Enhanced Quality in Electric Melt Grey Cast Irons

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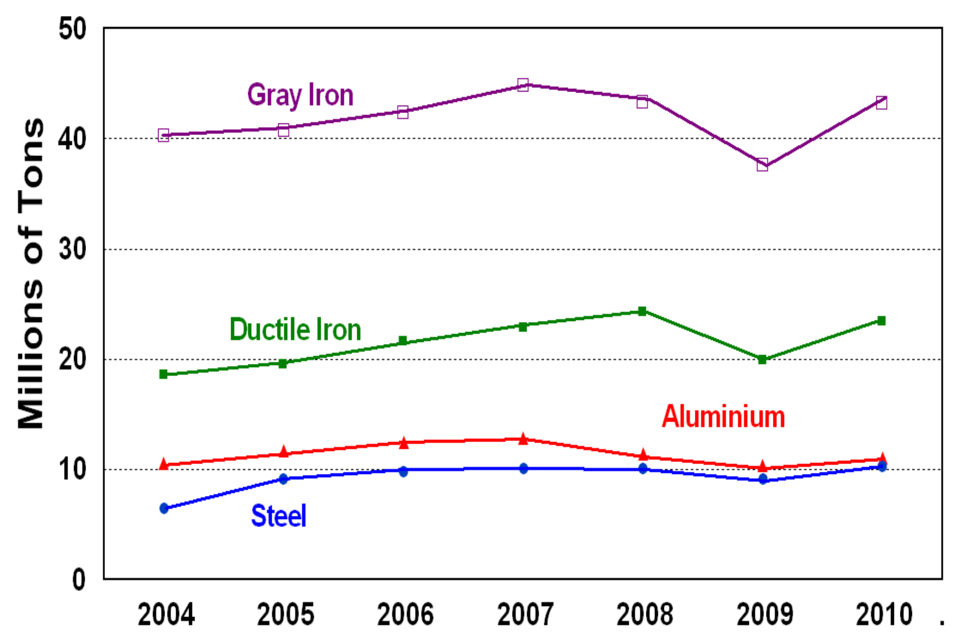
OUTLINE

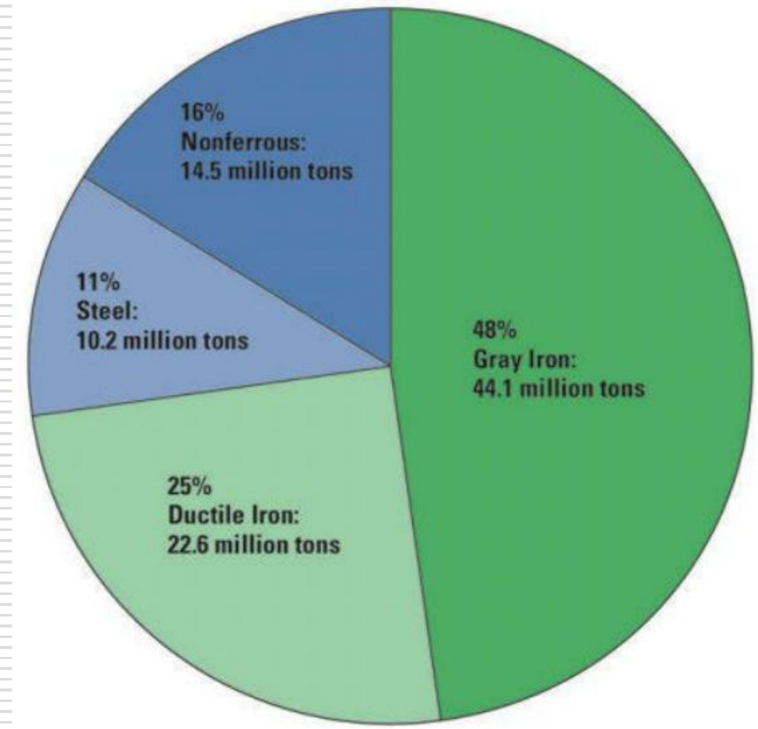
- **INTRODUCTION**
  - *Grey Iron: 48% of World Metalcasting Production
  - *Important Changes in Grey Iron Melting Technologies
- **HETEROGENEOUS GRAPHITE NUCLEATION IN GREY IRONS**
  - *Three – Stage Model of Graphite Nucleation in Grey Iron
- **LOW S / Al, SUPERHEATED GREY CAST IRONS**
  - *High Eutectic Undercooling and Chill Tendency
- **METALLURGICAL TREATMENT OF ELECTRIC MELT IRONS**
  - *Pre-treatment of the Iron Melt in a Melting Furnace
    - Carbon Material / Metallurgical Silicon Carbide / Aluminium
  - *Double Treatments [preconditioning + inoculation]
    - Al preconditioning + Ca-FeSi inoculation
    - Zr preconditioning + Sr-FeSi inoculation
    - Al,Zr,Ca-FeSi preconditioning + Ca,Ba-FeSi inoculation
- **RECOMMENDATIONS FOR FOUNDRY APPLICATION**

FOUNDRY METALLIC MATERIALS EVOLUTION WORLDWIDE

Grey Iron – The largest contributing material to global production



2010 World Casting Production



[*Modern Casting* – Census of World Casting Production, 2004 – 2010]

❖ IMPORTANT CHANGES IN GREY IRONS PRODUCTION

➢ Historically: Cupola Melted Irons

*** > 0.5%Mn, > 0.05%S, > 0.005%Al, (%Mn) x (%S) > 0.03**

* favourable conditions for MnS – type compounds

- major nucleation sites for flake graphite / low chill tendency

➢ Small or/and inefficient Cupolas – replaced by a new generation of Coreless Induction Furnaces

[200 – 1000 Hz, > 250 kW/t, acid lined]

* High melting rate, no heel, steel charge, stirring, > 1500°C

*** > 0.5%Mn, < 0.05%S, < 0.005%Al, (%Mn) x (%S) < 0.03**

- high chill / undercooled graphite tendency

➢ Grey, Ductile & Compacted Graphite Irons Production in the same Foundry

* Advantage : a single Low S Base Iron, single Inoculant, > 1500°C

*** < 0.5%Mn, < 0.03%S, < 0.005%Al, (%Mn) x (%S) < 0.02**

- the highest chill / undercooled graphite

[M. Chisamera, S. Stan, I. Riposan G. Costache, M. Barstow – *112 AFS Casting Congr.*, 2008, Atlanta, USA]

The main objective of the present paper

- **To explore what conditions are needed to improve the quality of electric melt grey iron**

  - superheated in acid lined, medium frequency coreless induction furnaces,
    - especially for thin wall iron castings production [automotive industry]

- **A review of original data obtained by the authors,** *relating to*
  - heterogeneous graphite nucleation model in commercial grey irons, ***and***
  - specific solidification pattern of low S - irons,

- **Examines how superheating affects the iron quality** *and*
  - which metallurgical treatments are effective.

I. HETEROGENEOUS GRAPHITE NUCLEATION IN COMMERCIAL GREY CAST IRONS

- **Only when liquid iron undercools sufficiently (200 - 230°C),**
  - can the smaller sizes of micro cluster $(C_6)n$ exist
    - as stable homogeneous nuclei for graphite particles.

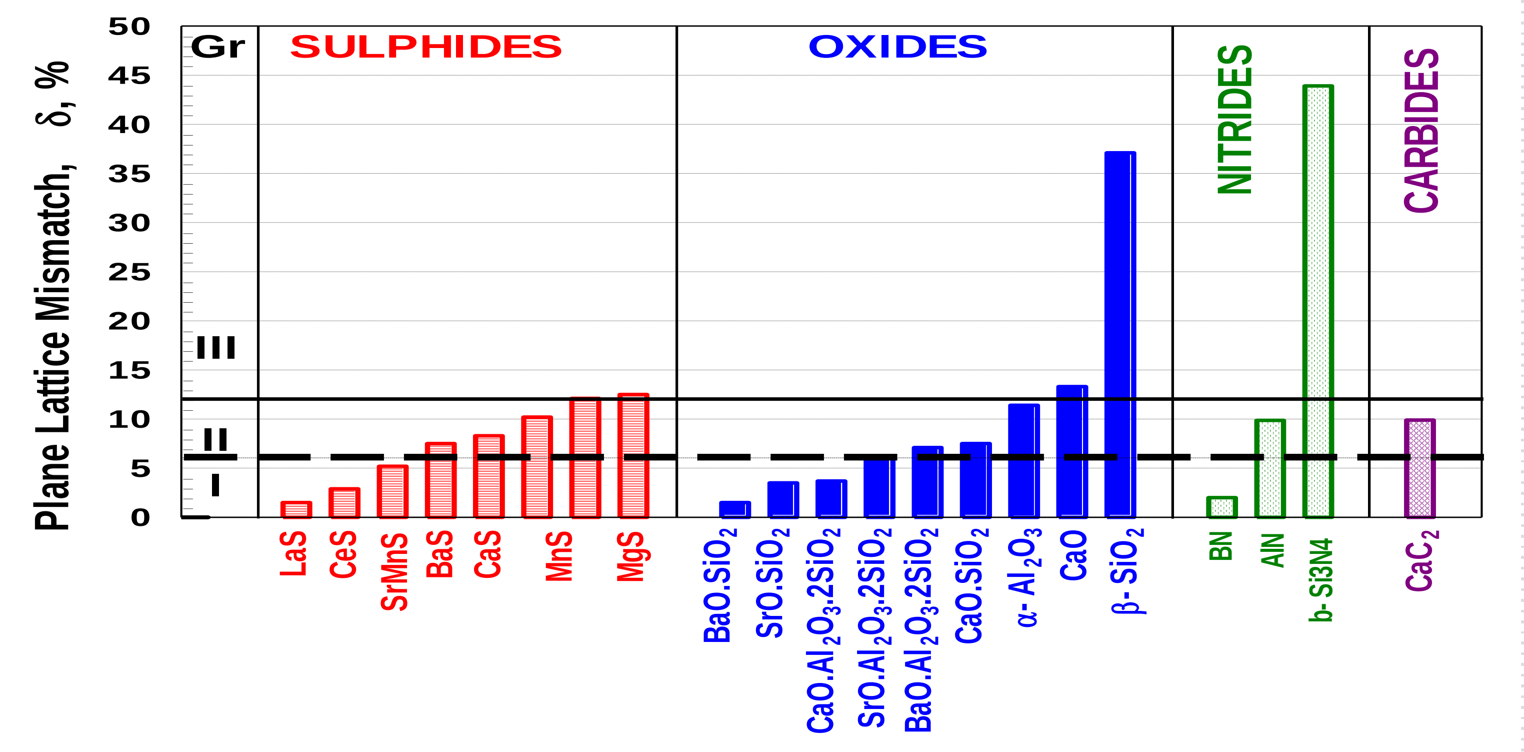
- **Under normal cond., such high undercooling is difficult to achieve**
  - therefore, the nucleation of graphite is mainly by heterogeneous nucleation:
    - residual graphite particles *and / or* non-metallic microinclusions

- **High Residual Graphite dissolution in the base iron, *especially for***
  - Low-S (<0.05%S), High superheating (>1500°C) irons, *typically for*
    - electric melting, new generation medium frequency induction furnaces

- **Practically, only existed *or / and* newly formed micro-inclusions act as graphite nuclei in commercial grey irons, *depending on***
  - melting practice, iron chemistry, molten iron treatments, solidification
  - thermodynamic conditions of compounds formation, *and*
  - lattice parameters difference compound - graphite [δ, %]

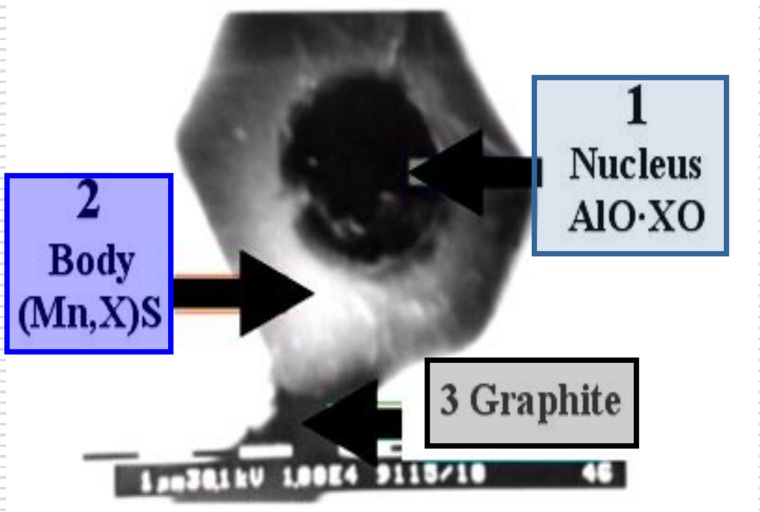
Mismatch (δ, %) between a special lattice face of Nucleants and (0001) face of Graphite

I - δ < 6% has the strongest nucleation ability
II - δ = 6 -12% has nucleation ability
III - δ > 12% has a weak nucleation ability



[I. Riposan – 115th *AFS Casting Congress*, Schaumburg, USA, 2011, Panel Paper 11-131]

A three-stage model for the nucleation of graphite in grey iron is proposed



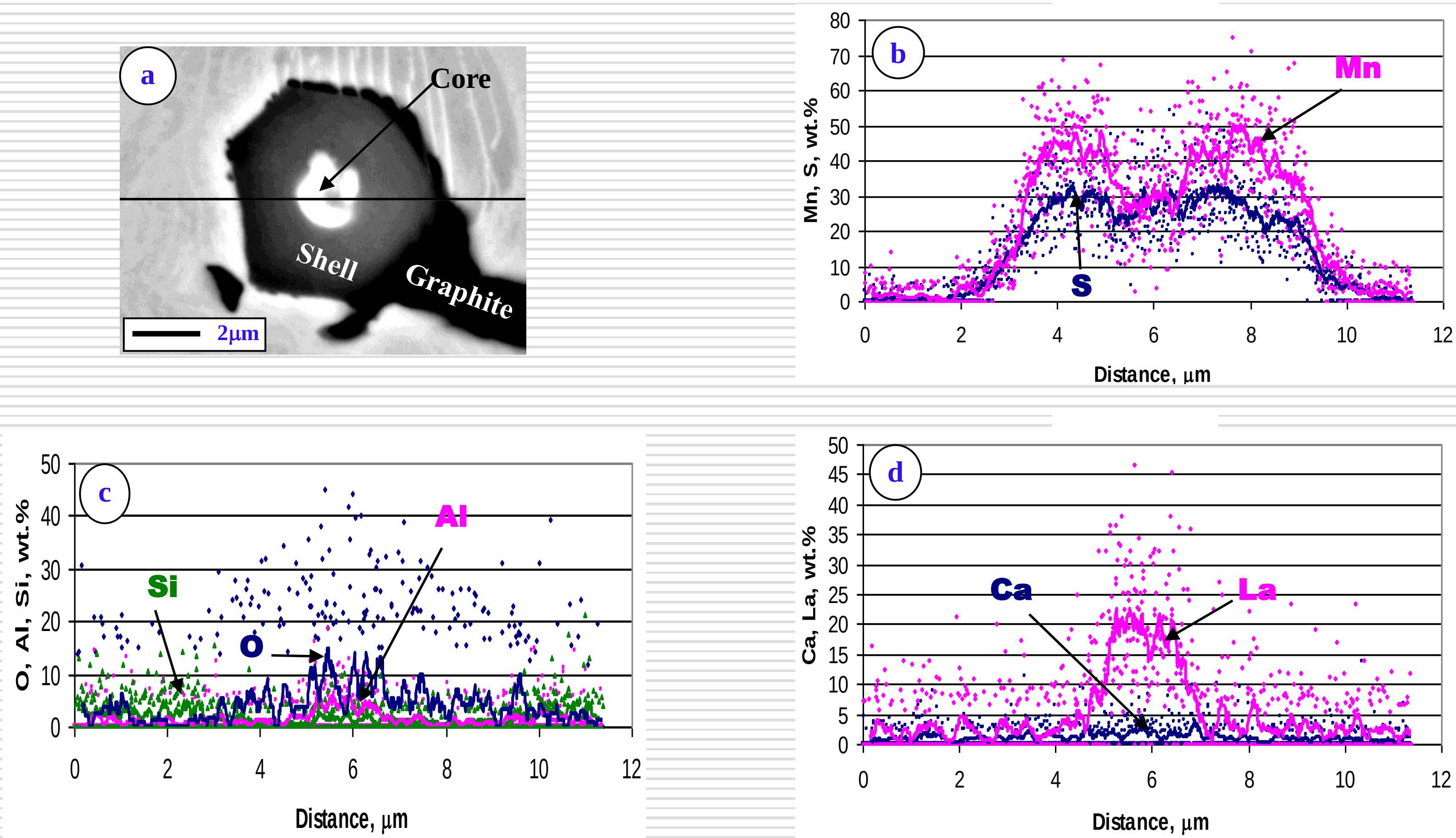
1) small oxide-based sites [< 3μm] are early formed in the melt as stable microinclusions of deoxid. elements such as **Mn, Si, Al, Ti, Zr…**

2) complex (Mn,X)S compounds [1…10μm] nucleate at these compounds [**Mn, S** importance] **[X = Fe, Si, Al, Zr, Ti, Ca, Sr, P, Ce, La..]**

3) graphite nucleates on the sides of the **(Mn,X)S** compounds with suitable crystallographic fit with graphite [**X**-Inoculating Element contribution]

[I. Riposan, M. Chisamera, S. Stan, T. Skaland. *AFS Trans.*, 2001 / *SPCI7*, 2002 / *Int. J. Cast Met. Res.* 2003 / *AFS Inoc. Conf.* 2005 / C. Loper Symp., 2009 / *Mat. Sci. & Techn.*, 2010]

Typical example of chemical analysis along cross-section of complex (Mn,X)S compound associated with graphite [a - Compo; b - Mn, S; c - O, Al, Si; d - Ca, La]



[I. Riposan, M. Chisamera, S. Stan, E. Stefan, C. Hartung – SPCI9-Luxor, Egypt, 2010; *Key Eng. Mater., 2011,* V. 457, pp. 19-24.]

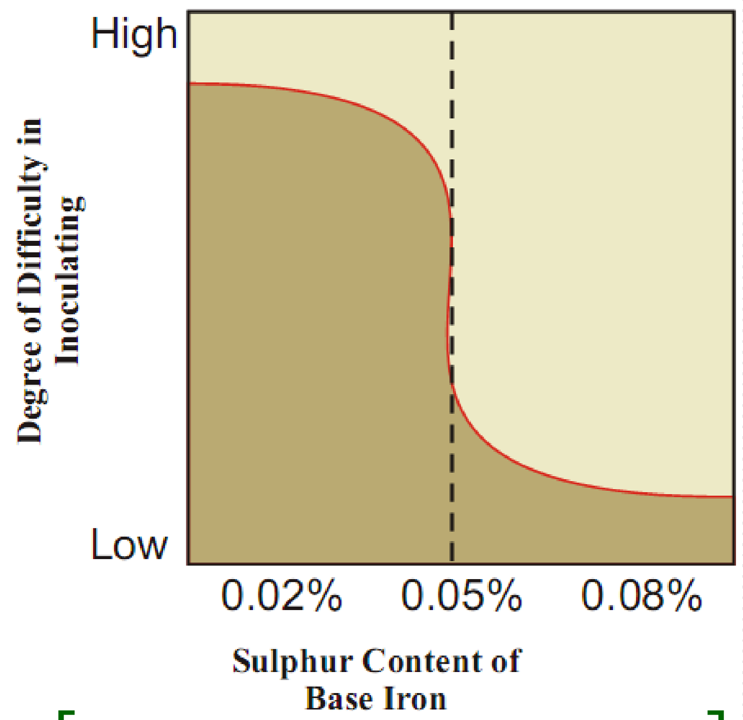
II. LOW S / Al GREY CAST IRONS CHARACTERISTICS

Typical problems of low S, low Al grey cast irons

- **Solidification with high eutectic undercooling**
  * Carbides and / or Undercooled Graphite (type D)
  * Low number of Eutectic Cells
  * Non homogeneous structure

Limited response to inoculation------→

- Unfavourable conditions for type A Graphite formation



[www.foundry.elkem.com]

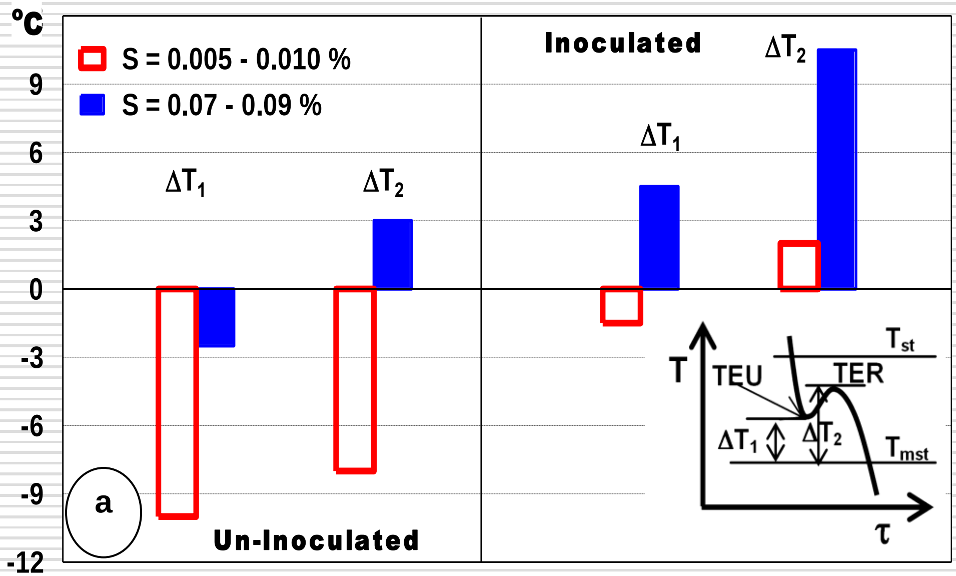
Inoculants: FeSiAlX: X = Ca, Ba, Sr....

traditionally inoculating elements

- to promote compounds [µm scale] in the iron melt, to act as active graphite nucleation sites, at lower eutectic undercooling

[I. Riposan, M. Chisamera, S. Stan G. Grasmo, C. Hartung, D. White.

113th AFS Casting Congress, 2009, Las Vegas, USA]



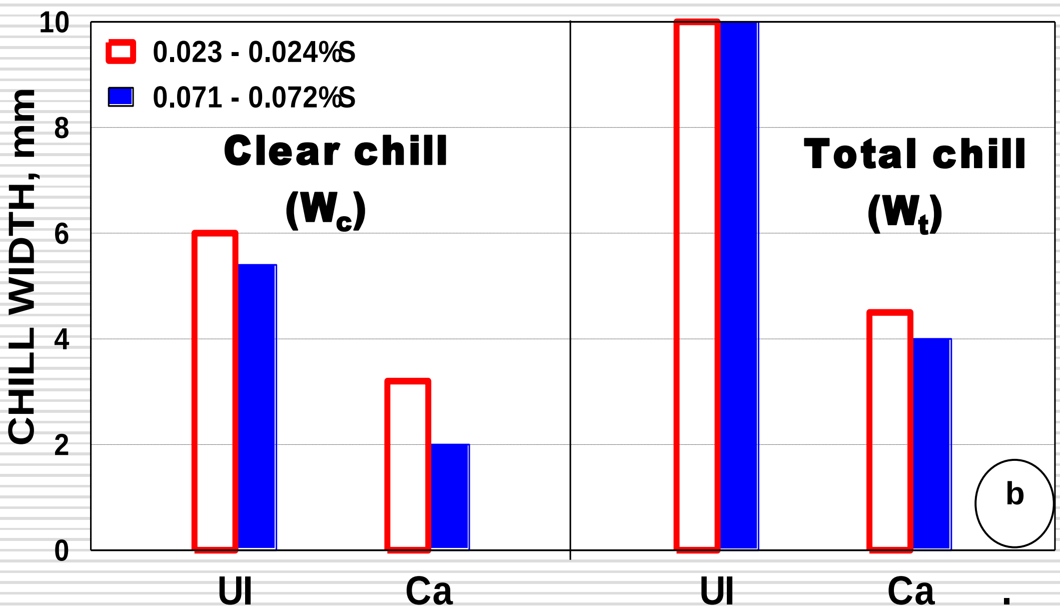
Base Iron:
As-Melted *vs* Resulphurized Irons
(%Mn) x (%S): 0.018 vs 0.055

[M.Chisamera, I.Riposan, S.Stan, D.White, G.Grasmo – *Asian Foundry Congress*, 2008, Japan; *Int. J. Cast Met. Res.*, 2008, 21(1- 4), 39..]

Base Iron:
Ductile Iron *vs* Grey Iron

[ΔT_1 = TEU – Tmst;
ΔT_2 = TER – Tmst]

[M. Chisamera, I. Riposan, S. Stan, T. Skaland. *64th World Foundry Congr.*, 2000,Paris, France]



III. SUPERHEATING OF IRON MELT IN ACID LINED CORELESS INDUCTION FURNACE [CIF]

➢ **There are different reasons for superheating grey iron in the acid lined, Coreless Induction Furnaces [CIF]**

(1) the production of thin wall (< 5 mm wall thickness) grey iron castings,
(2) correction after melting a steel charge needs power for stirring,
(3) post - furnace metallurgical treatment,
(4) numerous transfers and long holding time.

➢ **The new generation of CIF: high superheat temp. [> 1550°C],** ***due to***

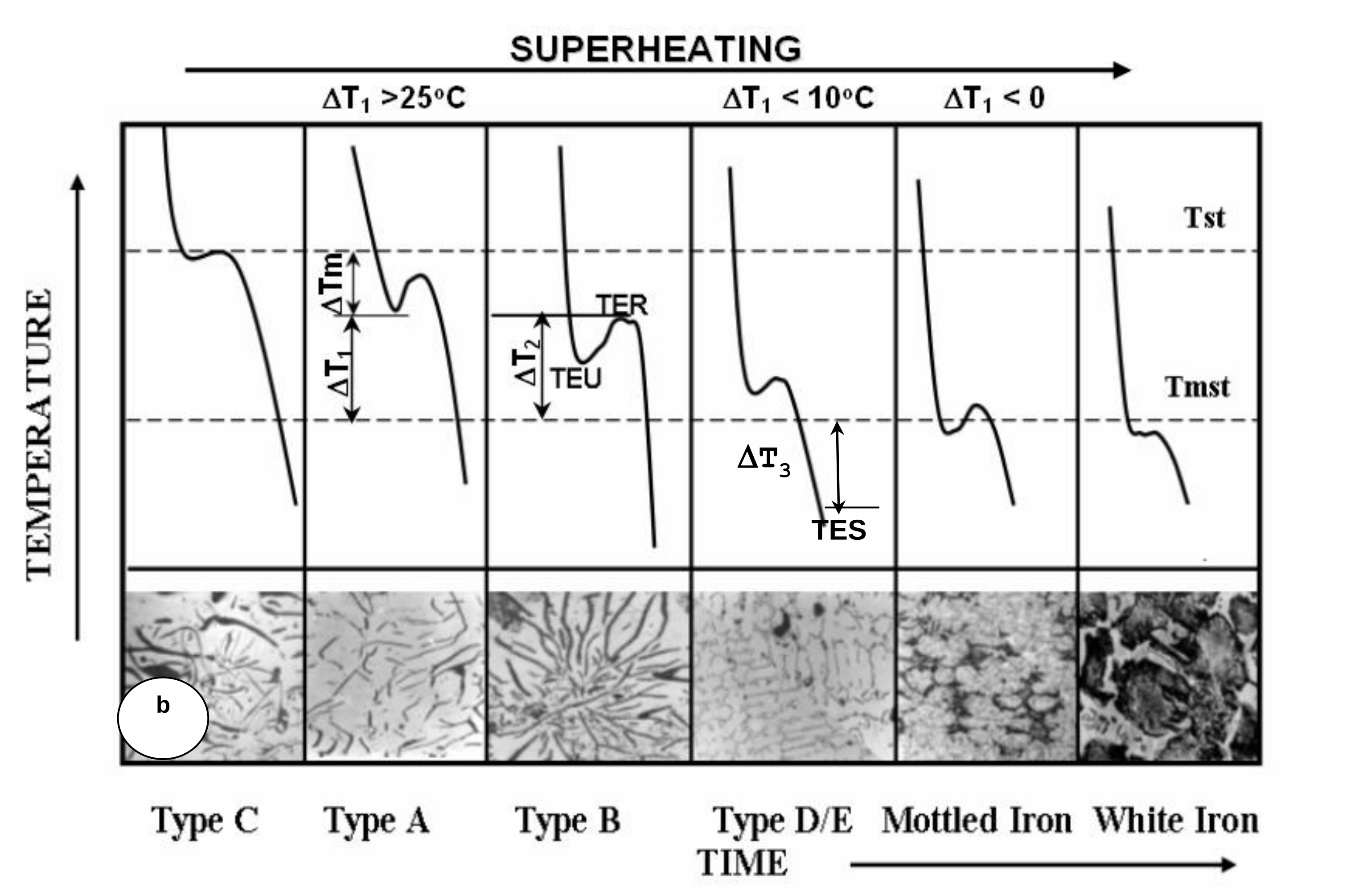
- high perform. electrical equipment with high specific power rating > 250 kW/t
- quality improvem. allow the acid refractory lining to withstand high temp.
- high purity SiO_2 mater., optimum crystalline structure, active agents addition

➢ **One application uses a SiC addition in a SiO_2 – B_2O_3 mass**

- leading to improved lining life (20-100%),
  - especially with high rust levels in the metallic charge
    - inclusively added to sustain Mn oxidation for ferritic ductile iron

[I. Riposan, M. Chisamera et al. Patent RO 110470-B1/1996; RO. Foundry J. 1996, 3, pp. 18-22]

Superheating - Cooling Curves - Structure Relationship

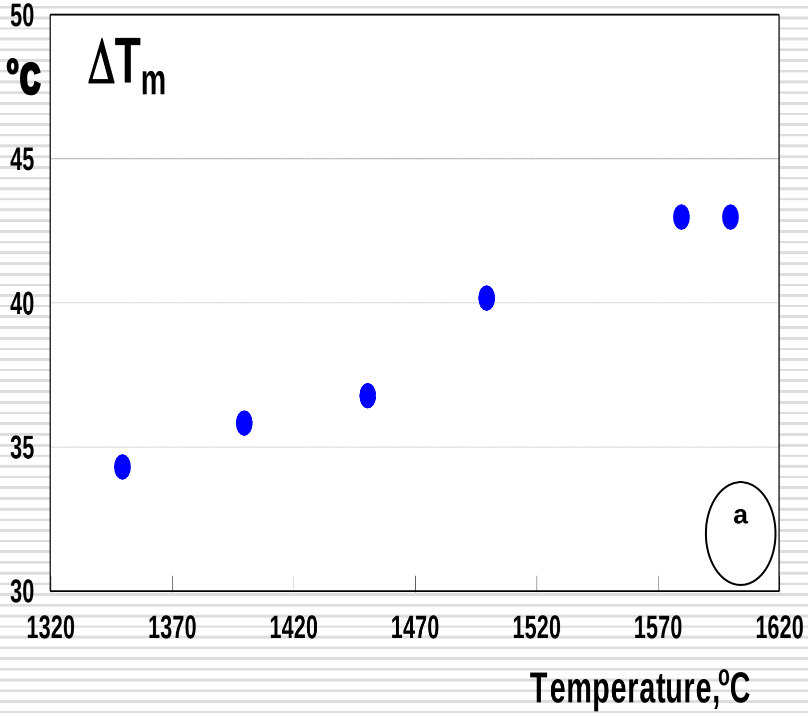


[S. Stan, I. Riposan, M. Chisamera, M. Barstow – Adv. Mater. Res., V. 23 (2007), pp. 307-310]

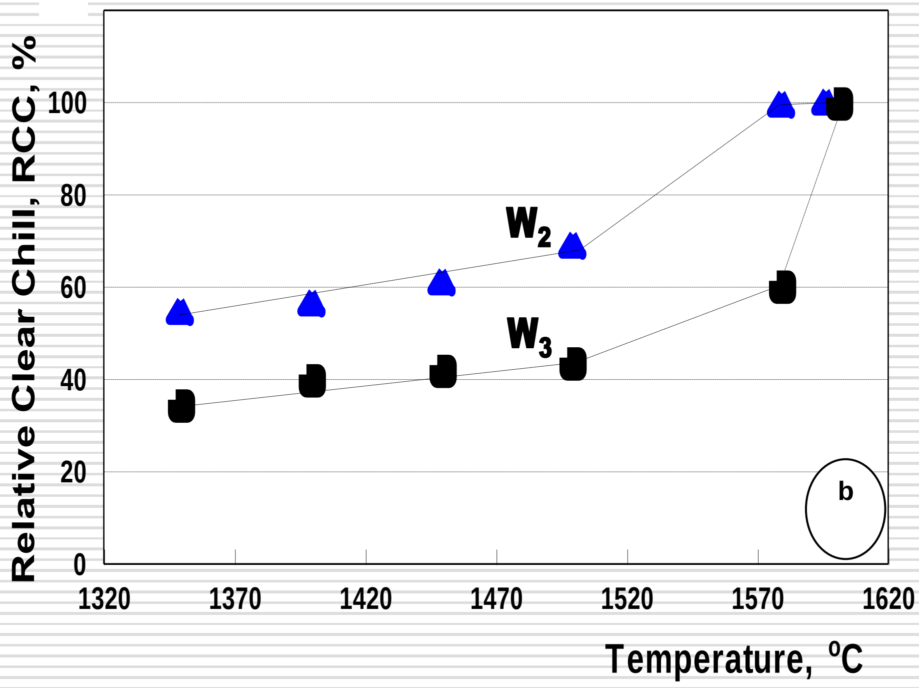
Eutectic Undercooling and Chill Tendency in Superheated Grey Irons

[3.9%CE, < 0.02%S, (%Mn) x (%S) < 0.01, < 0.005%Al, < 0.0005%Zr]

Eutectic Undercooling
[ΔTm = Tst –TEU]



Chill Tendency
[ΔTm = Tst –TEU]
[W2, W3 – wedges ASTM A367]
[RCC = (Wc / B) x 100]



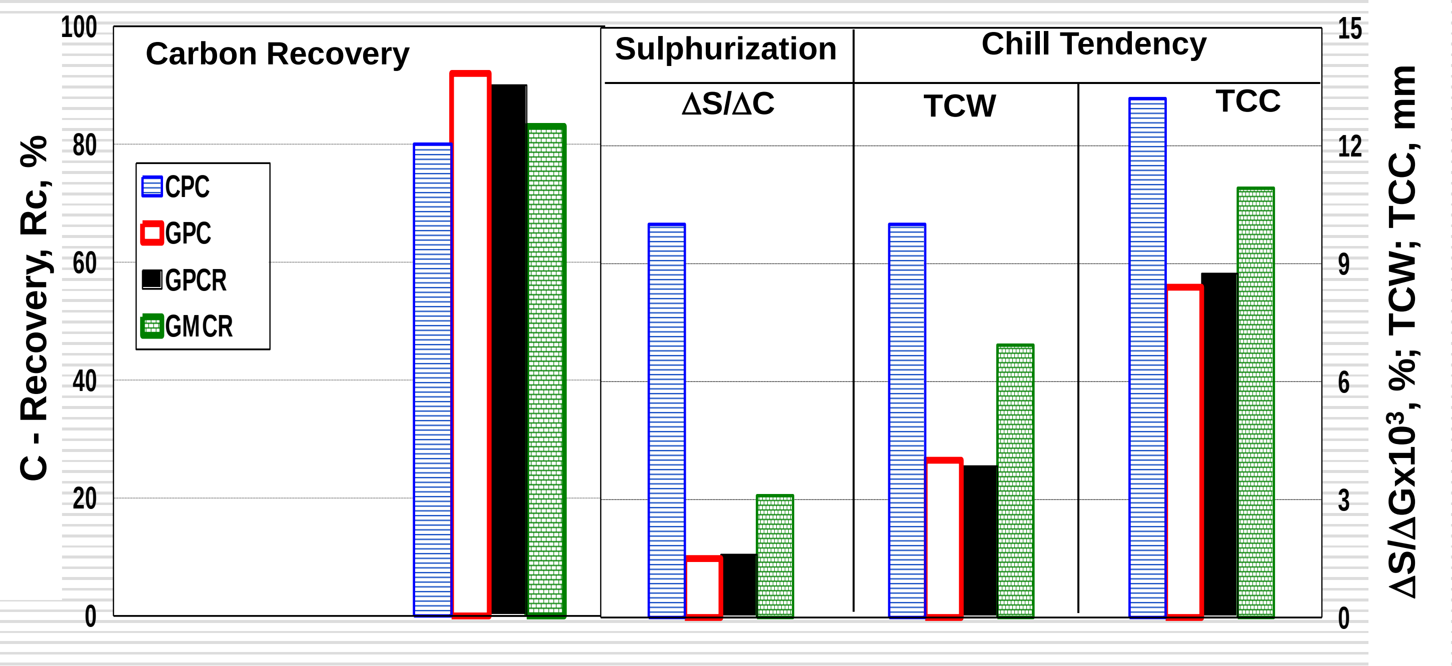
IV. METALLURGICAL TREATMENT OF ELECTRIC MELT GREY IRONS

A. PRE-TREATMENT OF THE IRON MELT IN A MELTING FURNACE

(1) Carbon materials

[Melt Iron: 3.0-3.25%CE, 2.5-2.9%C, 1.6-1.85%Si, 0.016-0.022%S, 1500°C]

[CPC – Calcined PC; GPC – Graphitized PC; GPCR – Graphitized Packing PC, a by-product; GMCR - Graphitized Packing Metallurgical Coke, a by-product]



[M. Chisamera, I. Riposan, L. Stan et al. *67th World Foundry Congr.*, 2006, Harrogate, UK; *Adv. Mater. Res.* 2007, 23, 287]

(2) Metallurgical Silicon Carbide [Met. SiC]

- **Worldwide foundry experience reports benefits from using Met. SiC:**
  - reduced chill; improved machinability; improved and more uniform mech. properties;
  - less scrap: hard edges, shrinkage and gas porosity, graphite degeneration; dross.
  - increased Mg-yield; higher nodule count.
  - higher durability of furnace acid lining;

- **The preconditioning / inoculation effect of Met. SiC**, ***promoted by***
  - presence of SiC molecules (not from melting but after dissolution), *and*
  - residual crystalline carbon, as graphite.

- **This effect benefits the formation of:**
  - fine iron structure / lower chill (carbide forming)
  - reduction, or even elimination, of the inoculant addition.

- **Possibility to improve the carburizing / preconditioning / inoculation performance of Met. SiC, *by***
  - optimizing the chemical composition,
    - especially by increasing the free graphite content
      - promotion of type – A graphite, less carbides

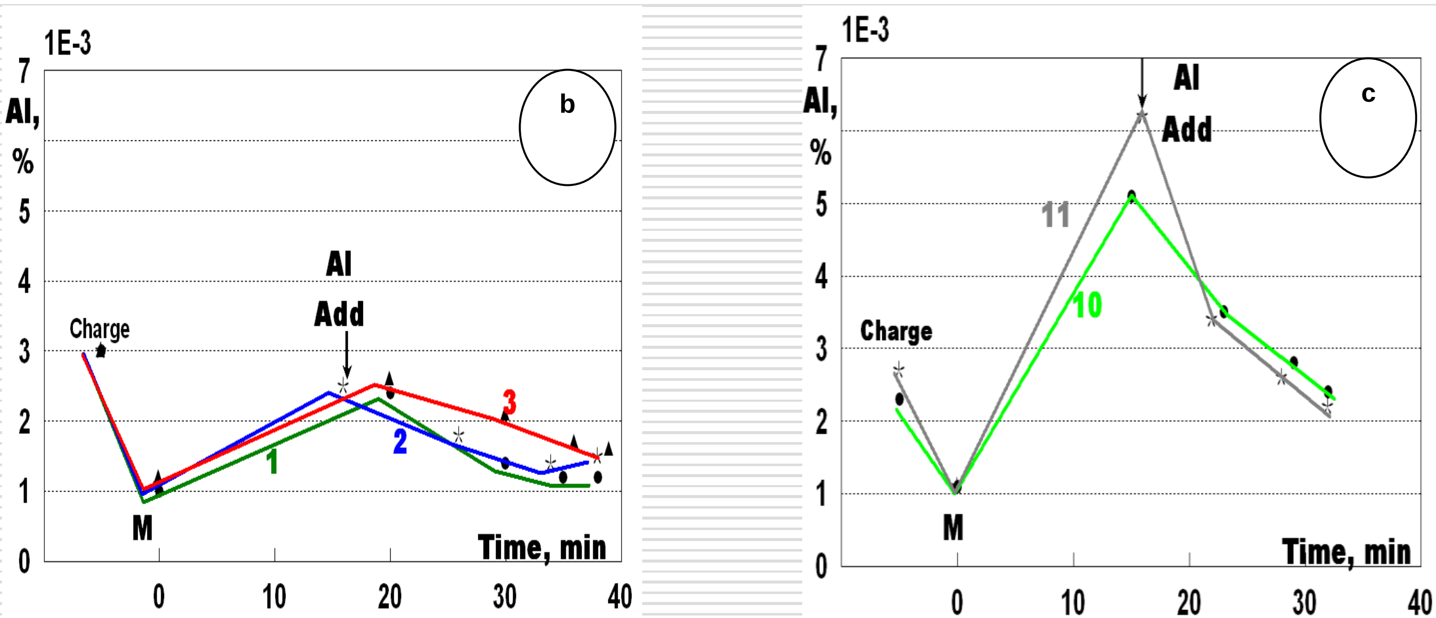
[I. Riposan, M. Chisamera, I. Petrus, V. Pintea. *Patents* RO 105.063-A/1991, RO 101.922-A/1990 / *60th World Foundry Congr.*, 1993, Netherlands; *ARABCAST Congress*, 2004, Egypt]

(c) Al recovery by charge and after melt. with in-furnace additions

[MF – CIF, acid lined, 1500 – 1600°C]

- **Al - a key element within complex (Mn,X)S acting as graph. nucl. sites**
  - experiments to control **Al** in acid lined, CIF melting with superheating
  - independent of the added **Al**, final **Al** was less than **0.003wt.% Al**
  - the final **Al** would be too low to sustain graphite nucleation

[> 0.004wt.%Al necessary]

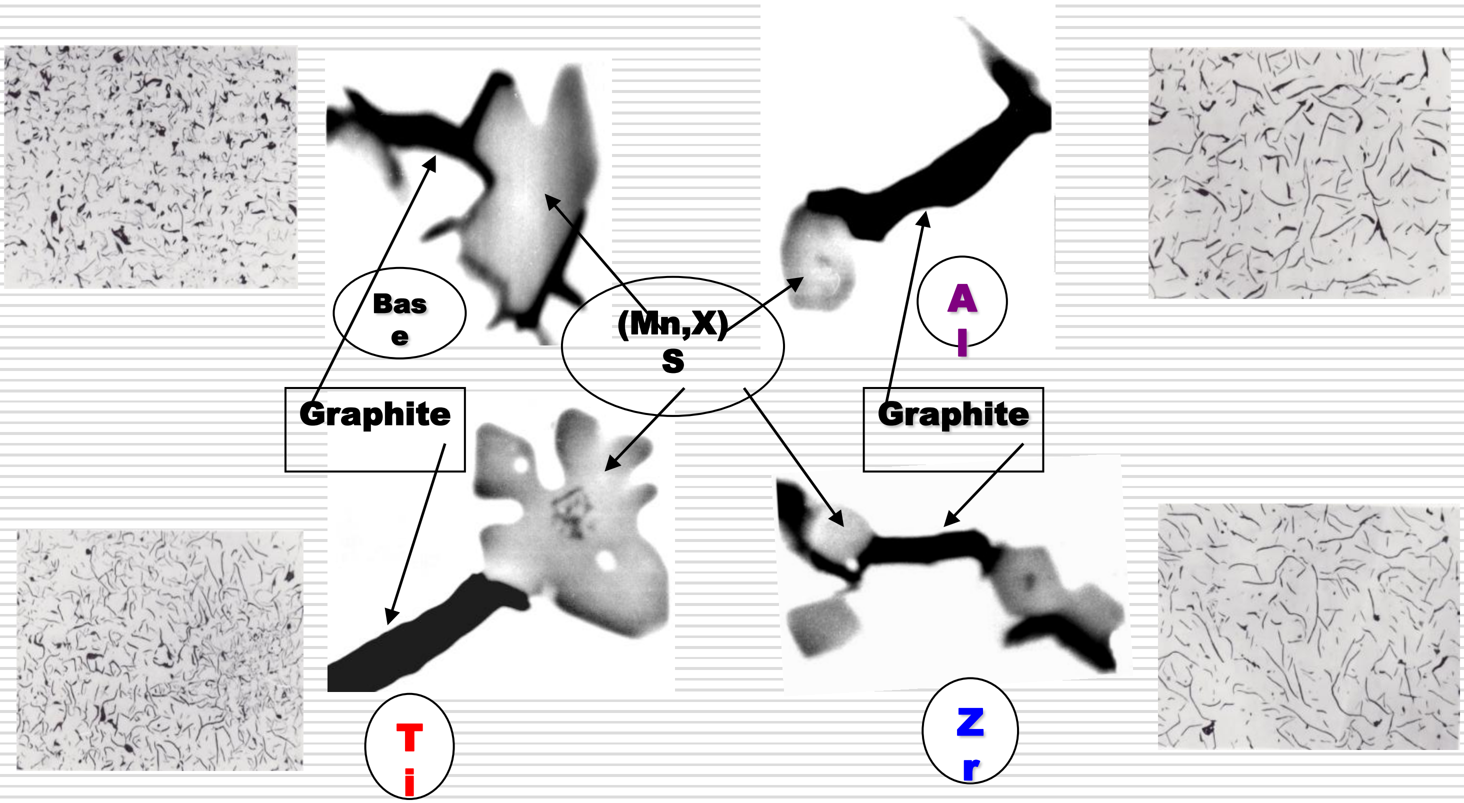


[I. Riposan, M. Chisamera, S. Stan, G. Grasmo, C. Hartung, D. White. *AFS Trans.*, 2009, 117,423-434]

B. COMPLEX TREATMENTS OF ELECTRIC MELT GREY IRONS

(1) Al, Zr *and* Ti Preconditioning Comparison

[0.003 – 0.03%Al, 0.0005 – 0.015%Zr, 0.005 – 0.03%Ti]



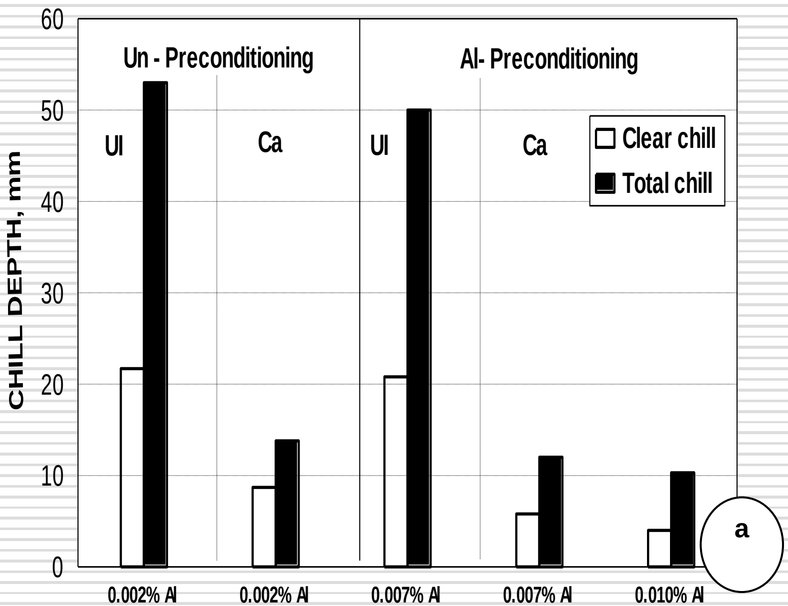
[I. Riposan, M. Chisamera, S. Stan, C. Hartung, D. White - *The Carl Loper Cast Iron Symp.*, 2009, Madison, USA / *Mater. Sci. Techn.*, 2010, 26 (12), 1439-1447]

(2) Double Treatments: Preconditioning + Inoculation

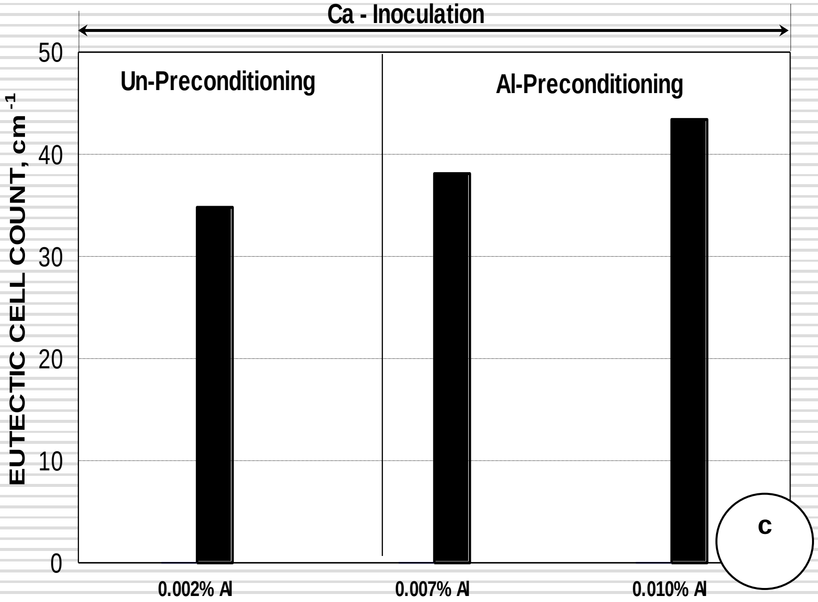
(a) Al preconditioning + Ca - FeSi inoculation

[3.6-3.7%CE, 0.44-0.46%Mn, 0.09-0.1%S, (%Mn) x (%S) = 0.04-0.05, 0.002 / 0.007 - 0.01%Al, 0.0005%Zr, 1520°C]

CHILL DEPTH [wedge sample]



EUTECTIC CELL COUNT

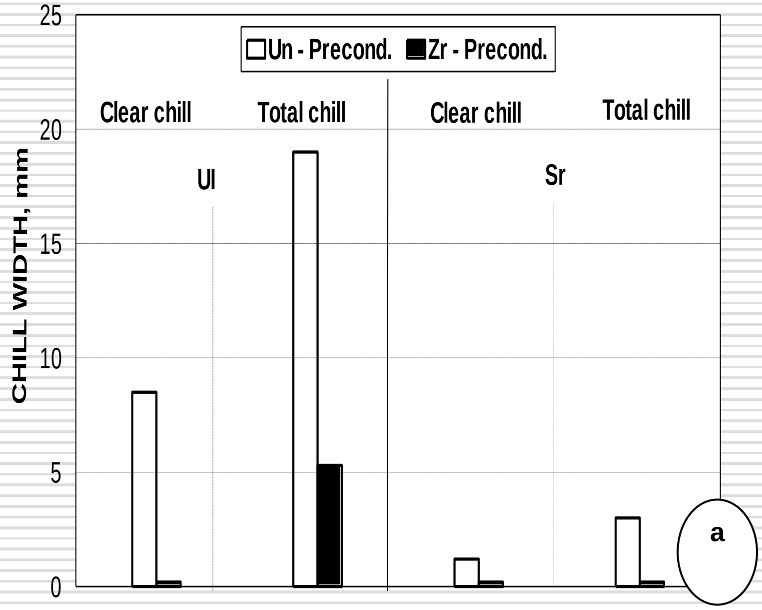


[M.Chisamera, I.Riposan, S.Stan, D.White, G.Grasmo – *Asian Foundry Congr.*, 2008, Nagoya, Japan; *Int. J. Cast Met. Res.*, 2008, 21(1- 4), 39-44]

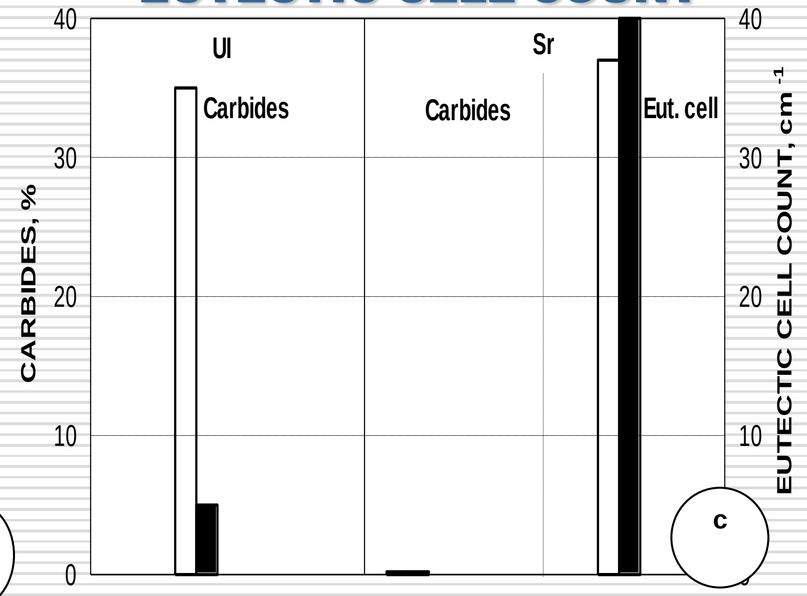
b) Zr preconditioning + Sr - FeSi inoculation

[3.7-3.9%CE, 0.55-0.65%Mn, 0.095-0.1%S, (%Mn) x (%S) = 0.05-0.06, 0.002-0.004%Al, 0.0005 / 0.013%Zr, 1520°C]

CHILL DEPTH [wedge sample]



CARBIDES / EUTECTIC CELL COUNT



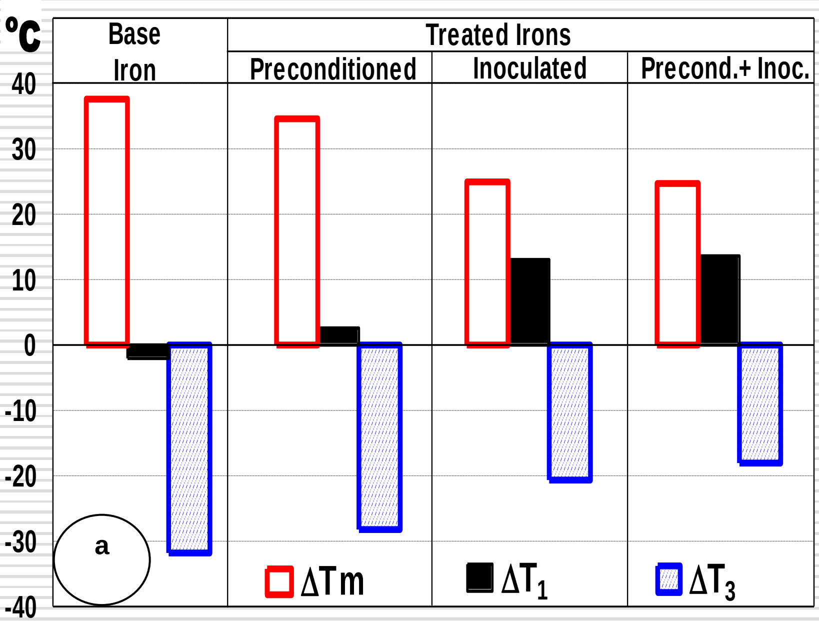
[M.Chisamera, I.Riposan, S.Stan, D.White, G.Grasmo – *Asian Foundry Congr.*, 2008, Nagoya, Japan; *Int. J. Cast Met. Res.*, 2008, 21(1- 4), 39-44]

c) Al,Zr,Ca - FeSi preconditioning + Ca,Ba - FeSi inoculation

[3.9-4.0%CE, 0.7-0.8%Mn, 0.012-0.015%S, (%Mn) x (%S) < 0.015, < 0.005%Al, < 0.0005%Zr, 1530°C]

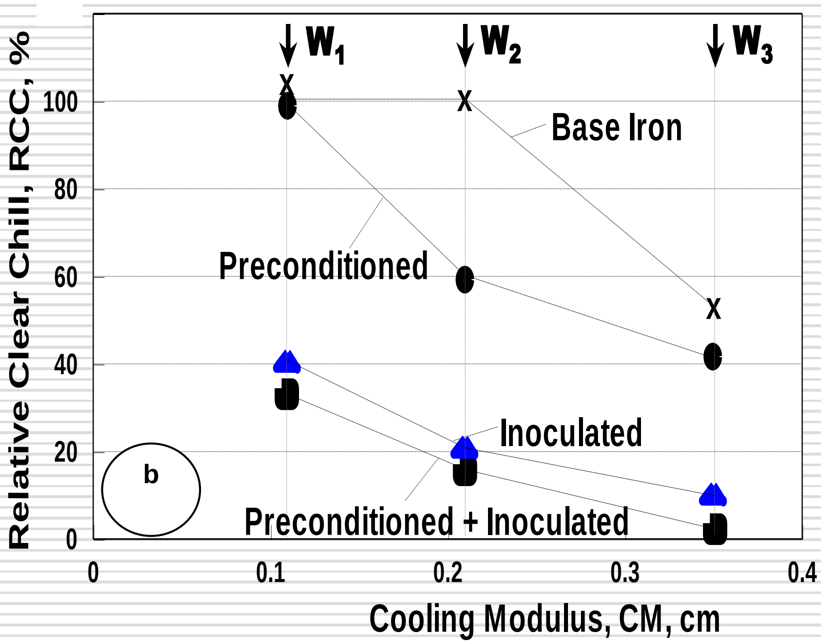
EUTECTIC UNDERCOOLING

[ΔTm = Tst – TEU; ΔT_1 = TEU – Tmst; ΔT_3 = TES – Tmst]



CHILL TENDENCY

W_1, W_2, W_3 – wedges ASTM A367]
[RCC = (W_c / B) x 100]



RECOMMENDATIONS FOR FOUNDRY APPLICATION

OBJECTIVE

To sustain (Mn,X)S Compounds formation, compatible to graphite nucleation at lower eutectic undercooling:

- lower size / higher compactness / higher count particles suitable crystallographic fit with graphite

EXPECTED FINAL RESULTS

- ✓ Solidification at lower eutectic undercooling / recalescence
- ✓ Graphite nucleation at lower undercooling
  - A-type graphite promotion / D-type graphite avoidance
- ✓ Carbides avoidance
- ✓ Higher eutectic cell count
- ✓ Thin wall grey iron castings especially
  - no Carbides or / and D - type graphite

Three groups of elements are important to sustain graphite nucleation in grey irons

1) **strong deoxidizing elements**, such as **Al** and **Zr**, to promote formation of very small micro-inclusions [0.005 – 0.010%**Al** benef.; I. Riposan et al]

2) **Mn** and **S** to sustain **MnS** type sulphide formation [(%**Mn**) x (%**S**) = 0.03 – 0.06; R. Gundlach]

3) **inoculating elements** (such as **Ca, Sr** etc) which act in the first stage and / or in the second stage of graphite formation, to improve the capability of **(Mn,X)S** compounds to nucleate graphite.

Three technological steps appear to be necessary to produce high performance grey cast iron

1) furnace super-heating of the molten iron, to eliminate un-desired heredity influence of charge:

- depending on the charge characteristics *and* melting practice

2) pre-conditioning with oxide forming elements (Al *or / and* Zr) of the base iron, especially for:

- low quality charge materials *or / and* melting practice, *or*
- low performance inoculation procedure or / and pouring practice

3) inoculation (such as Ca, Sr....) of pre-treated iron, as final treatment:

- to control eutectic undercooling
  - *according to the quality of base iron
  - *according to the castings characteristics

FOUNDRY APPLICATION RECOMMENDATIONS

No.	Step	Characteristics
1	Melting	* Minimum 1500°C superheat / Induction furnace * Scrap steel and Iron charge; * C and Si correction; * Met. SiC beneficial; * Recovered (by-product) graphit. carbon mater. beneficial; * S correction for optimum (%Mn) x (%S) Factor [0.03-0.06] - generally, in a 0.4-1.2%Mn / 0.04-0.12%S range
2.	Precon-ditioning	* Al, Zr - FeSi alloys beneficial * 0.05 – 0.15wt.% addition before furnace tap (0.1% usually) * 0.005-0.015wt.%Al / Zr in final iron [max. 0.01% usually]
3.	Inocula-tion	* Different inoculation techniques * Normal to lower addition rates * Sr - FeSi / Ca - FeSi / Ca,Zr - FeSi / Ca,Ba - FeSi alloys

ACKNOWLEDGMENTS

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❖ Authors thank to ELKEM AS Foundry Products Division, Norway, which partially supported the laboratory experiments and approved reference to those results for publication.

THANK YOU