Rio Tinto

Defects in Heavy Section Ductile Iron Castings: Chunky Graphite , Dross and Intercellular Carbides.

Martin Gagné
Rio Tinto
Iron & Titanium

Ankiros, October 2008

Istanbul, Turkey

Heavy Section Ductile Iron Castings: A Rapidly Growing Market!

Wind Energy is one of

the faster growth sector!

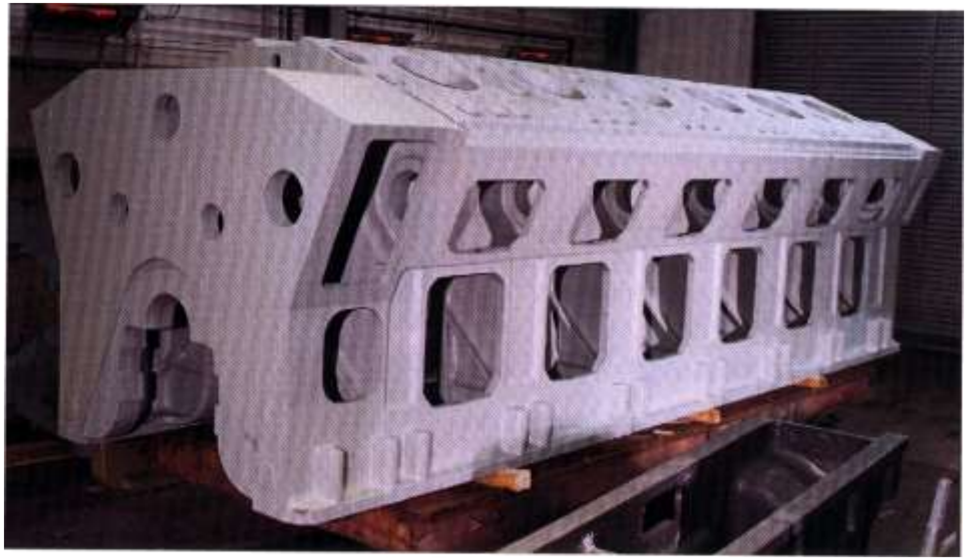
Ankiros, Istanbul, Turkey

October 2008

RioTinto

Heavy Section Ductile Iron Castings: A Rapidly Growing Market!

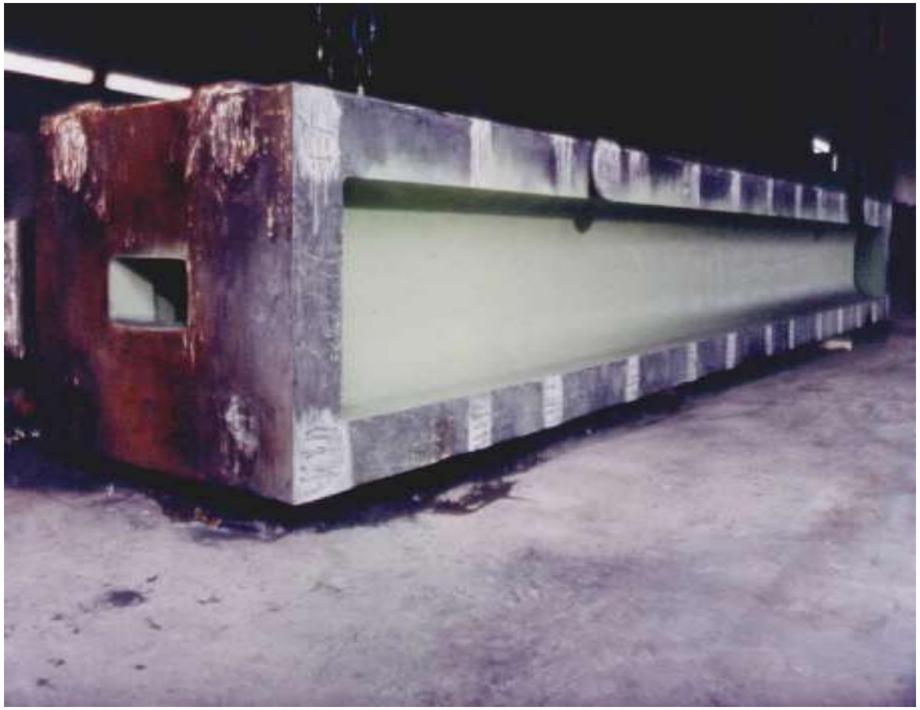
Hub for wave enegy generator (9 tons)



Engine block (35 tons)

Heavy Section Ductile Iron Castings: A Rapidly Growing Market!

Turbine Housing (45 tons)



Press Frame (232 tons)

Rio Tinto

Heavy Section Ductile Iron Castings: Easy to produce?

- Most of these castings must fulfill the requirements of iSO (GGG 40.3), which includes specifications on Impact resistance at –20C.
- As a result, they are very sensitive to microstructural defects.
- Because of their size (weight), such castings exhibit very long solidification/cooling time that results in structural inhomogeneities that are exacerbated by this factor.
- Handling of very large quantity of liquid Ductile Iron also means larger exposure of the liquid metal to reoxidation (during handling, pouring, in the gating system,…).
- Most of these castings are manufactured using the riserless technique that improves metal yield and ensures shrinkage-free parts if well designed but the rejection may be the results of the occurrence of structural defects.
- **Rejecting one casting, because of the mouding, iron processing and recycling costs, represents significant losses for the foundry!**

RioTinto

What Are the Major Defects Typical/Critical to Heavy Section Ductile Iron Castings

- Degenerated graphite particles (chunky, spiky, intercellular flakes,….)
- Non-metallic inclusions (dross, slag, sand)
- Intercellular embrittling structures (carbides, phophides, porosities)

RioTinto

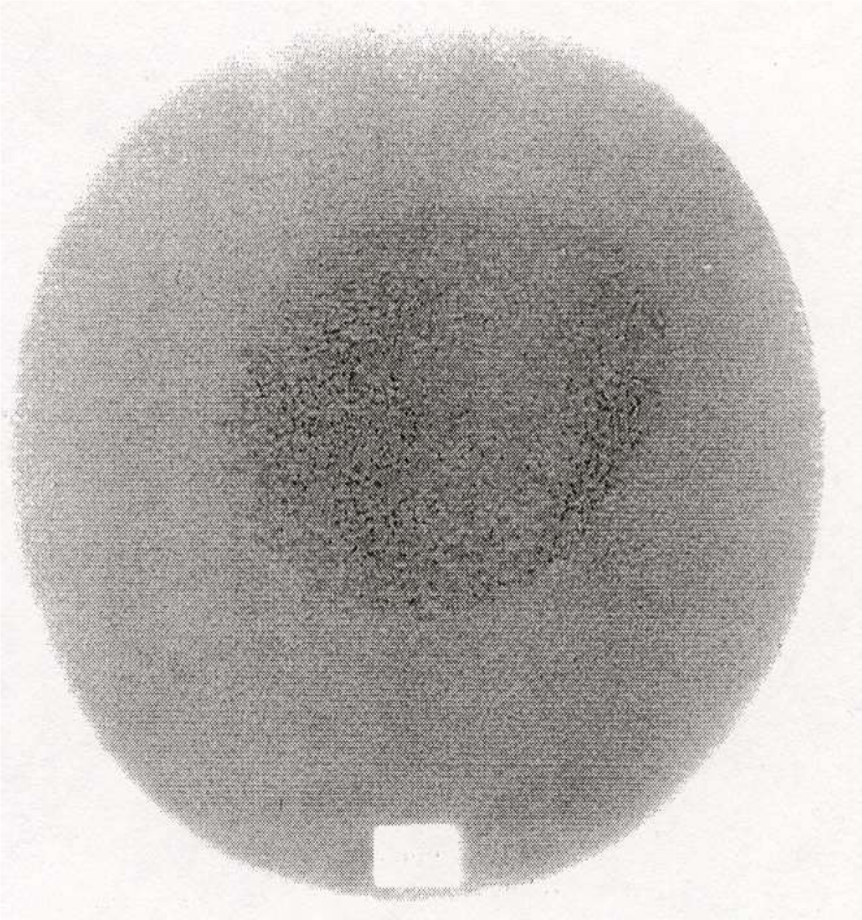
Chunky Graphite: Formation, Effect on Properties and Prevention

Ankiros, Istanbul, Turkey

October 2008

RioTinto

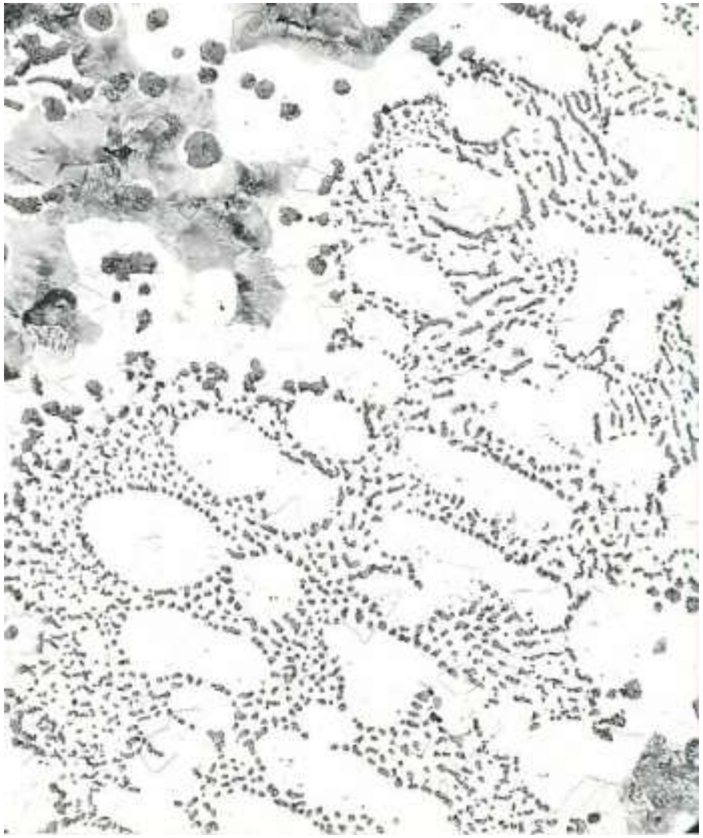
Chunk Graphite: Macrographic Appearance in a Heavy Section Ductile Iron Casting



Diameter of the cylinder: 20 cm

RioTinto

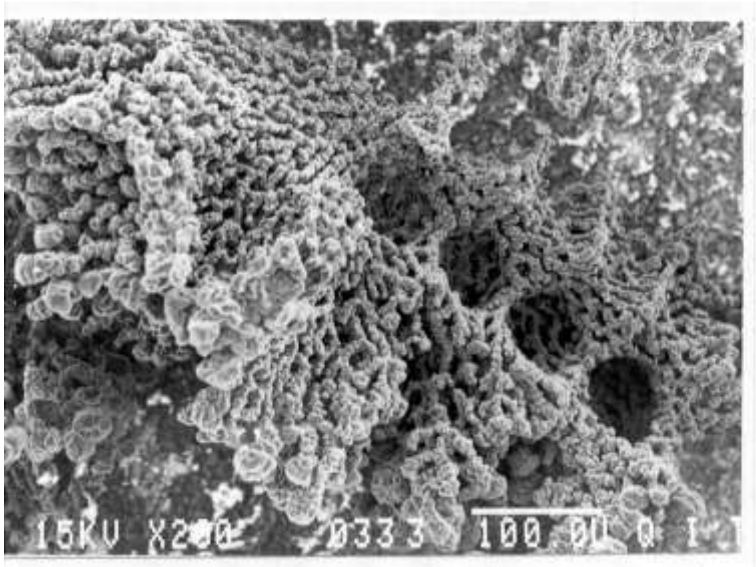
Chunk Graphite: 2-D Appearance

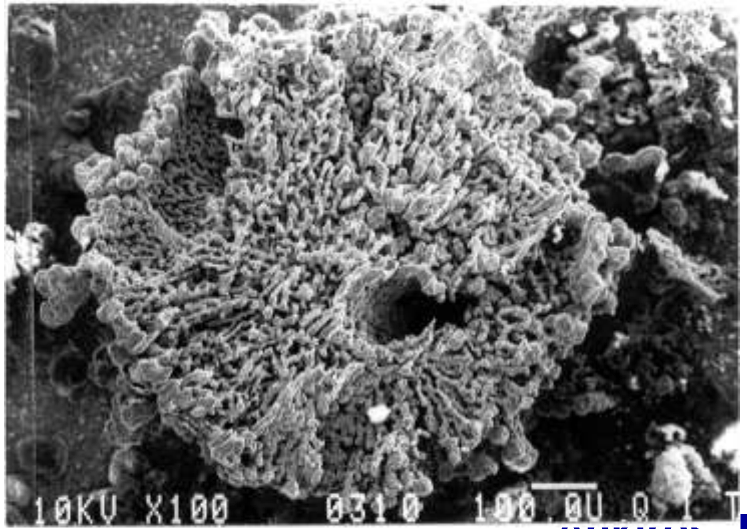


Appearing as either interdendritic or as clusters under optical microscopy, chunk graphite may appear as ASTM Type D graphite but it lacks the characteristic flake nature of Type D graphite.

Chunk Graphite: 3-D Appearance

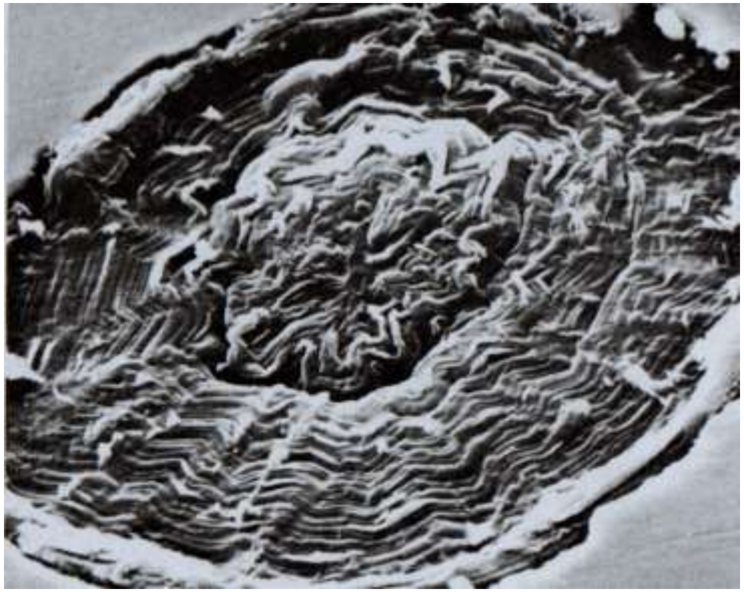
Chunk Graphite Particles





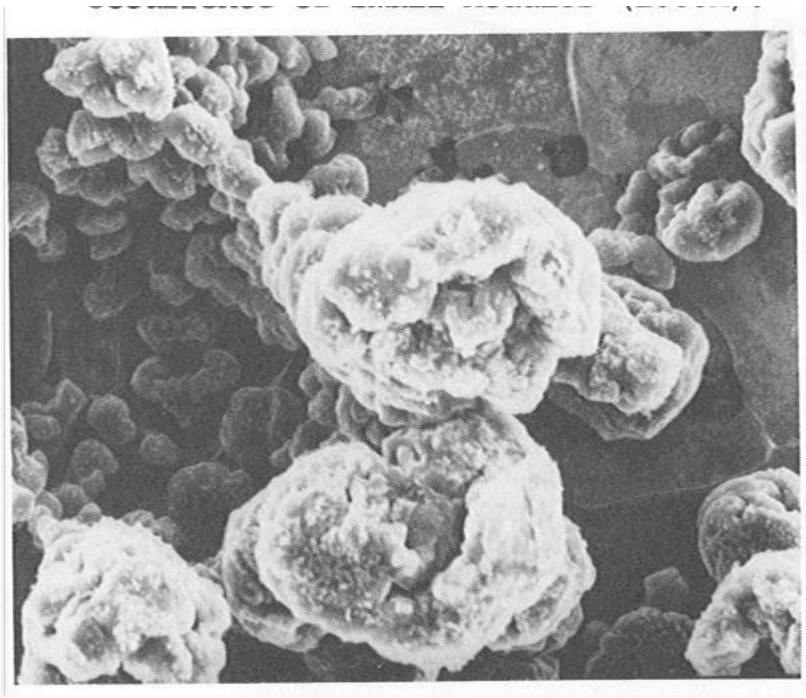
Diameter: up to 1 mm

Type I Graphite Particle

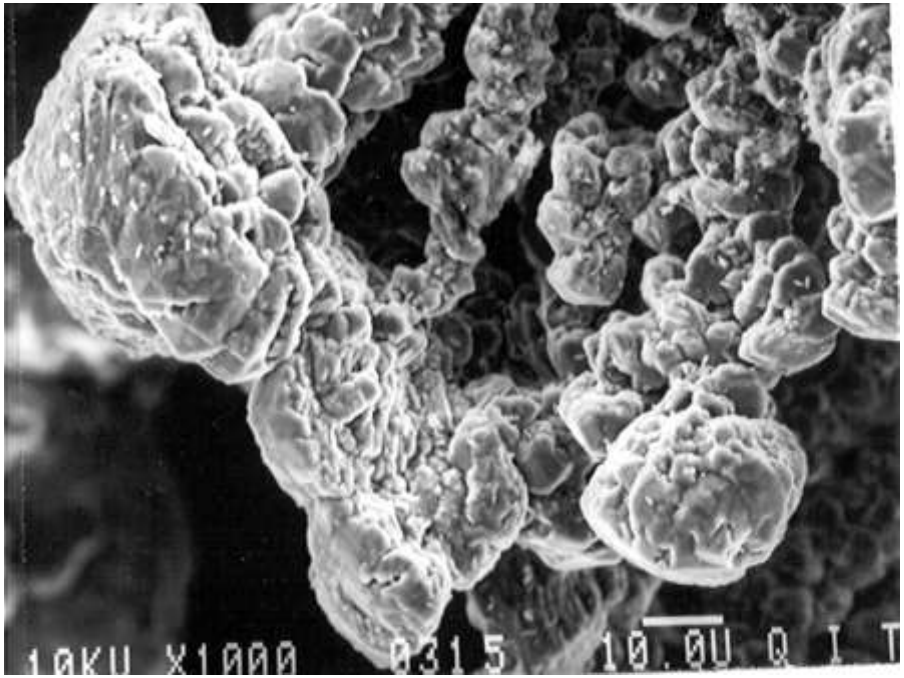


Diameter: up to 0,1 mm

Chunk Graphite: Structural Details



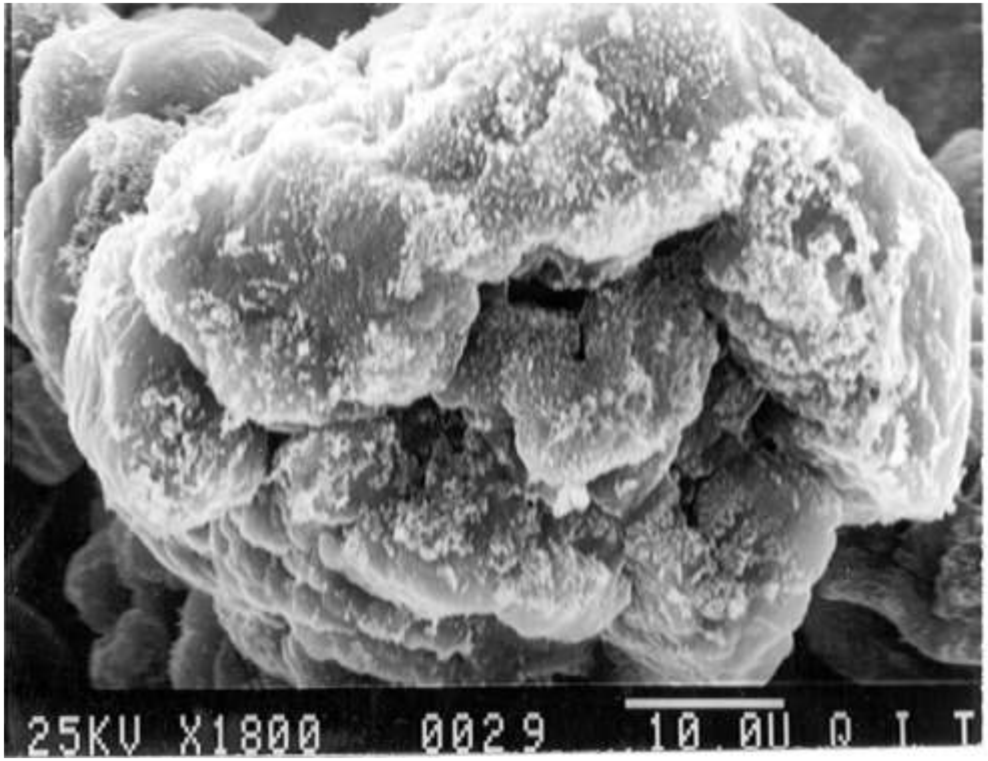
Thin graphite filaments interconnected and highly branched



Each graphite filament is terminated by a small spherical protuberance (nodule)

RioTinto

Chunk Graphite: Growth Mechanism



Fractured extremity of a chunk graphite filament

Chunk graphite filaments grow via a spiral growth mechanism on the « c » axis of the graphite crystals. Such a growth (which is very rapid) can only occur in presence of high driving forces in the liquid iron.

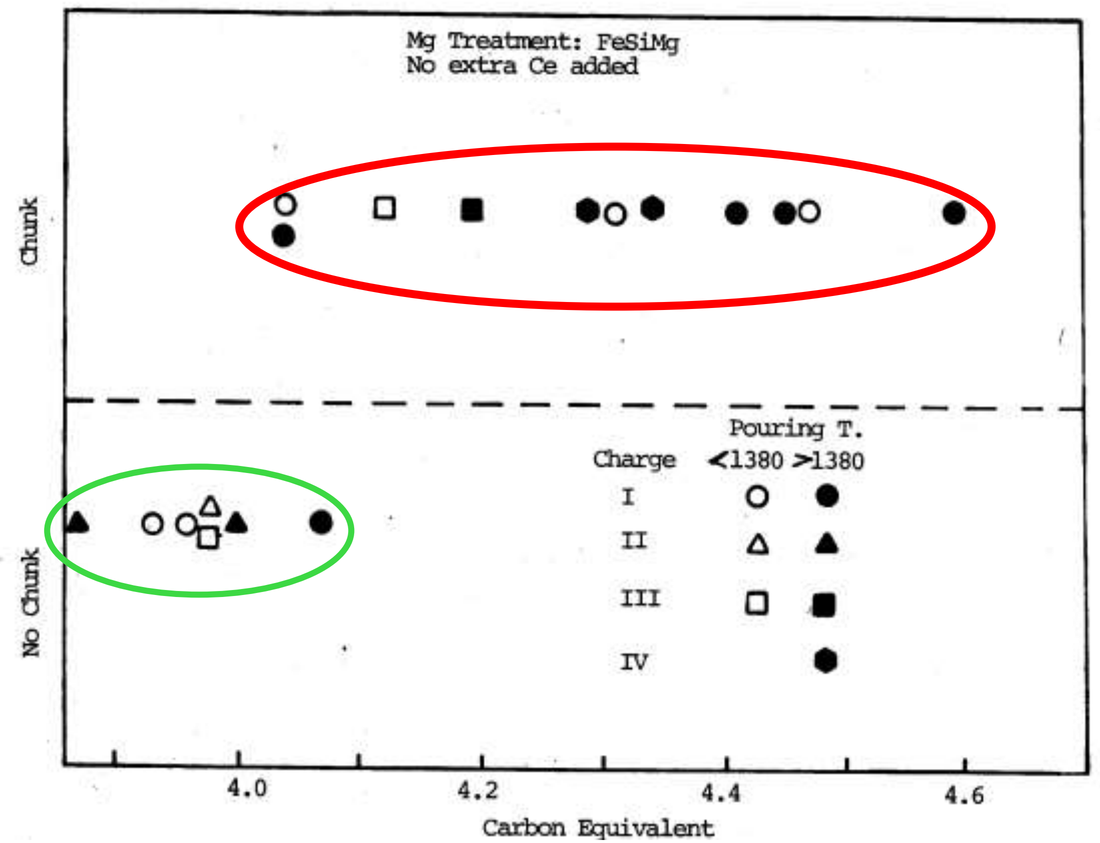
As the parameters causing the high driving forces decreases, the growth pattern changes to become that of nodular graphite, explaining the nodular shape of the extrimities of the chunk grahite strings.

RioTinto

Chunk Graphite Driving Forces: Carbon Equivalent

High carbon equivalent, which results in high local supersaturation of carbon, forces the instantaneous precipitation of carbon atoms on the base « C » plan of the graphite crystals.

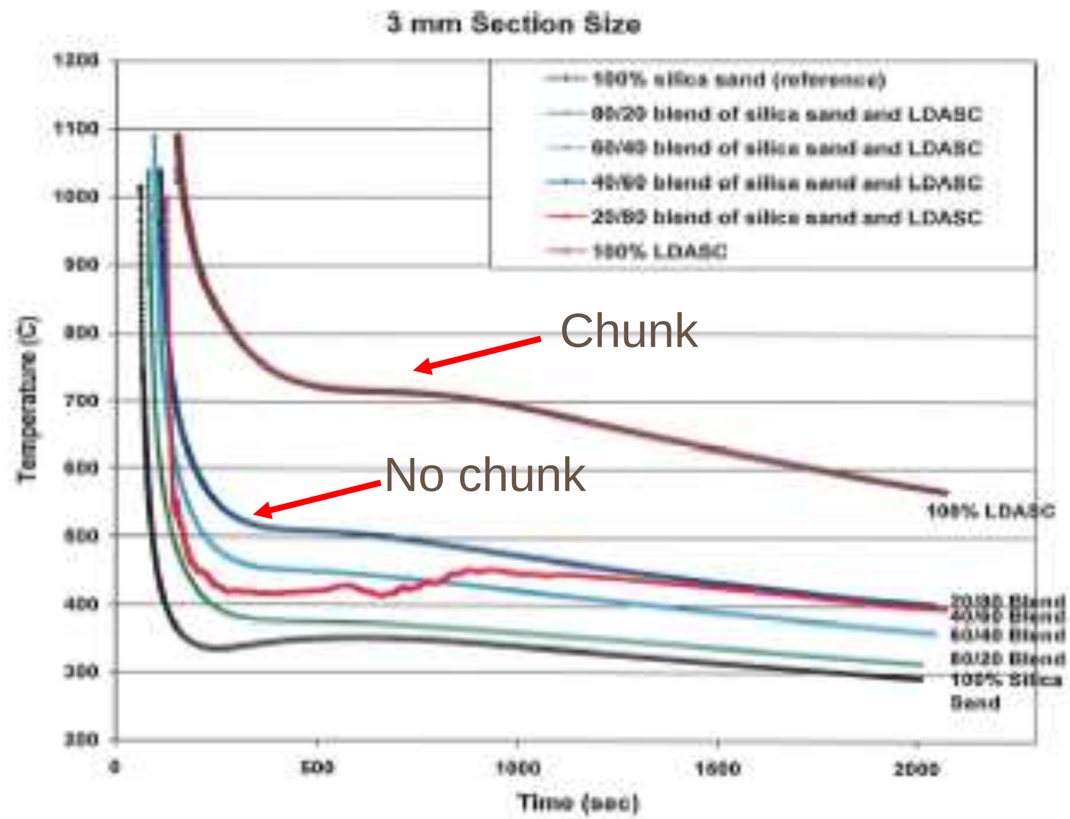
Carbon equivalent should be maintained below 4,1!



RioTinto

Chunk Graphite Driving Forces: Low Nucleation Potential

Low nucleation potential due to unsufficient undercooling, lack of oxygen in the last liquid to solidify to form suitable nuclei or poor inoculation in a high (or limit) carbon equivalent iron creates condition for carbon supersaturation and chunk graphite formation.



Cooling curves obtained in 3 mm high CE castings solidified with different undercooling levels

RioTinto

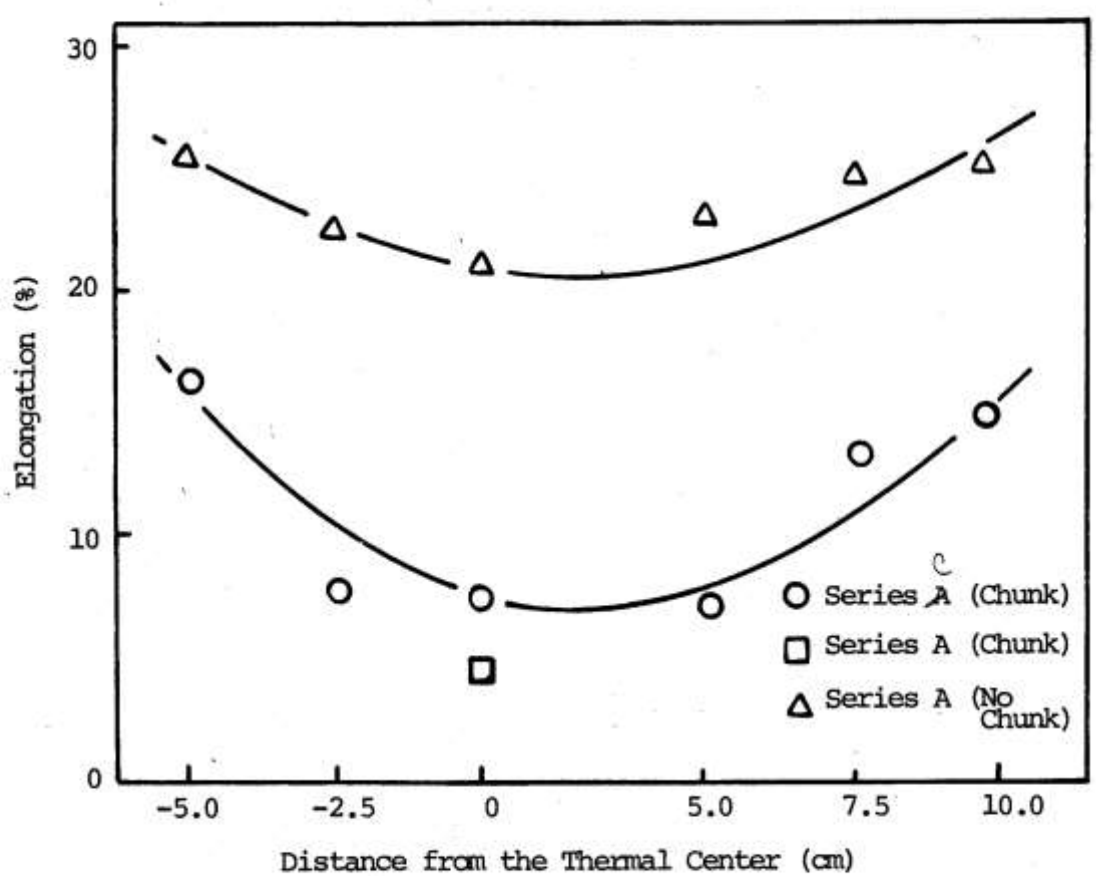
Chunk Graphite Driving Forces: Others

- Published R&D work indicate that no relationship exist between chunk graphite and segregation, either micro- or macro-, in the thermal center of the castings.

- Cerium has been reported to favor chunk graphite formation but recent work published by Källbom et al failed to to find a direct relationship between cerium and chunk graphite; the possible influence of cerium is believed to « complementary » to the factors previously indicated by further decreasing the nucleation potential in the last liquid to solidify by strongly deoxidizing and desulphurizing the remaining liquid iron.

RioTinto

Chunk Graphite: Effect on Mechnical Properties



The typical elongation of a chunk/ferrite structure is <5% compared to 20%+ for nodular/ferrite. A similar behavior is observed for impact resistance.

The yield strength is marginally affected but the UTS is reduced by 20%.

Fatigue resistance has been reported to be reduced by 25%.

RioTinto

Chunk Graphite: Prevention

- Maintain the carbon equivalent as low as allowed by the manufacturing process and the the properties targetted for the casting;
- Maintain a high nucleation potential until the end of the solidification;
- Change the solidification pattern to favor thermal mixing in tha casting, per example by using chills;
- Although shown as not critical by R&D work, maintain the Ce content at the lowest possible level;
- If chunk graphite persists, add elements that create a diffusion barrier around the graphite particle and limit the growth on the « C » plan of the graphite crystals; Sb, Cu and Sn have been shown efficient but the use of Sb at very low concentrations (<40 ppm) is recommended.

RioTinto

Dross: Formation, Effect on Properties and Prevention

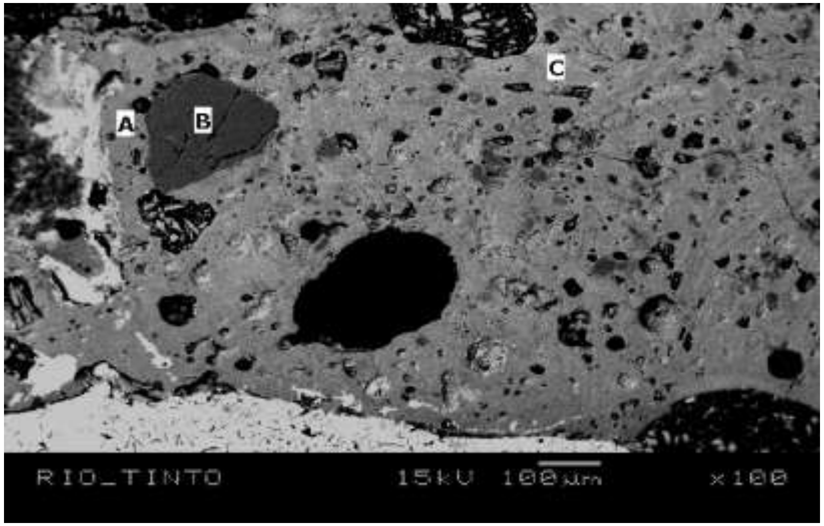
Ankiros, Istanbul, Turkey

October 2008

RioTinto

What is Dross?

Sand Inclusions



Inclusion
A= 54%SiO_2, 17%MgO,18%CaO;
B= SiO_2 100% grain de sable;
C voir figure 2

Slag Inclusions

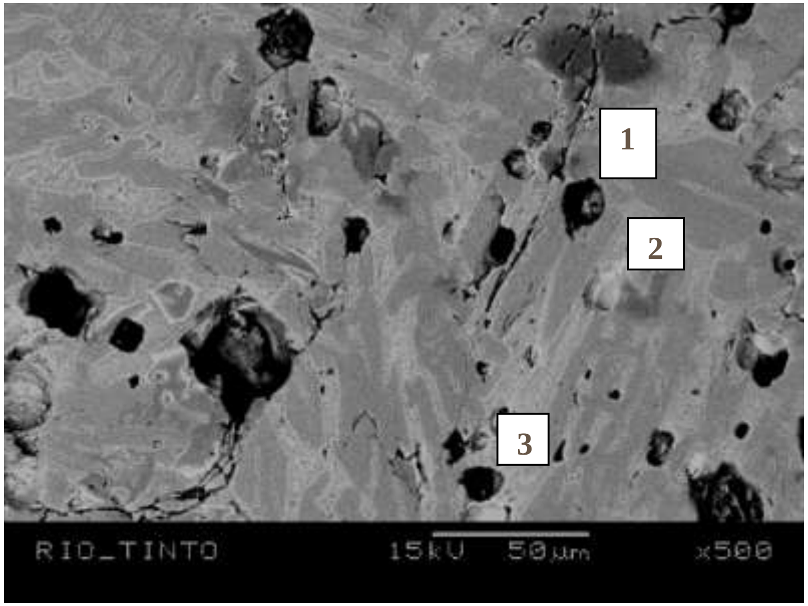
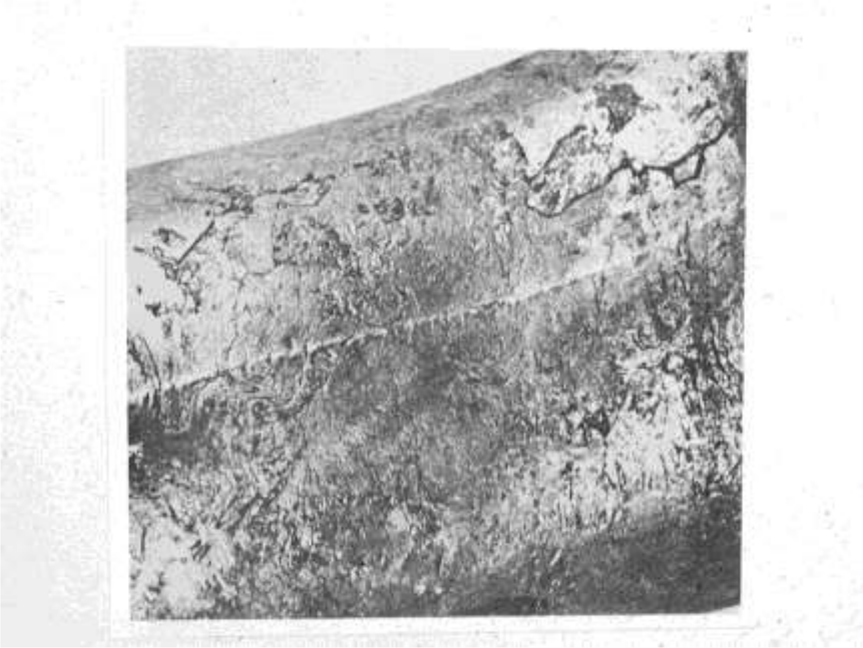


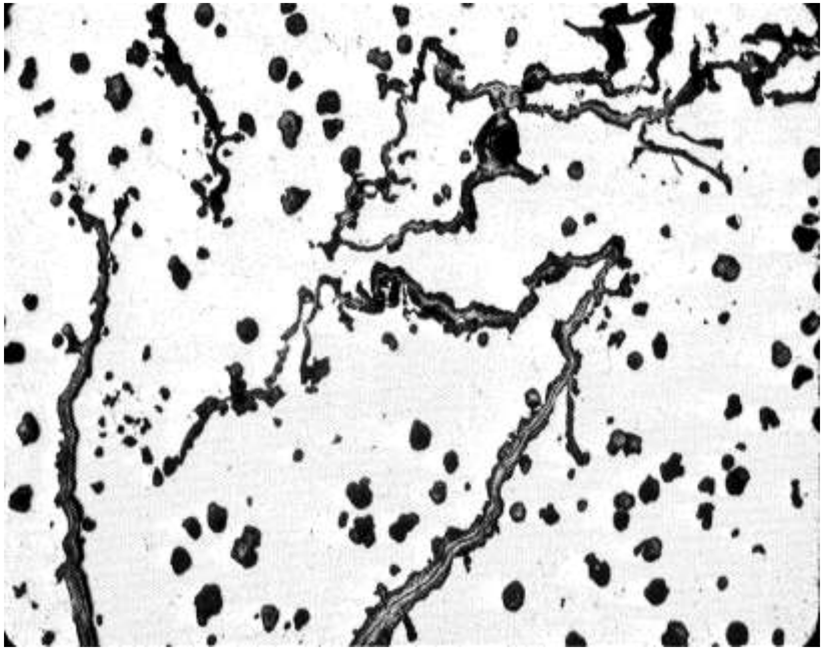
Figure 2 : Agrandissement de la zone C
1= 44%SiO_2, 52%MgO;
2= 53%SiO_2 , 18%CaO, 16%MgO;
3 = 54%SiO2, 18%Al_2O_3, 10% CaO, 15%FeO

RioTinto

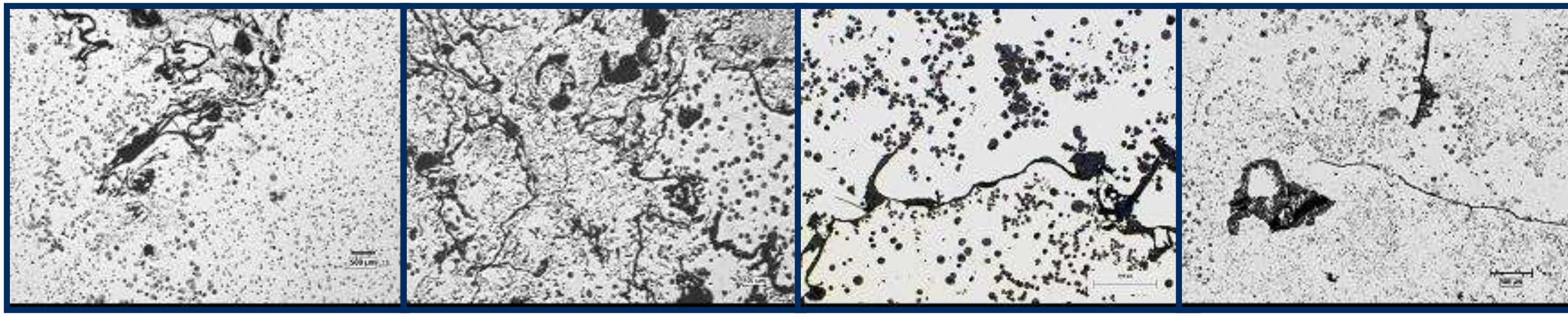
What is Dross?

This is **DROSS**: it appears as a filamentary inclusion but is a planar sheet of oxydes; Drosses are endogeneous, i.e. that they form in the liquid metal





What is Dross? Other Examples



Analysis no.	1	2	3	4	5	6
MgO	25%	14	16	48	40	24
SiO_2	56%	55	62	44	36	33
Al_2O_3	7%	5	8	5	6	1
CaO	0.5	-	-	-	-	-
MnO	5	23	11	-	3	8
FeO	4	3	2	2	16	31

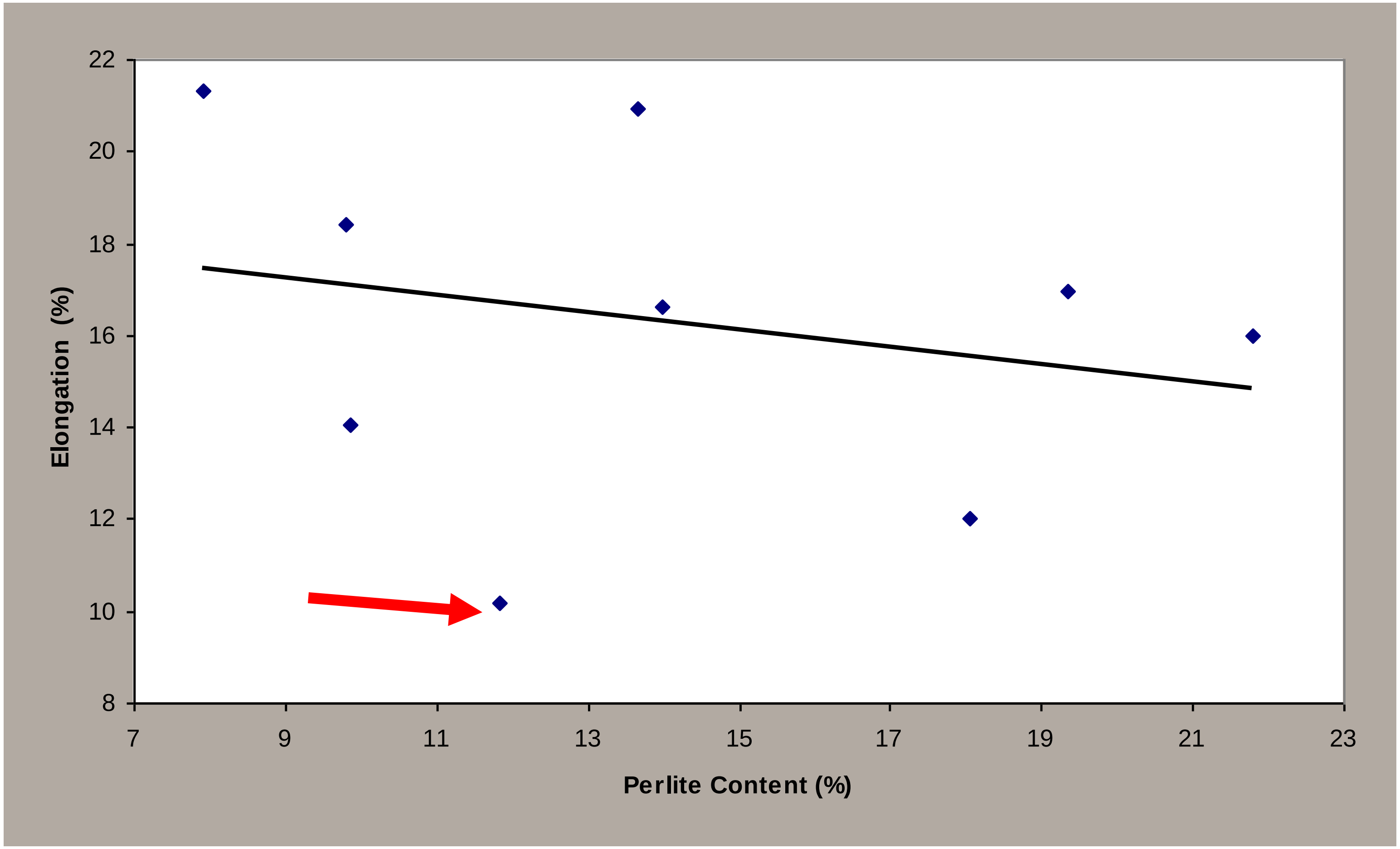
Ankiros, Istanbul, Turkey

October 2008

RioTinto

Dross: Effect on Mechanical Properties

Ductility

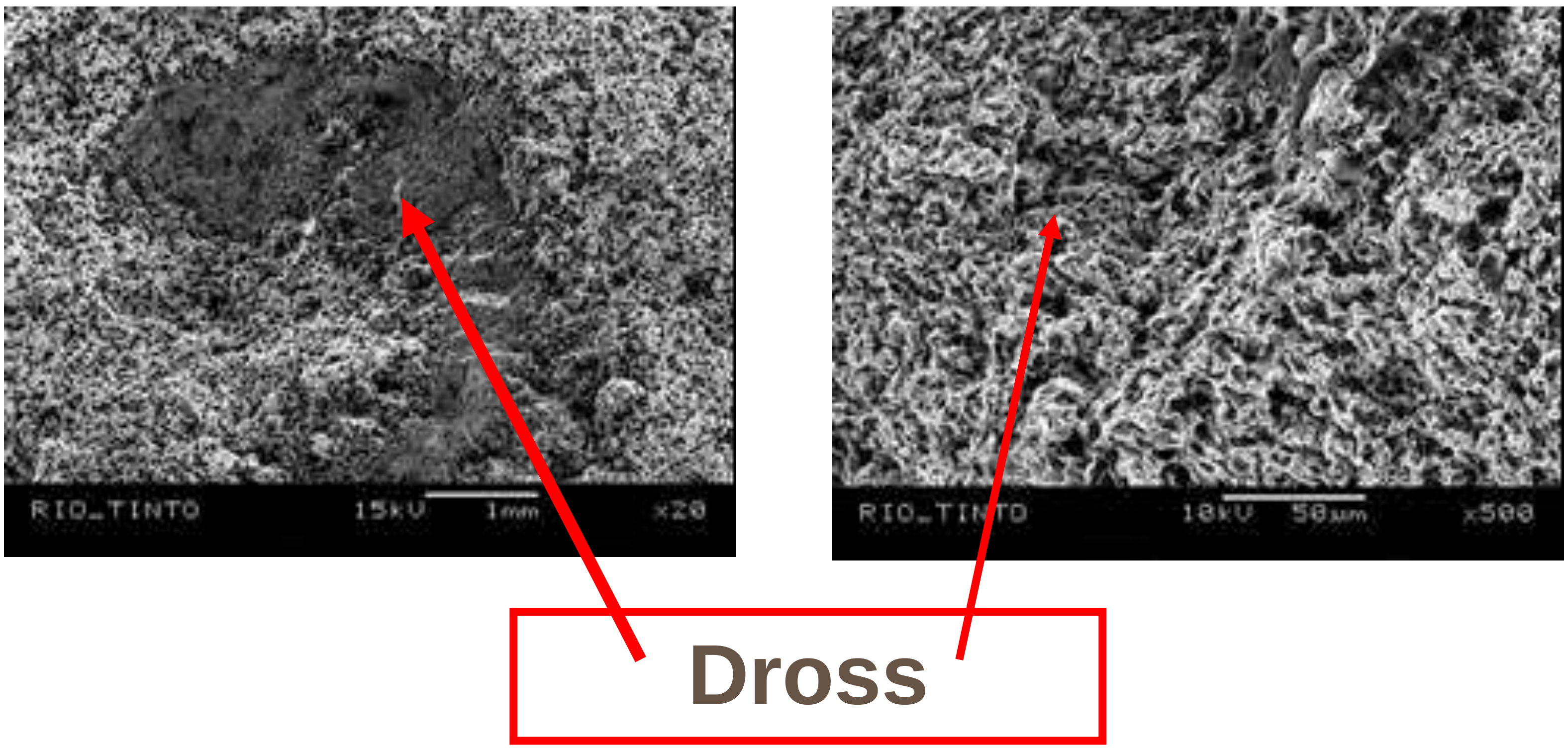


Ankiros, Istanbul, Turkey

October 2008

Dross: Effect on Mechanical Properties

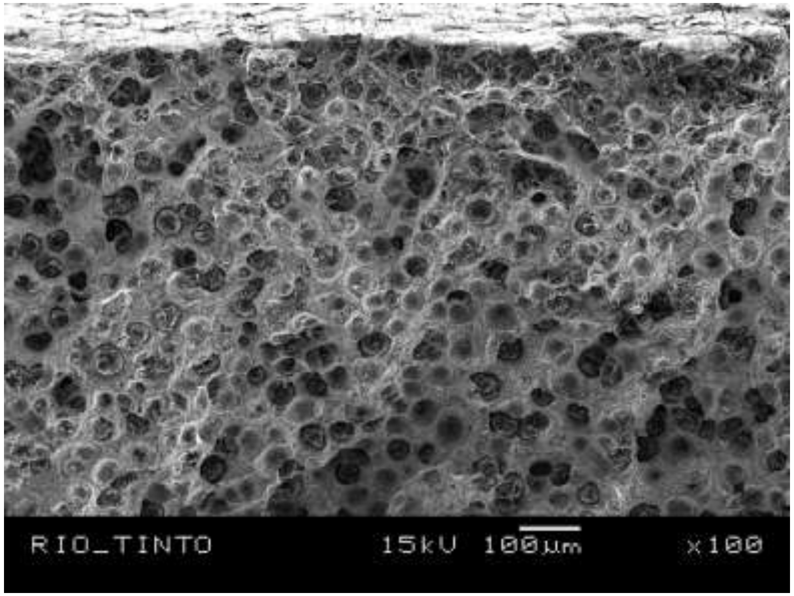
Low Ductility: Dross on Fracture Surface

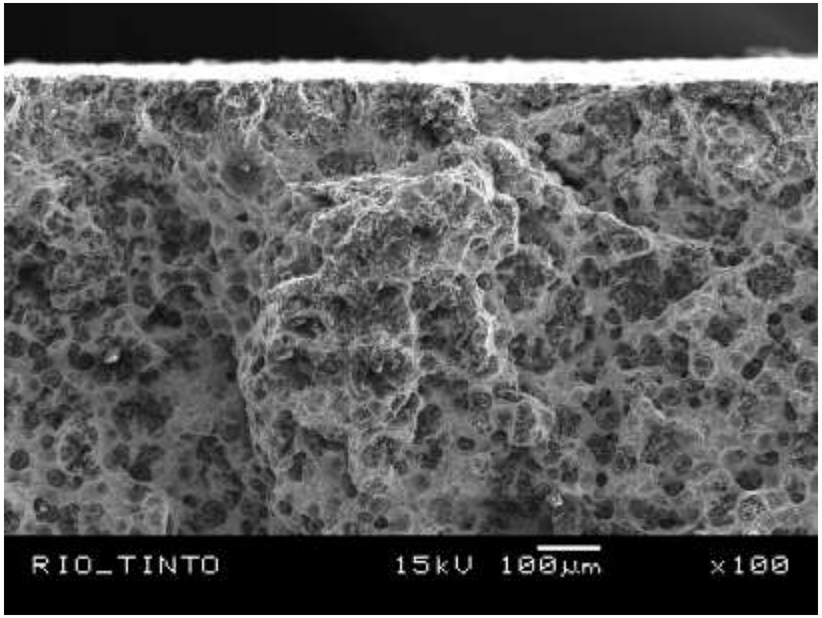


RioTinto

Effect of Dross on Mechanical Properties

Impact Energy: Dross on Fracture Surface





No Dross: 114 lb-ft

With Dross: 52 lb-ft

ADI: un-notched Charpy specimens

RioTinto

Effect of Dross on Mechanical Properties

Fatigue Strength

Defect	Rel. Fatigue Endurance
None	1.00
Dross	0,54
Micro shrinkage.	0,73
Macro shrinkage	0,50
Chunk graph.	0,75
Anomalies	0,83

RioTinto

Prevention/Minimization of Dross Formation: Thermodynamical Modelling

✓Thermodynamic simulations were carried out to determine the conditions favoring dross formation

✓General Parameters:

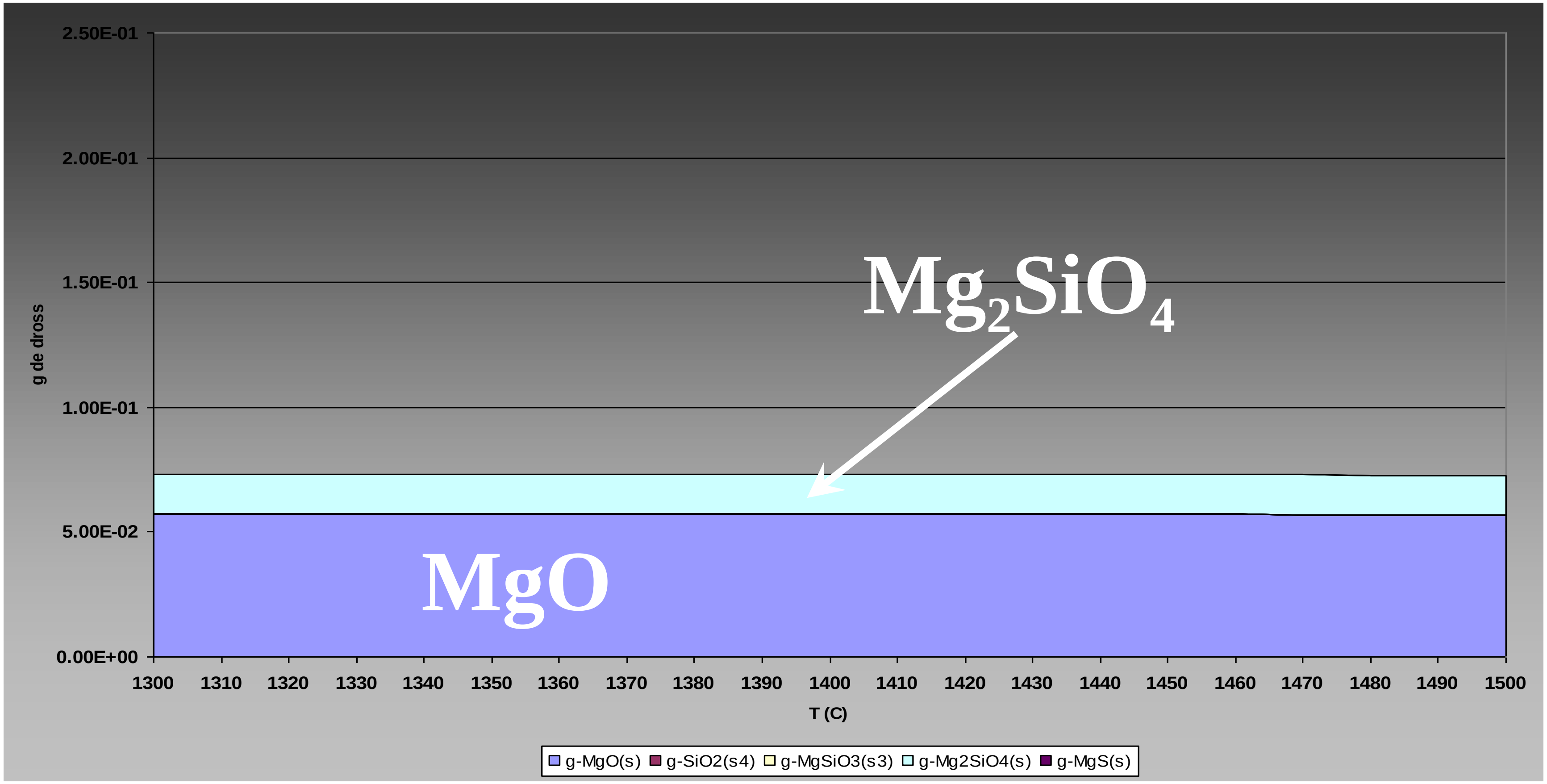
- %S : 0,010 & 0,020;
- %Si: 2,0 & 2,5;
- %Mg: 0,04 – 0,06%;
- Temp.: 1300 to 1500C;
- Oxygen: 10 to 1000 ppm.

✓Simulation by FactSage software (developed at École Polytechnique de Montréal); this software assumes equilibrium is reached.

RioTinto

Prevention/Minimization of Dross Formation: Thermodynamical Modelling

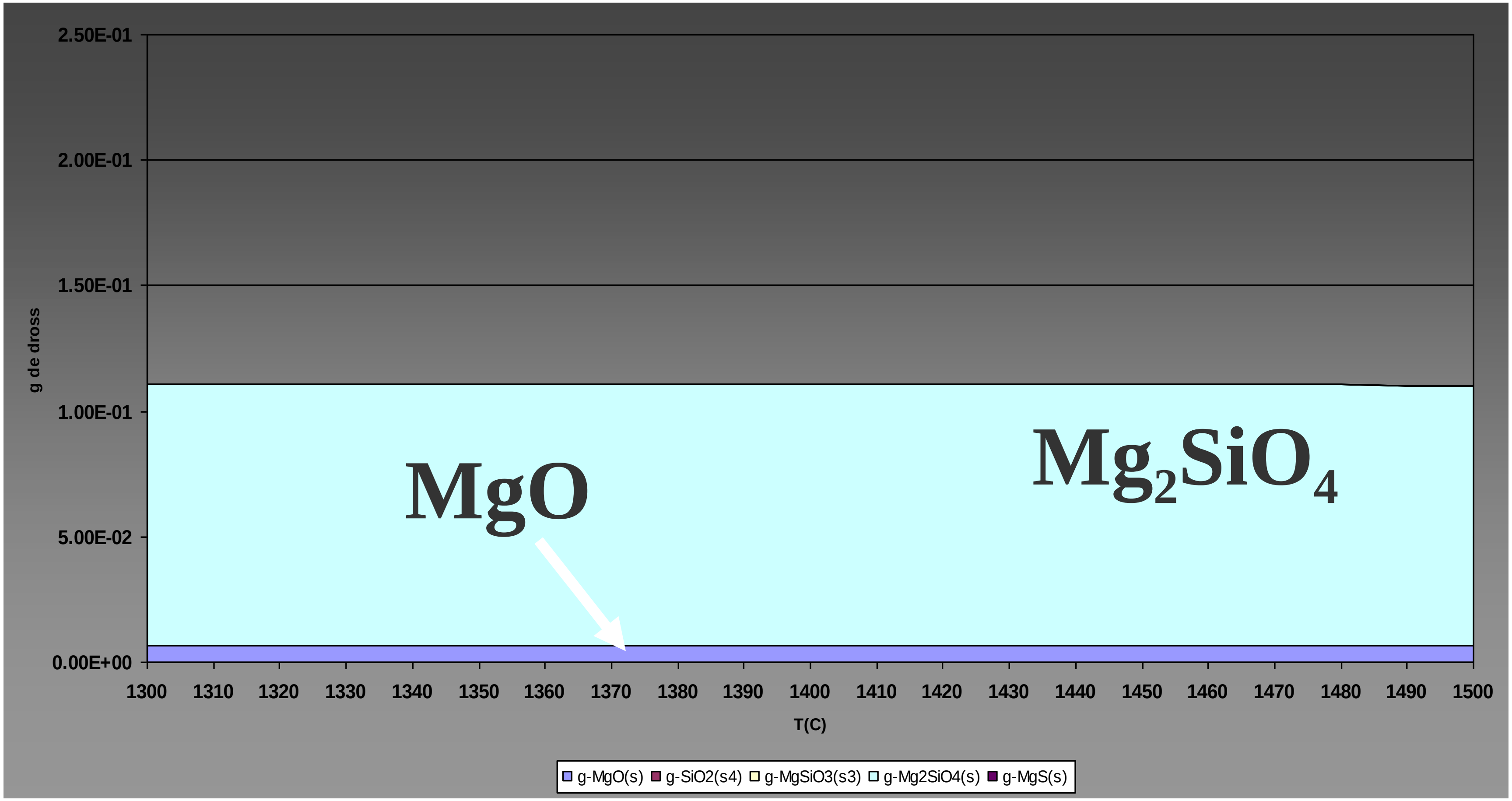
Dross formation vs Temperature for 0.04% Mg, 2% Si & 300ppm O_2



RioTinto

Prevention/Minimization of Dross Formation: Thermodynamical Modelling

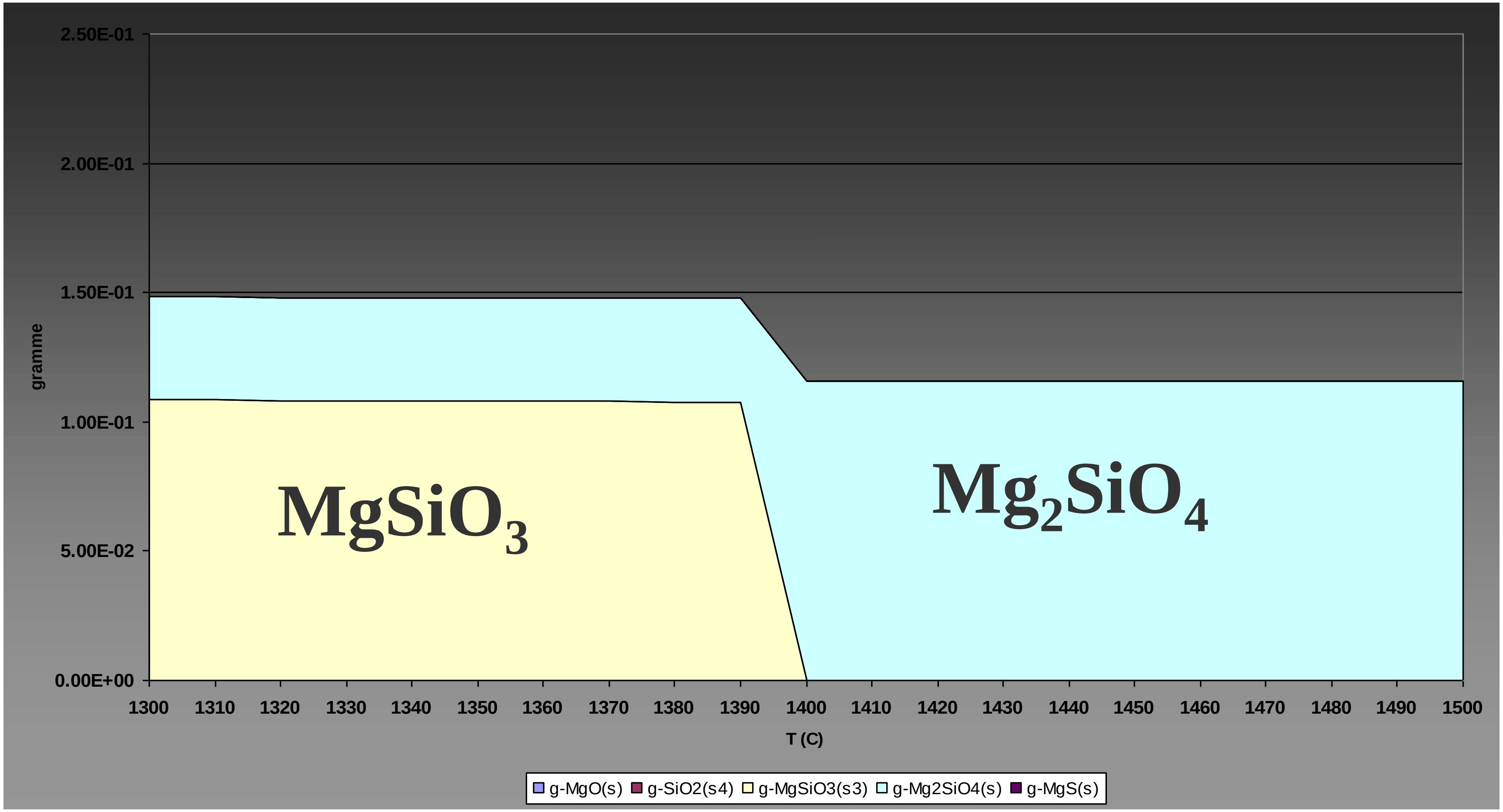
Dross formation vs Temperature for 0.04% Mg, 2% Si & 500ppm O_2



RioTinto

Prevention/Minimization of Dross Formation: Thermodynamical Modelling

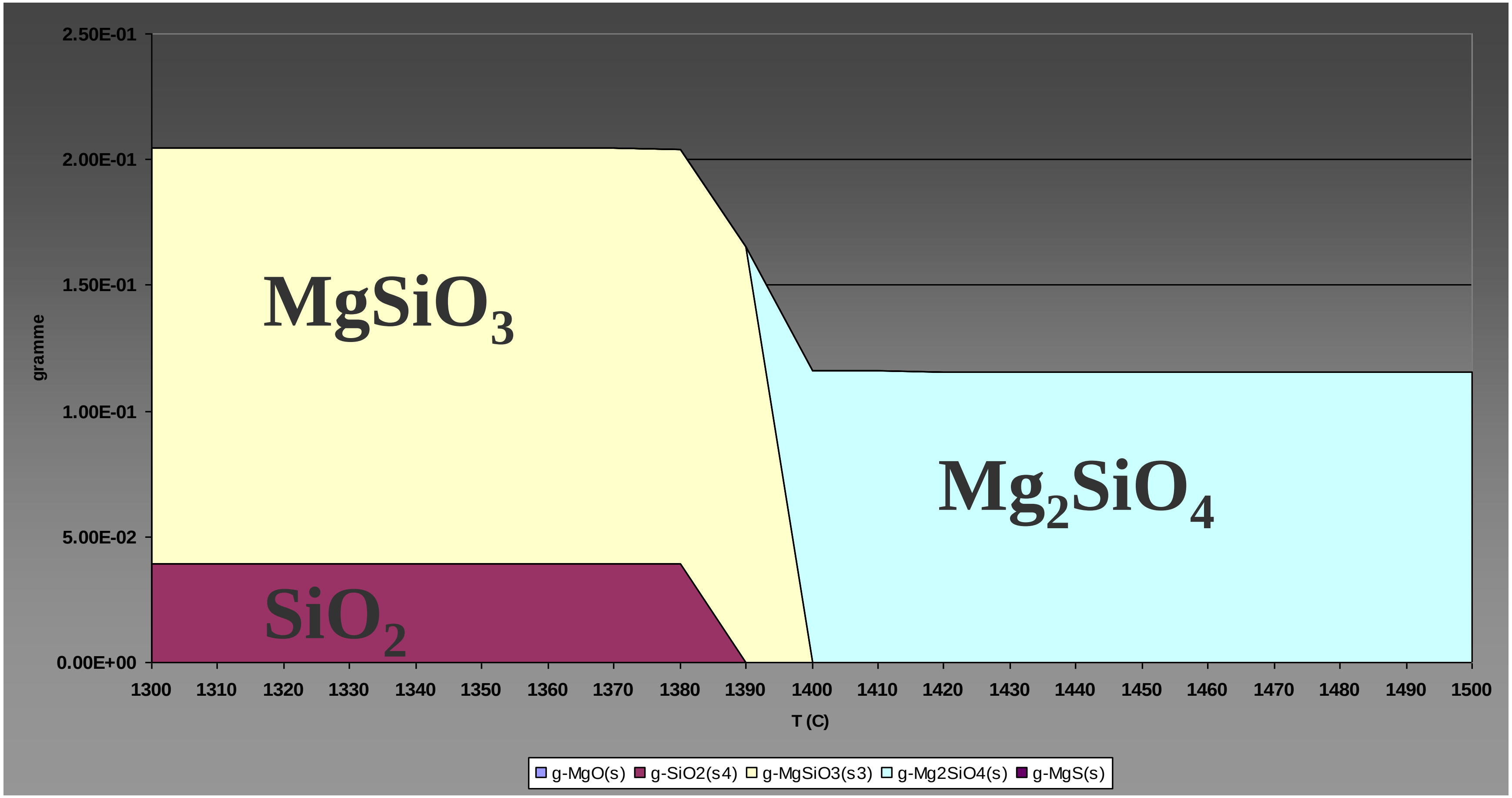
Dross formation vs Temperature for 0.04% Mg, 2% Si & 700ppm O_2



RioTinto

Prevention/Minimization of Dross Formation: Thermodynamical Modelling

Dross formation vs Temperature for 0.04% Mg, 2% Si & 1000ppm O_2



RioTinto

Prevention/Minimization of Dross Formation: Conclusions

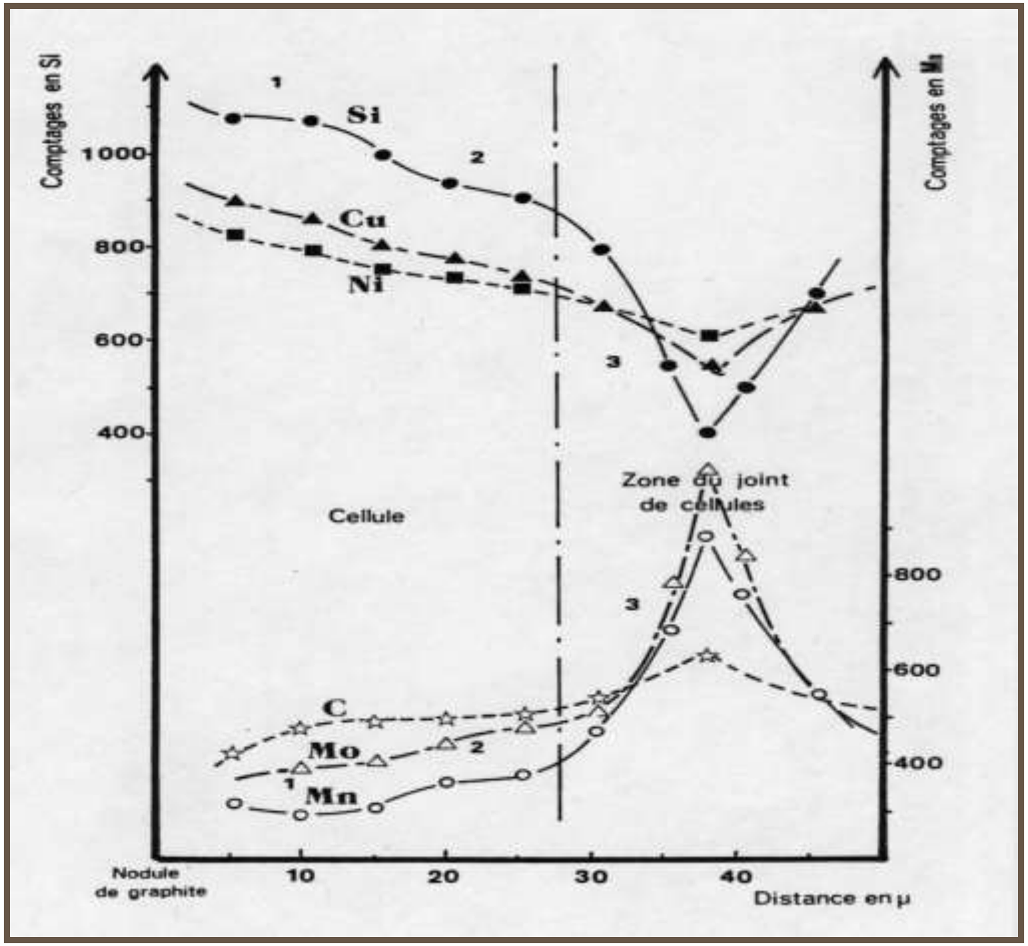
- ✓ **Formation of dross is mainly controlled by oxygen content; the level of oxygen required suggests that exposure to an external source of oxygen is needed: turbulence!**
- ✓ **Dross is mainly a "mixture" of magnesium silicates;**
- ✓ **Dross formation is favored by low pouring temperature, turbulence, high %Mg and high %Si;**
- ✓ **If all other parameters are kept under control, the effect of pouring temperature is minimum;**
- ✓ **Sulphur, at low level, does not interact with dross formation.**
- ✓ **Composition of dross changes with temperature.**

RioTinto

Intercellular Embrittling Phases

RioTinto

Intercellular Embrittling Structures: Result of Chemical Segregation



Segregation is the result of partitioning of elements at the solid-liquid interface.

Factors controlling segregation are:

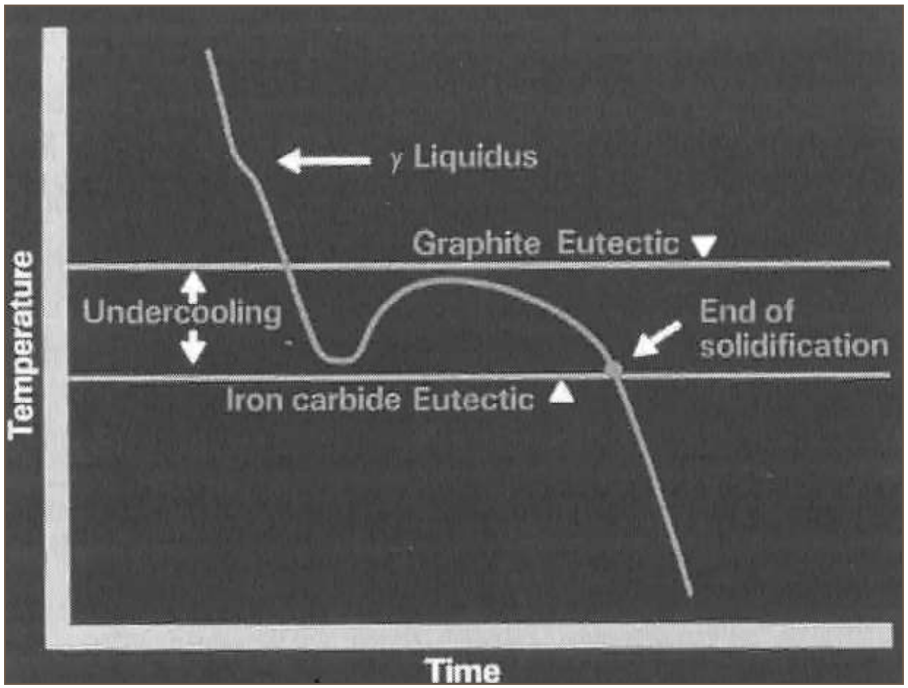
1. Concentration of the elements;
2. Solidification rate
3. Nucleation rate.

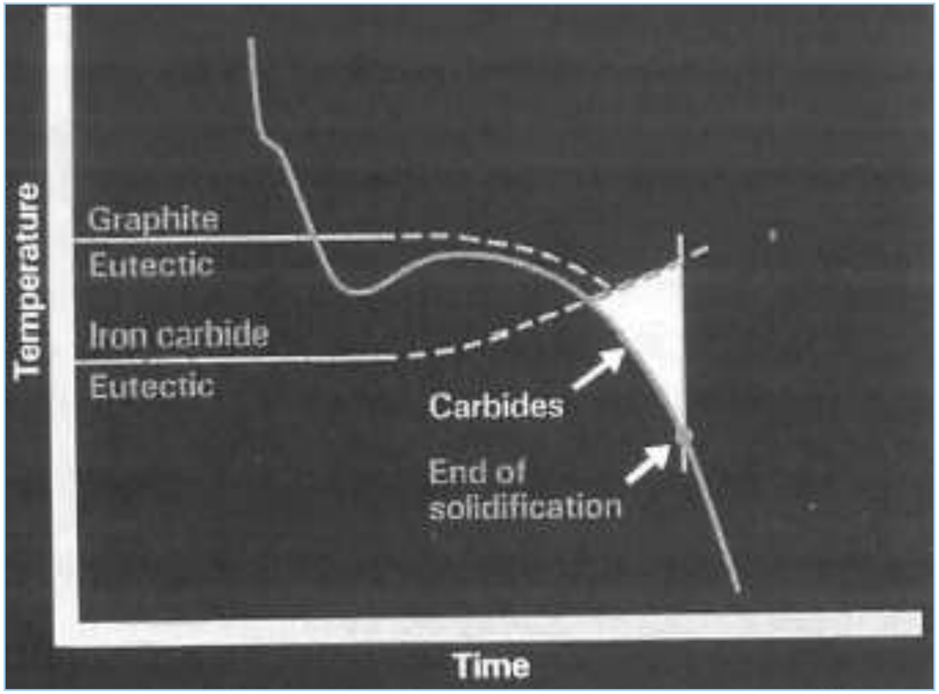
Major defects are:

1. Intercellular carbides
2. Intercellular Porosities
3. Intercellular flakes (not discussed below)

RioTinto

Intercellular Embrittling Structures: Solidification Model



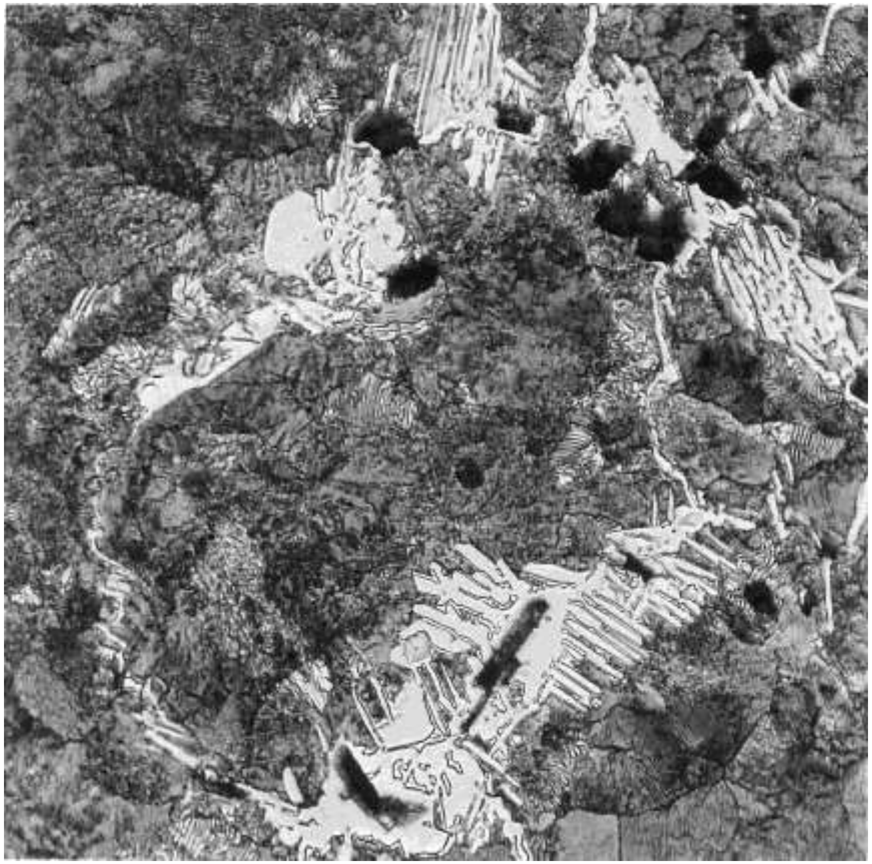


The first-to-freeze (FTF) volume has a composition differing from that of the LTF

Iron carbide and phosphide eutectic in last- to-freeze volume (LTF)

RioTinto

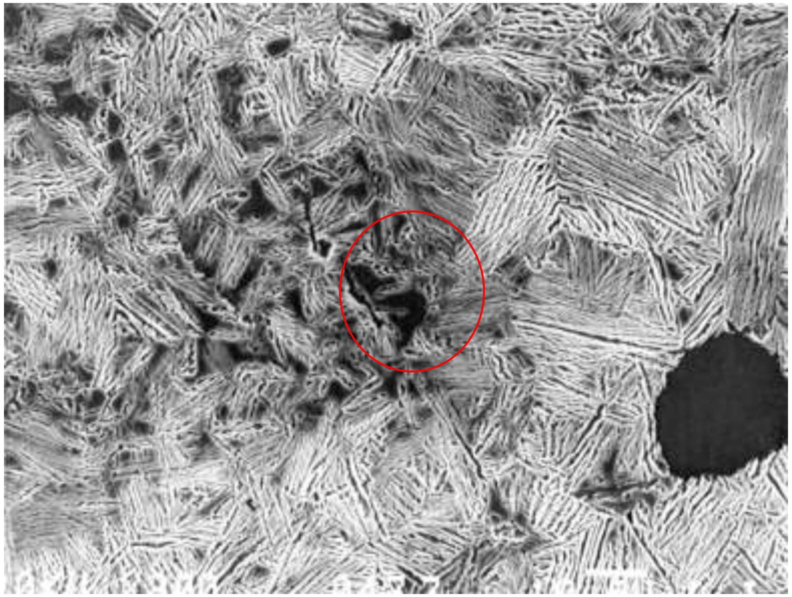
Intercellular Embrittling Structures: Example of Mn and Cr Segregation

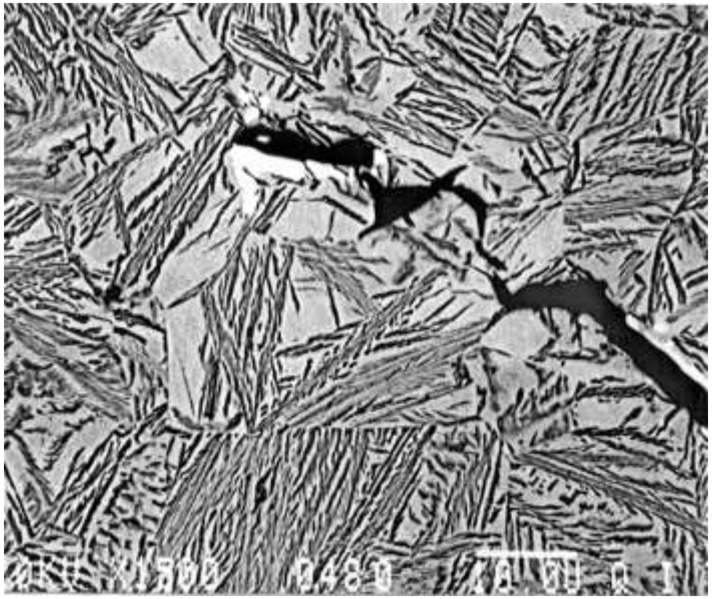


Intercellular Carbides in a 7,62 cm diameter Ductile Iron bar containing 0,4%Mn and 0,2% Cr; it is worth noting that the effects of Cr and Mn on carbide formation are synergetic, not simply additive!

RioTinto

Intercellular Embrittling Structures: Example of Mo Segregation

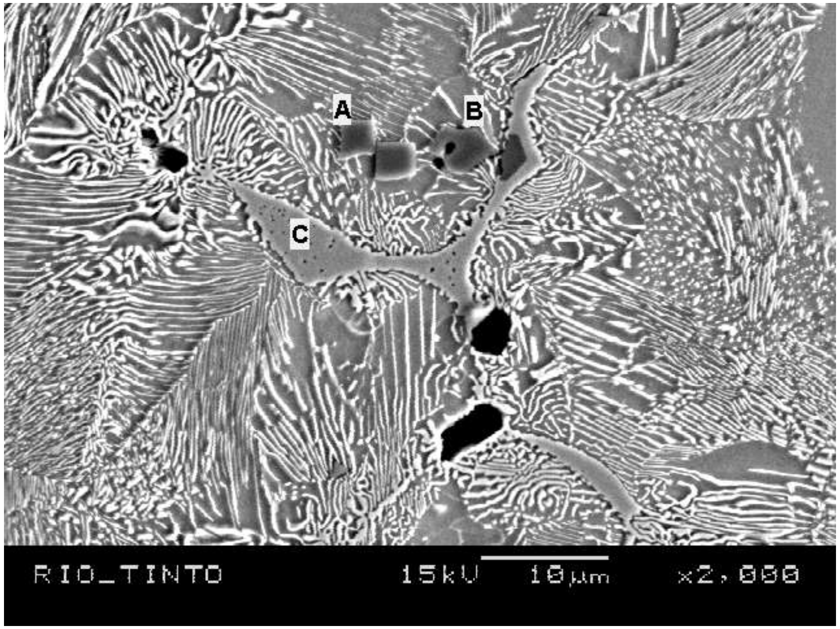


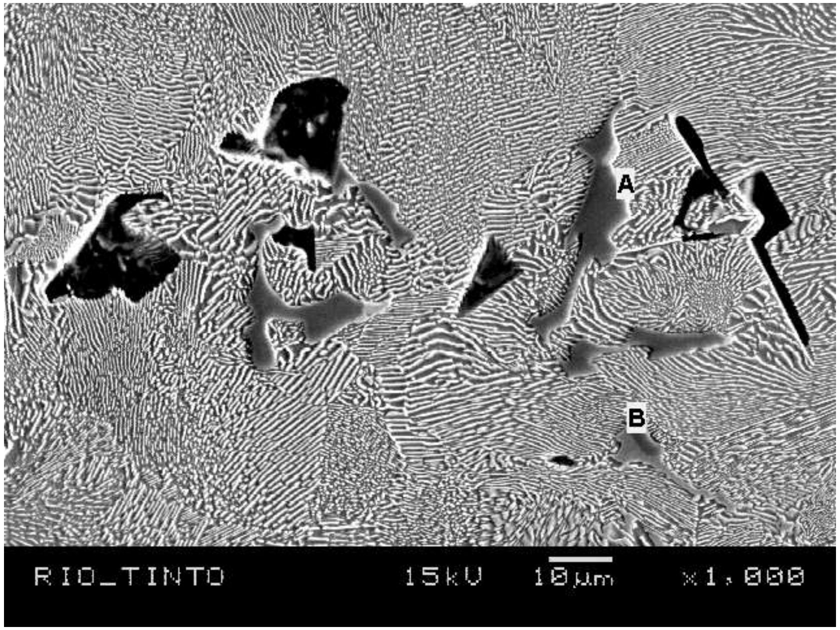


SEM image of Mo-rich intercellular phase in a 2,5 cm diameter cylinder containing1% Cu, 0,2% Mn, 0,2% Mo austempered at 360°C for 1 hour; the white phase on the right figure is Mo carbide.

RioTinto

Intercellular Embrittling Structures: Example of P Segregation

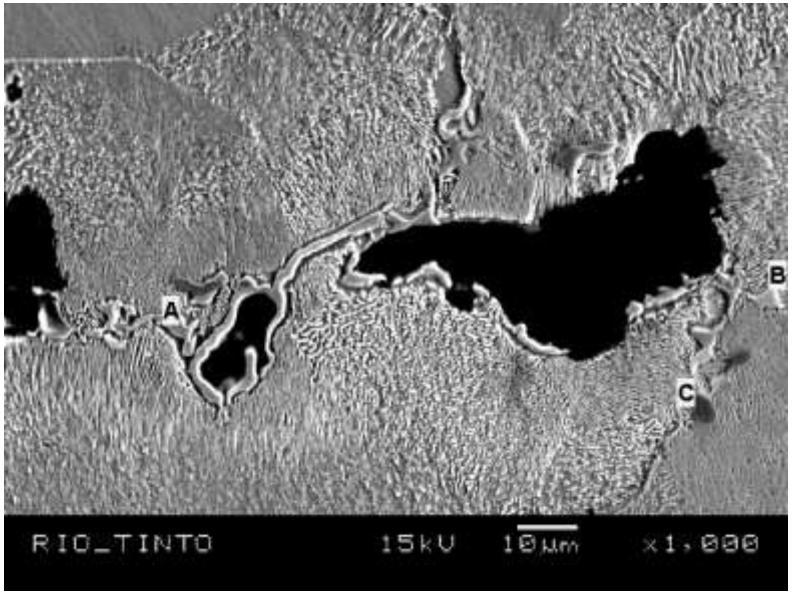




Complex Fe(P,C) particles at the cell boundaries of a 20 cm diameter Ductile Iron cylinfer containing **0,043%P**; the segregated intercellelular particles are containing up to **18%P**!

RioTinto

Intercellular Embrittling Structures: Example of Zr Segregation



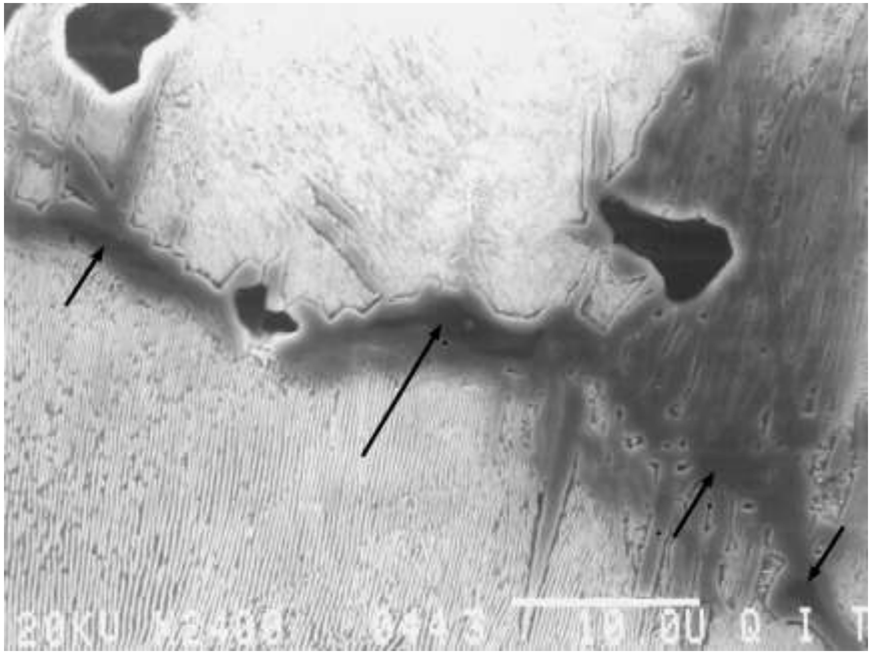
Bulk [ ]
Zr (0,004%)
Cr (0,04%)
V (0,02%)
Ti (0,009%)

(A) 1,74%Cr, 1,65%V
(B) 4,4%Cr, **76%Zr**, 13%Ti

Zirconium found in Ductile Iron castings typically originates from inoculants; although resulting in very low concentration in the casting, it is reported to strongly segregated to cell boundaries where it can be found in concentrations as high as 2000 times the bulk concentration!

RioTinto

Intercellular Embrittling Structures: Example of V Segregation



Segregated V-rich carbides found in a low nodule count 20 cm diameter Ductile Iron casting containing 0,024%V.

The arrows are pointing towards a darker central phase rich in V that serves as nuclei for the formation of an intercellular cementite network.

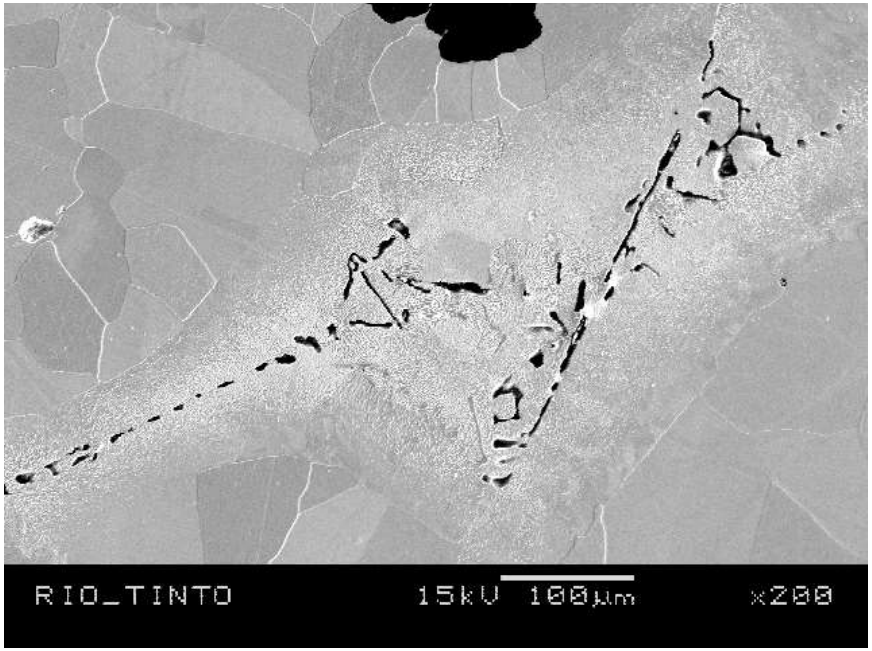
Rio Tinto

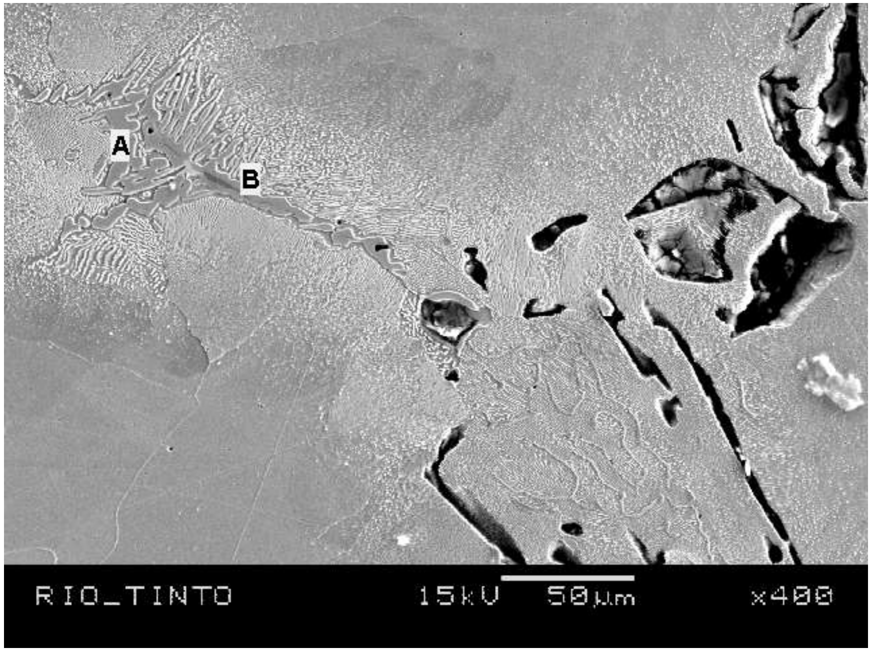
Intercellular Embrittling Structures: Other Elements to Control

- **Boron;**
- **Titanium;**
- **Niobium;**
- **Tellurium;**
- **…..**

RioTinto

Intercellular Embrittling Structures: Microshrinkage





Intercellular microshrinkage is often seen in intercellular regions, and more often in intercellular regions featuring intercellular pearlite/carbides. Carbides, which occupy a smaller volume than graphite + ferrite, are at least partially responsible of their formation.

RioTinto

Intercellular Embrittling Structures: Effect on Mechanical Properties

- Intercellular phases, either carbides or P rich conmpounds, increase the brittleness of the material and significantly reduce the machinability of the castings.
- Increasing phophorus content from 0,01% to 0,04% (resulting in steadite formation) was reported by Labrecque to decrease the tensile elongation from 22 to 16% and impact energy at room temperature from 18 to 8 joules. Similar effects will be produced by intercellular carbides.
- Microshrinkage at cell boundaries is reported to reduce the fatigue endurance limit by 25% and +, depanding on its extent.

RioTinto

Intercellular Embrittling Structures: Causes of Formation

- In heavy section Ductile Iron castings, a nodule count of 100 per mm2 should be targetted; a minimum nodule count of 50 is considered as an absolute minimmum. Therefore, an efficient inoculation process is a requirement for the production of heavy section Ductile Iron castings.

- The concentrations of carbide forming elements have to be maintained at a very low level because of the very high tendency of these elements to segregate to cell boundaries. As a consequence, the selection of charge materials is key to avoid/minimize the formation of intercellular embrittling phases. **A particular concern for Ductile Iron foundries then become the degradation of the steel scrap quality!**

RioTinto

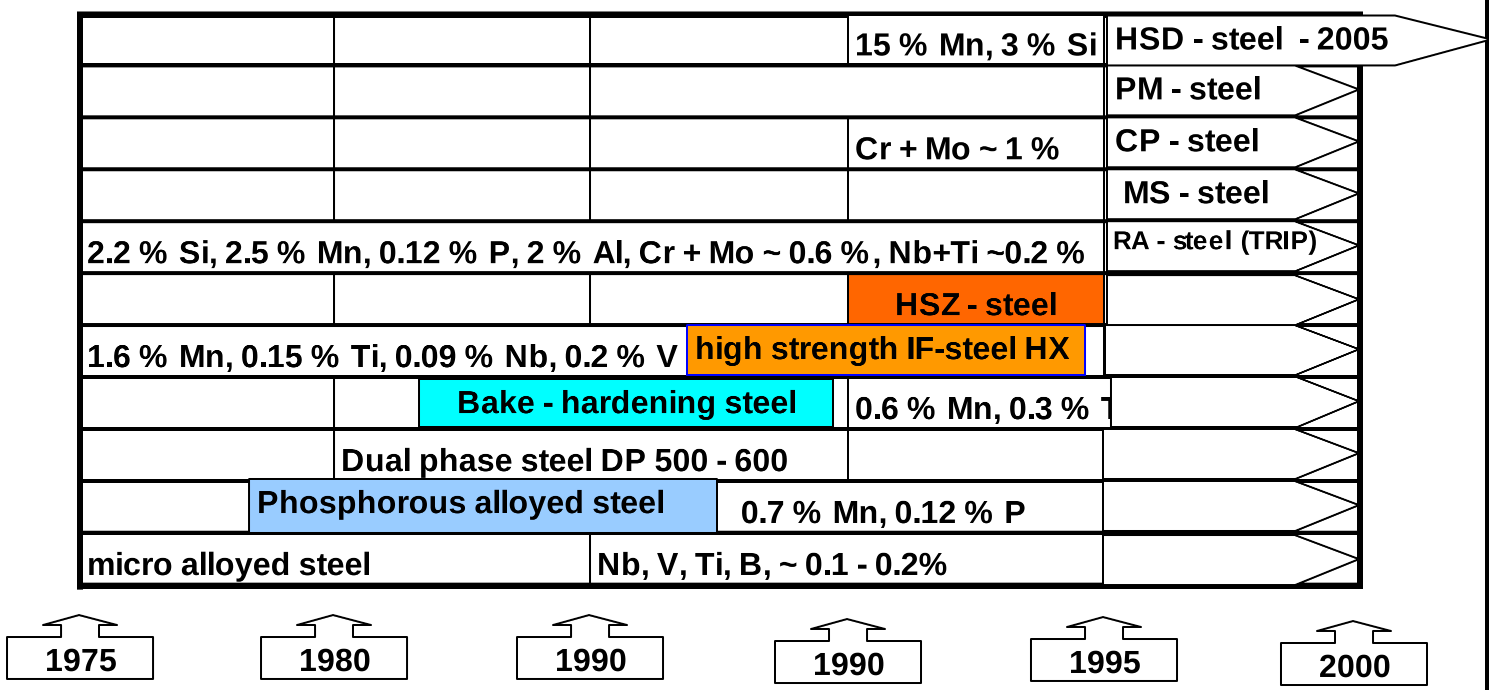
Intercellular Embrittling Structures: Recommended Concentrations

Element	Wt%	Comments
Boron	0,002	
Chromium	0,05	Lower if %Mn>0,3%
Manganese	0,3	0,2% for low T applications
Molybdenum	0,2	To avoid, if possible, in ADI
Phosphorus	0,03	Lower for low T applications
Titanium	0,05	
Vanadium	0,03	
Zirconium	0,003	Originate from inoculants

Steel Scrap Quality: Evolution of Steel Composition

Steelscrap - Analyses changes over the years

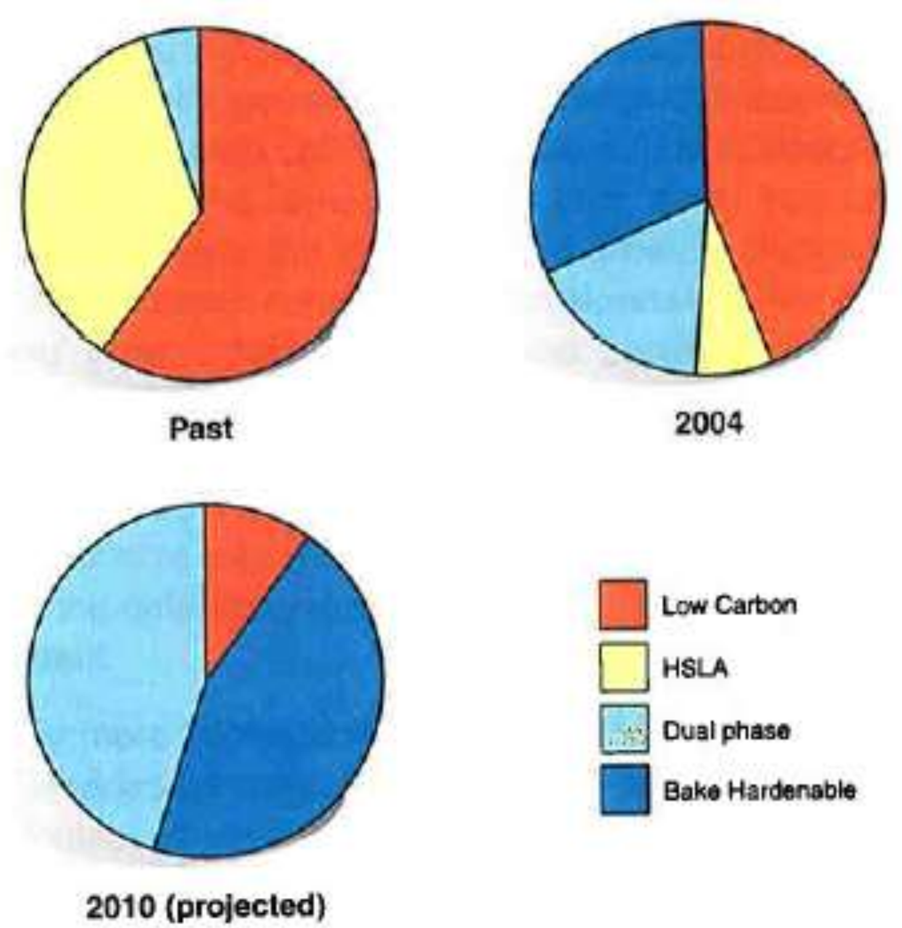
Development of high strength steel scrap over the years



ref.: TKS

RioTinto

Steel Scrap Quality: Evolution of Steel Composition in North American Auto Industry



RioTinto

Concluding Remarks

- The market for heavy section Ductile Iron castings expands because of the unique combination of castability and mechanical properties of this material.
- The sringent requirements for such castings, particularly in the wind energy sector demands a high level of quality that means that structural defects must be avoided/minimized.
- The major defects to prevent are chunk graphite, dross and intercellular embrittling phases. As shown previously, these can be maintained at a very low level in the castings if the foundryman carefully control its processes and the chemical composition of the castings.

Rio Tinto

Mersi!

Ankiros, Istanbul, Turkey

October 2008