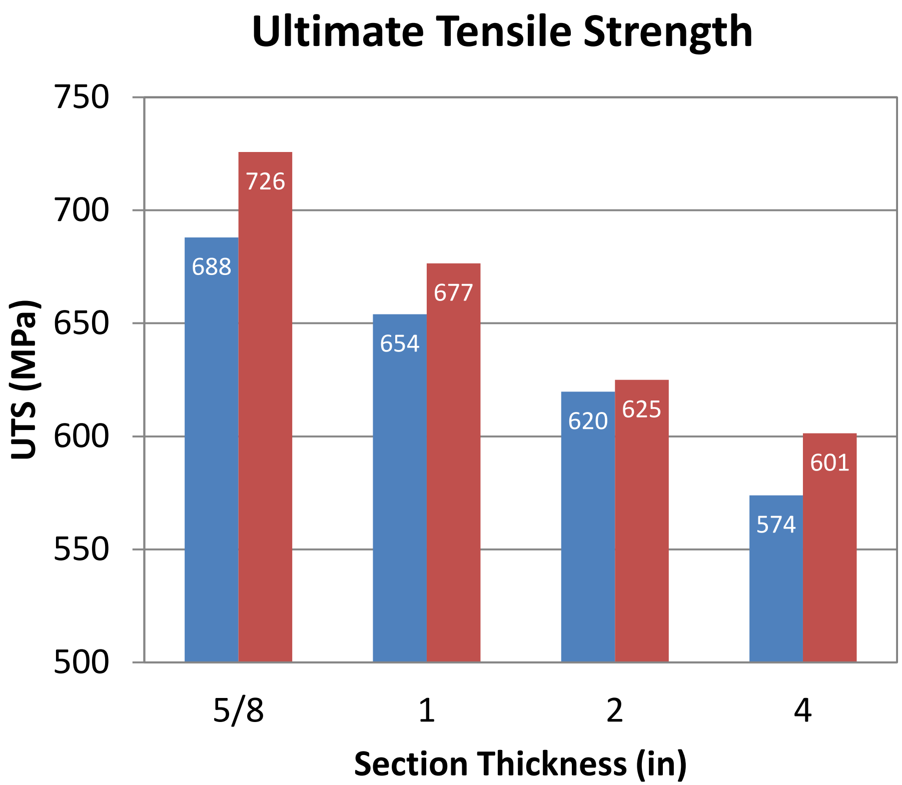
Casting Trials – Example Graphite Structure

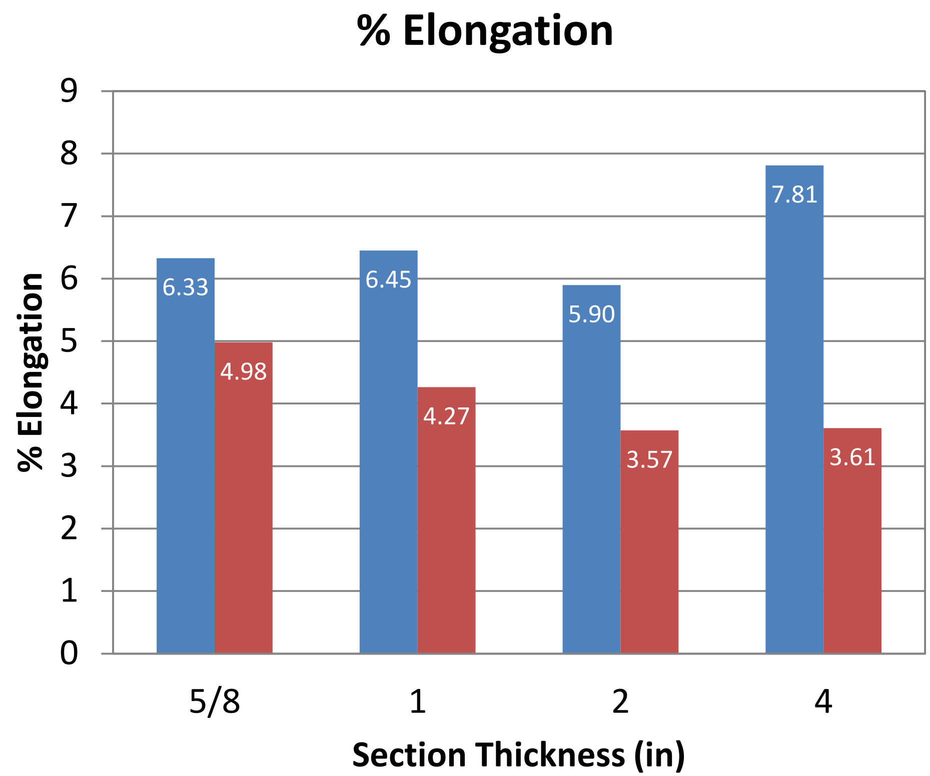


B – Baseline Casting – No Post-Inoculant

#1 – Post-Inoculant 1

Casting Trials – Example Properties



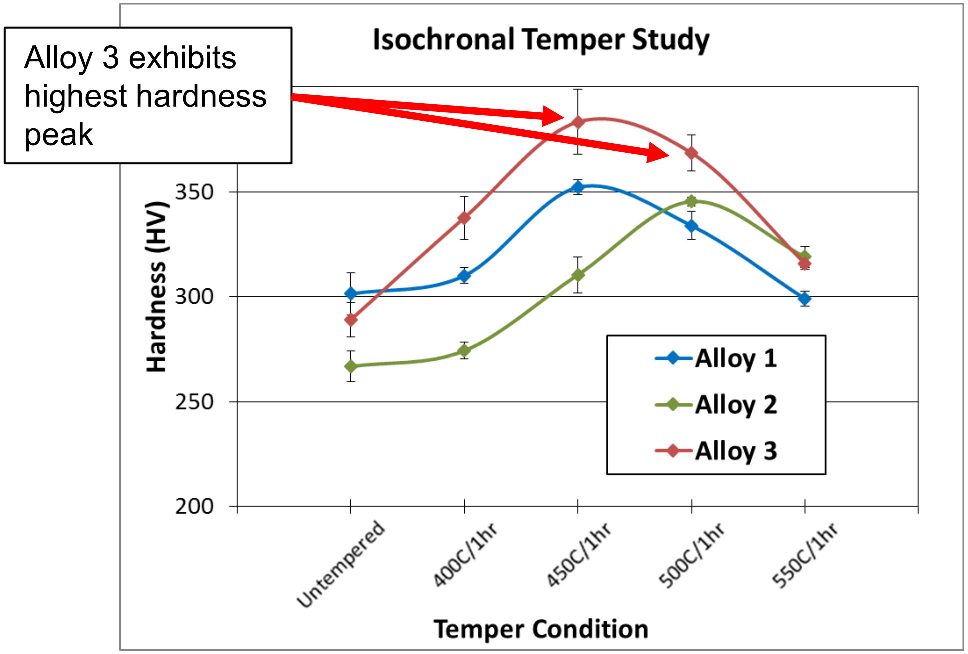


Baseline – No Post-Inoculant

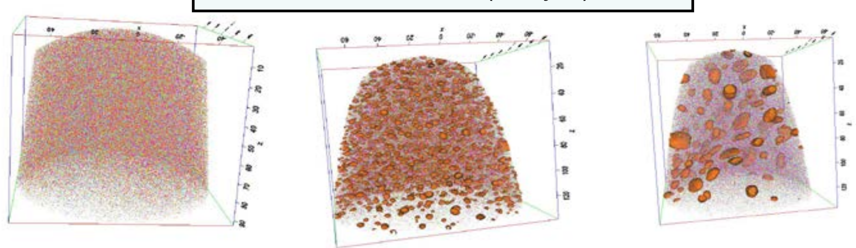
Post-Inoculant #1

Pearlite (Ferrite) Nano-precipitation Strengthening

- Strengthen pearlitic matrix during stress relief 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



LEAP Results (Alloy 1)



As homogenized | Peak hardness | Over-aged

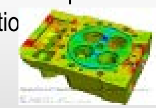
Response to Reviewers Comments

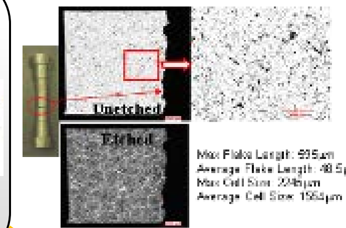
- Program not reviewed last year

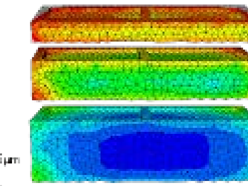
Collaboration – Project Team

Project Lead →

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

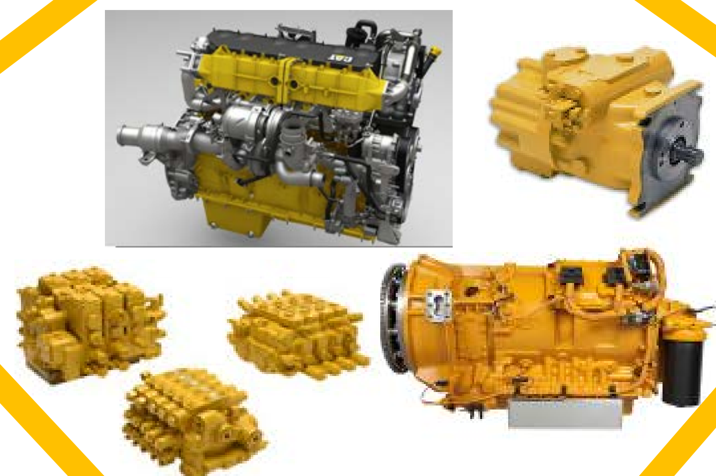




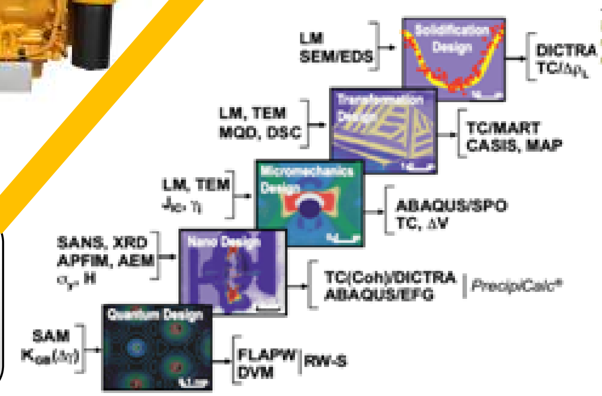


215 – 300 MPa

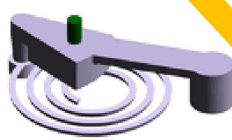
Argonne NATIONAL LABORATORY
- Material Evaluation using Advanced Photon Source (APS) X-Ray and MTS Testing Machine
- In-Situ Microstructure and Damage Measurements



QuesTek INNOVATIONS LLC
- Computational Material Design
- Solidification Design
- Transformation Design
- Nano Design
- Material Characterization



Addition Support:
- Northwestern University
  - Dr. P. Voorhees
  - Dr. C. Wolverton
- Bradley University
  - GI Fatigue Testing



Fluidity Spiral Test Casting

UAB THE UNIVERSITY OF ALABAMA AT BIRMINGHAM
- Experimental Casting Material Samples
- Liquid Metal Fluidity Evaluation
- Hot Tear Resistance

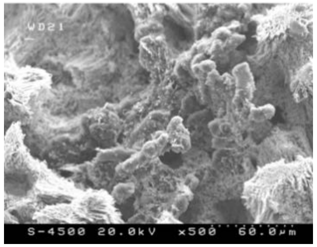
Remaining Challenges and Barriers

- Nucleation and growth of austenite + graphite is not completely understood.
  - There could be a theoretical limit to the nucleation density possible and the resulting microstructure refinement
  - Level of control of the eutectic growth that is attainable through control of alloying and casting conditions has not been quantified
- Material design that meets the mechanical properties targets while simultaneously satisfying thermal conductivity and manufacturing cost requirements has not been achieved.
  - Can mechanical properties be achieved with a vermicular graphite morphology?
- Satisfactory ICME tools for the fundamental material modeling to design cast iron alloys are not available.

Future Steps

- Nucleation
  - FIB + SEM serial sectioning of deep etched graphite (see figure on right) structures to identify nucleants
  - Graphite core structure identification by X-ray micro-beam fluorescence to identify potential nucleant locations in complex vermicular shaped graphite
  - X-ray *in-situ* cast iron solidification experiments
  - Refine precipitation models of strengthening phases and inoculants
    - Graphite/austenite precipitation modeling
    - DFT calculations of inoculant/graphite interfacial energies
- Growth
  - Perform directional solidification experiments at various solidification velocities and levels of alloying elements (Si, Mn, Cu, Al, etc.)
    - Quantitative evaluation on the influence of alloying elements and solidification conditions on the length scales of developing microstructure
  - Fine tune the theoretical model for calculating LECZ

Deep-etched Vermicular Graphite



Future Steps

- Casting Trials
  - Continue step block casting trials to evaluate concepts to refine the microstructure, control the graphite morphology and strengthen the matrix
    - Post-inoculant studies to refine the austenite and eutectic nucleation and control the graphite morphology
    - CGI DOE to investigate the effects of carbon equivalent and alloying elements on microstructure and mechanical properties
    - DOE on high-thermal conductivity DI
    - Casting process methods to achieve desired solidification rates in actual castings
- Precipitation Strengthening
  - Further isochronal/isothermal studies + LEAP to identify strengthening precipitates (Alloy 3)
  - Evaluate hardening potential of nano-precipitation strengthened alloys in pearlitic microstructure
    - Evaluate quench suppressibility

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
  - Increased mechanical properties will allow the mass of heavy-duty engines to be reduced, which will improve fuel-economy at the vehicle level
- FY13-14 focused on identifying and modeling the critical mechanisms governing the microstructure development during cast iron solidification
  - X-ray methods established to reveal complex 3-D graphite network in cast irons and identify the composition to locate potential nucleants in complex graphite shapes.
  - Progress made on modeling the nucleation potency (lattice disregistry and interfacial energies) of inoculants.
  - Eutectic Coupled Zone (ECZ) solidification model extended to multi-component alloys for use with high strength iron alloy compositions.
  - Experimental foundry upgraded to 500 lb. heat capacity. Ramping up step block casting experiments for inoculation and alloying experiments.
  - Alloys have been identified that show a precipitation strengthening effect in the target temperature ranges

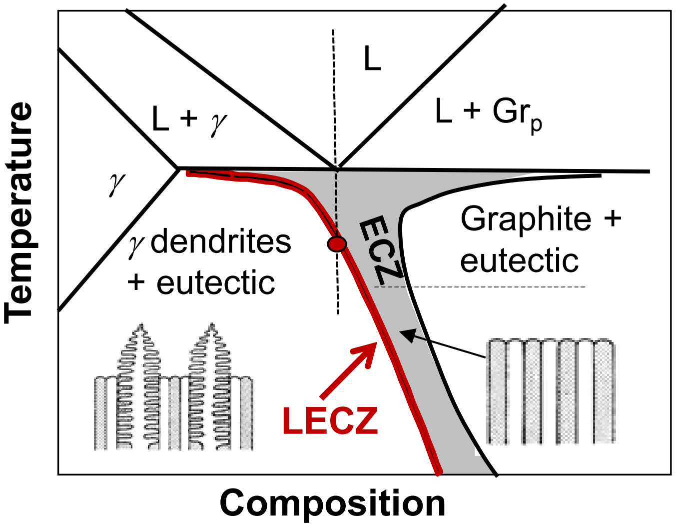
Technical Back-up Slides

Improved Mechanical Properties by Solidification at The Limit of Eutectic Coupled Zone (LECZ)

➢Background on Eutectic Coupled Zone (ECZ)

- Cast Iron solidifies with an irregular eutectic microstructure and exhibits a skewed ECZ
- Inside the ECZ graphite and austenite grow in a cooperative manner as alternating lamellae; the graphite flake (lamella) size is comparable to that of eutectic cell size
- In certain solidification conditions, an alloy of eutectic or slightly hypereutectic chemistry can solidify outside the ECZ with austenite dendrites + eutectic microstructure; this is because the skewedness of ECZ
- Solidification outside the ECZ leads to refining of graphite flakes (*i.e.*, shorter length) and increased tensile and fatigue strength of the material
- Determining the limit of ECZ will allow selecting and imposing the solidification conditions leading to refined microstructure and improved mechanical properties of the material

Skewed Eutectic Coupled Zone of Fe-C



➢ Objectives

- Determine LECZ of the alloy by means of theoretical modeling (dendritic and eutectic growth)
- Improve on eutectic growth theory to account for multicomponent alloys and irregular microstructure of cast iron
- Validate theoretical developments against directional solidification experiments
- Validate the concept on test castings solidified inside and outside the ECZ
- Application of LECZ approach to cast engine components

Eutectic Solidification Model for Multicomponent Fe-C Based Alloys

- Developed improved theoretical model for solidification of eutectic alloys accounting for:
  - multicomponent alloys
  - irregular eutectic microstructure in cast iron
  - density difference between phases in microstructure
  - phase fraction change with respect to solidification conditions (*e.g.*, undercooling temperature or imposed solidification velocity) – fig.(a)
- For binary Fe-$C_{graphite}$ system the model was validated against published experimental data the minimum eutectic spacing corresponds to the minimum growth undercooling (λ_{ex} in fig.(a))
  - the average growth undercooling and average lamellar spacing depend on the fraction of faceted phase (graphite) in the microstructure – fig.(b) and fig.(c); the same relationships also hold for Fe-Fe_3C and Al-Si irregular eutectics
- Validation for multicomponent alloys is currently underway

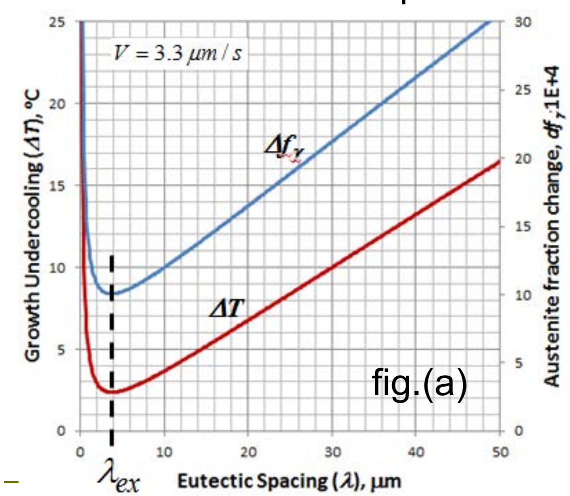


fig.(a)

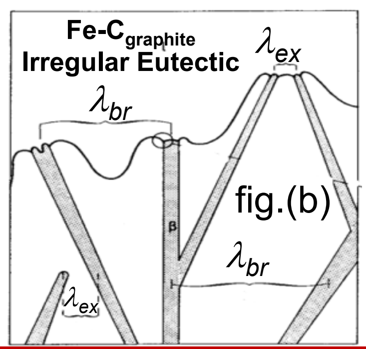


fig.(b)

$$\lambda_{av} = \lambda_{ex} / \sqrt{f_{vol.graphite}}$$
$$\lambda_{br} = e \cdot \lambda_{av}$$

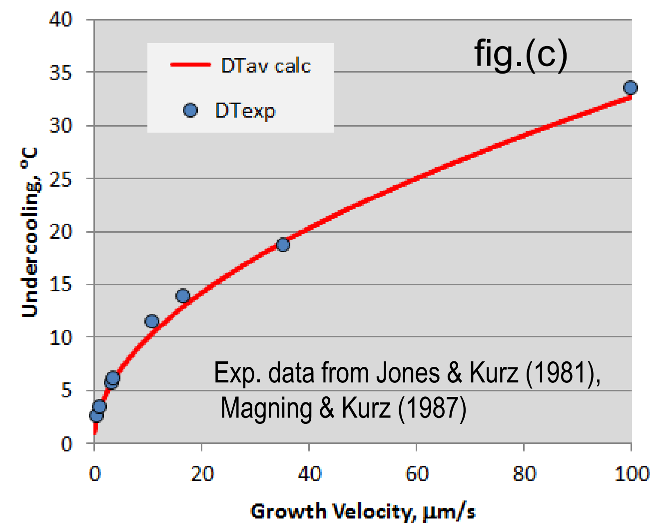
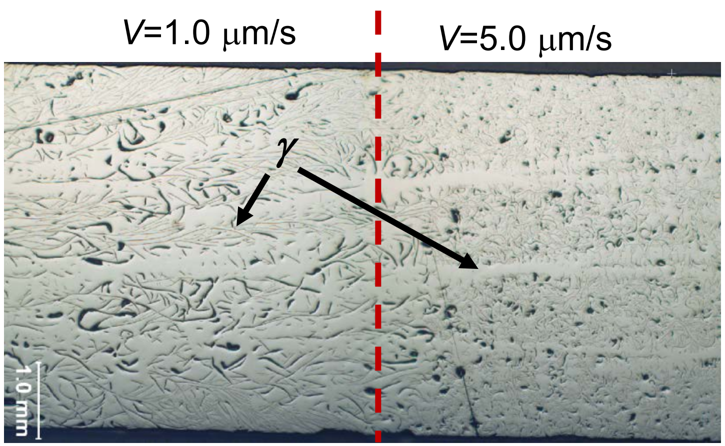


fig.(c)

Technical Accomplishment: Limit of Eutectic Coupled Zone in Fe-C Based Alloys

- LECZ was theoretically determined by using the developed eutectic growth model and the dendritic growth model available in literature (Lipton *et al*, 1984) which was extended to multicomponent alloys
- For binary Fe-$C_{graphite}$ system the theoretical calculations agree well with the point of slope change of graphite lamellar spacing *vs* solidification undercooling (V_{LECZ} = 6.5 μm/s)
- Ternary Fe-3.78 wt%C-1.67wt%Si alloy (*i.e.*, slightly hypereutectic) alloy:
  - Directional solidification experiments, at solidification velocities of 1.0 μm/s and 5.0 μm/s, revealed that V_{LECZ} < 1.0 μm/s
  - theoretical calculations showed V_{LECZ} = 0.85 μm/s and 1.03 μm/s for values of carbon diffusion coefficient in liquid of $1.0 \cdot 10^{-9}$ m^2/s and $1.25 \cdot 10^{-9}$ m^2/s, respectively. This reveals the need for improved knowledge on the diffusion coefficients of alloying elements in liquid iron
- Current findings:
  - Si lowers V_{LECZ} and increases the eutectic lamellar spacing as compared to binary Fe-C eutectic
  - for the same undercooling, the solidification velocity of eutectic alloy with 1.67wt%Si is 21% higher as compared to that of binary Fe-C eutectic
  - at solidification velocities $V > V_{LECZ}$ austenite dendrites appear in the microstructure of an alloy of eutectic or hypereutectic composition also leading to refinement of graphite lamellae. Improved mechanical properties (tensile & fatigue strength) are expected for a material exhibiting more austenite dendrites and finer graphite in the microstructure



Austenite dendrites (γ) in Fe-C-Si alloy of hypereutectic composition solidified at $V > V_{LECZ}$