Some Observations of the Role and Importance of Oxide Films in Castings.

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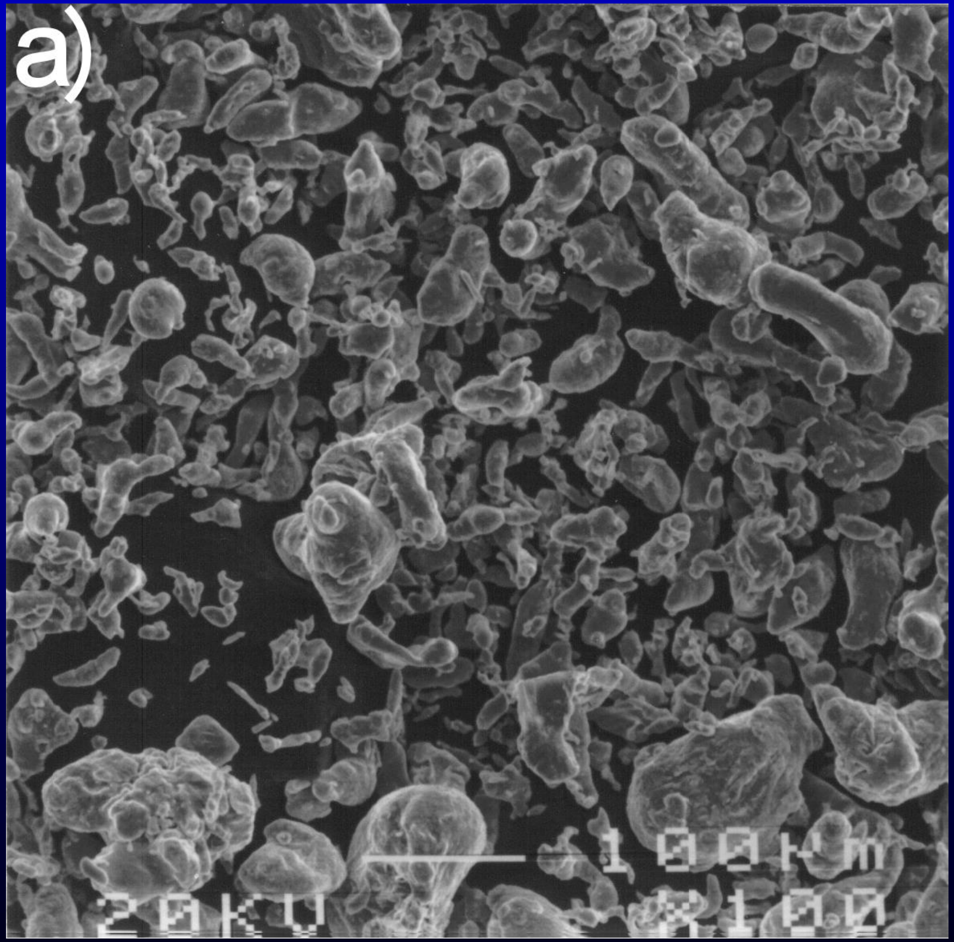
Todays Presentation

- The oxide problem for sintering aluminium.
- The role of magnesium
- Heat treatment of High Pressure Diecastings and the mechanism of blister formation.
- Complex defect structures.
- Defect Hierarchies
- Investment cast aluminium.
- Some other materials of interest.
- Different kinds of oxides.

The Oxide Problem for Sintering Aluminium

- **Al powders have about 0.5% by weight of oxide.**



So how can they be successfully sintered?
Each powder has an oxide layer corresponding to its surface.
Reducing atmospheres required are not achievable.

Evidence for a role of Mg_3N_2 (similar to vacuum brazing) but then requires interconnected porosity.

R.Lumley, 1998

Role of Magnesium

Al-XMg

Mg 0 to 1.5%
Bal. Al.

Minimum to no transient liquid phases.

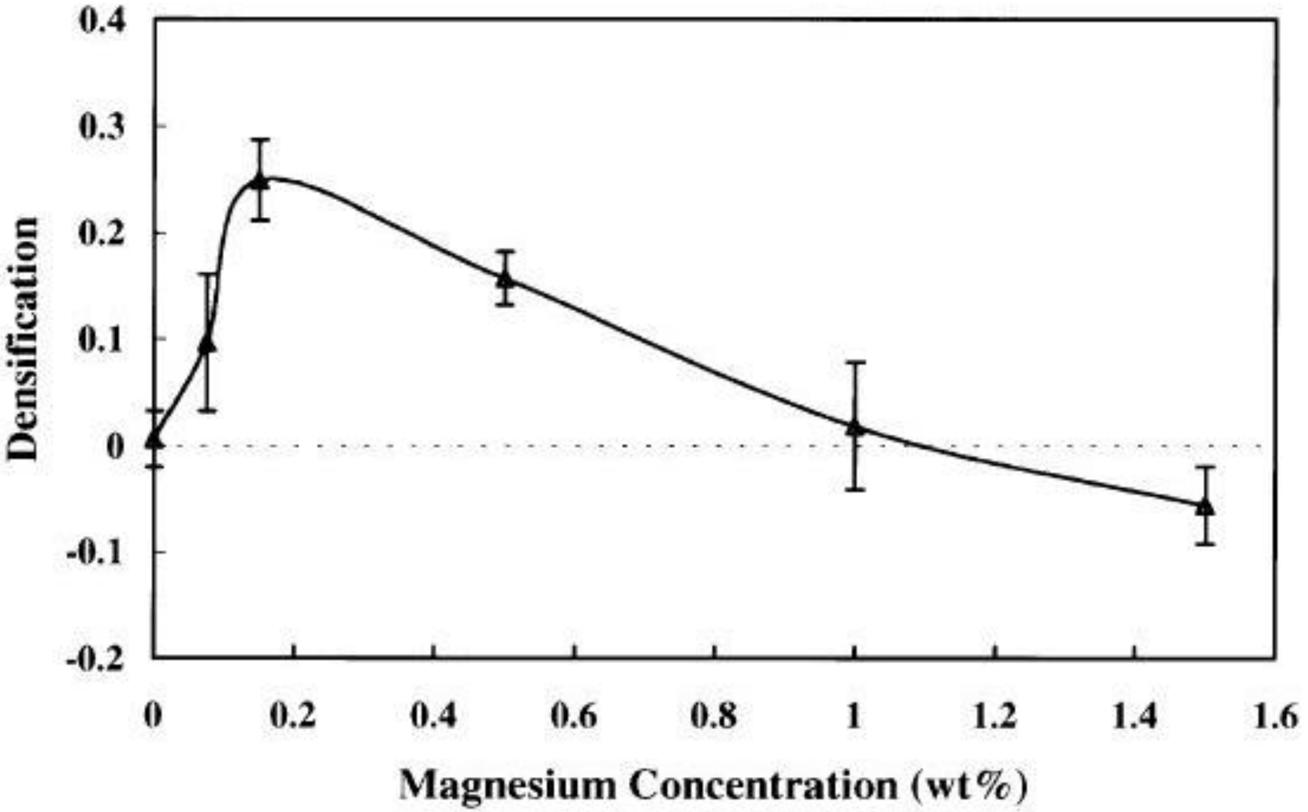
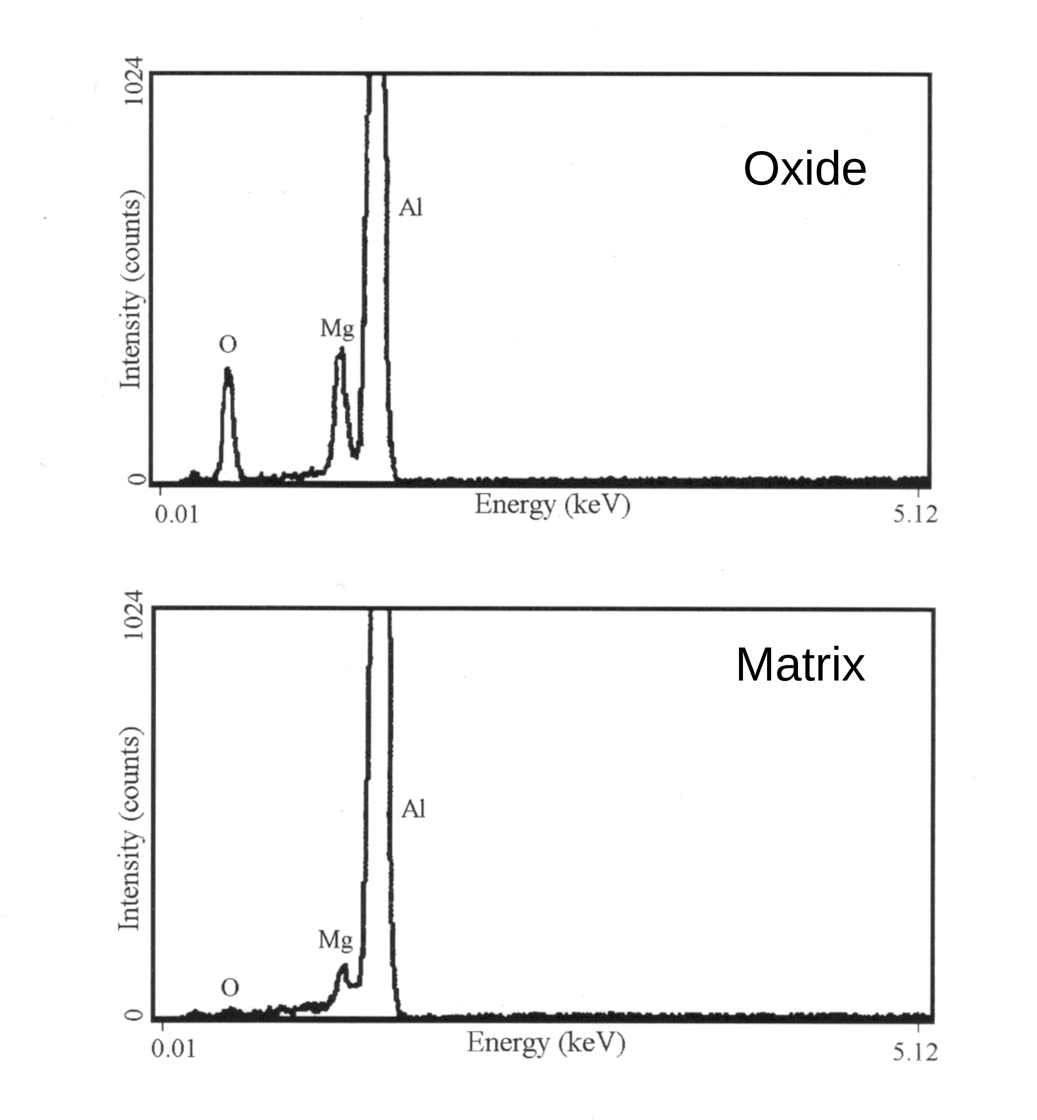


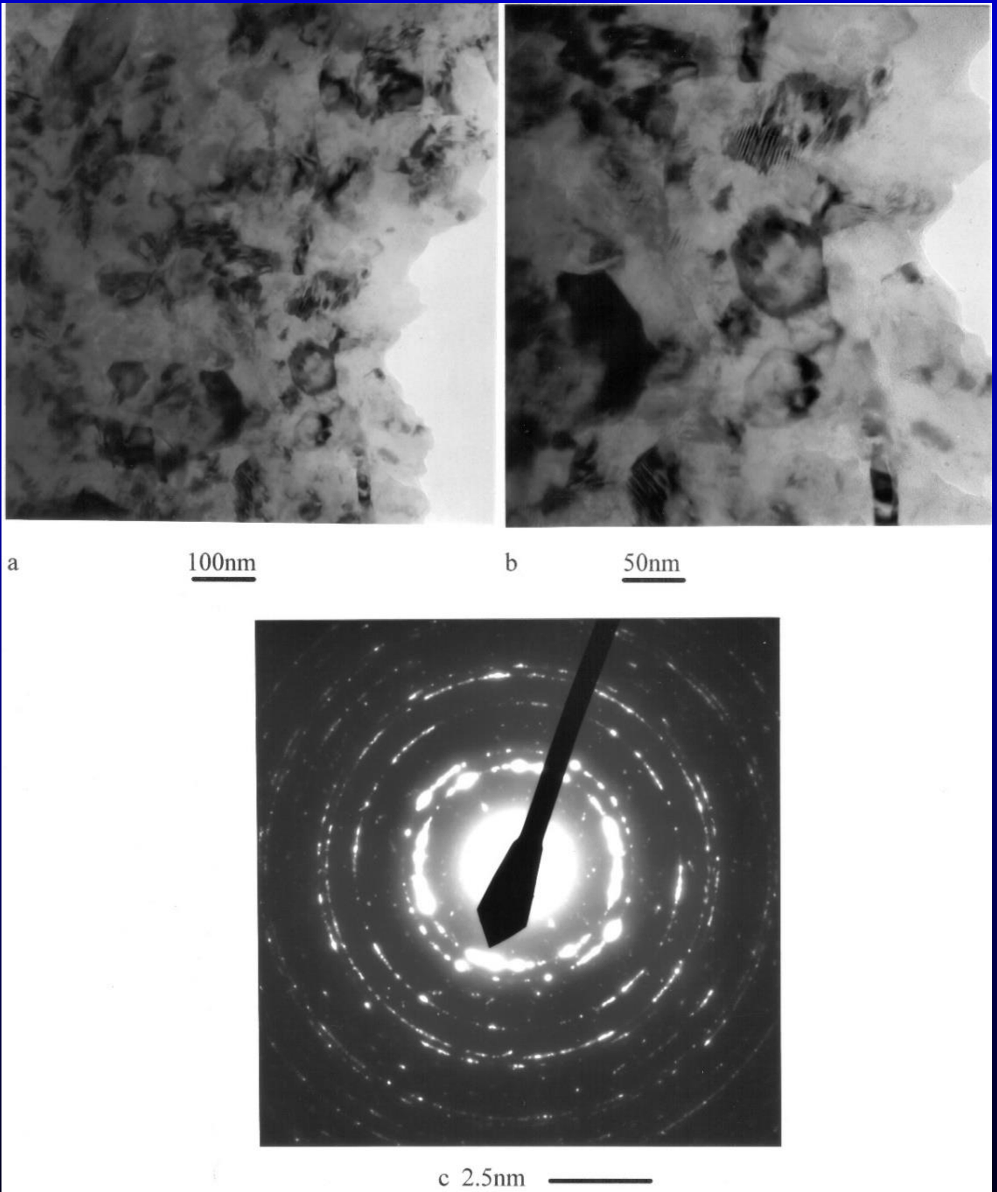
Fig. 2—The effect of magnesium on the densification of aluminum powder. The densification is maximized at 0.15 pct Mg, and there is net expansion at concentrations > 1 pct (the densification is defined by Eq. [7]; positive numbers indicate shrinkage). The samples were pressed at 200 MPa, dewaxed at 200 °C, heated at 20 °C/min, sintered at 620 °C for 30 min, and air cooled.

R.N Lumley, T.B Sercombe and G.B Schaffer, Surface Oxide and the role of Magnesium During the Sintering of Aluminium, Metallurgical and Materials Transactions A, 30A, (2), 457-463, 1999.

Role of Magnesium



Spinel forms as fine crystals where oxide films were.

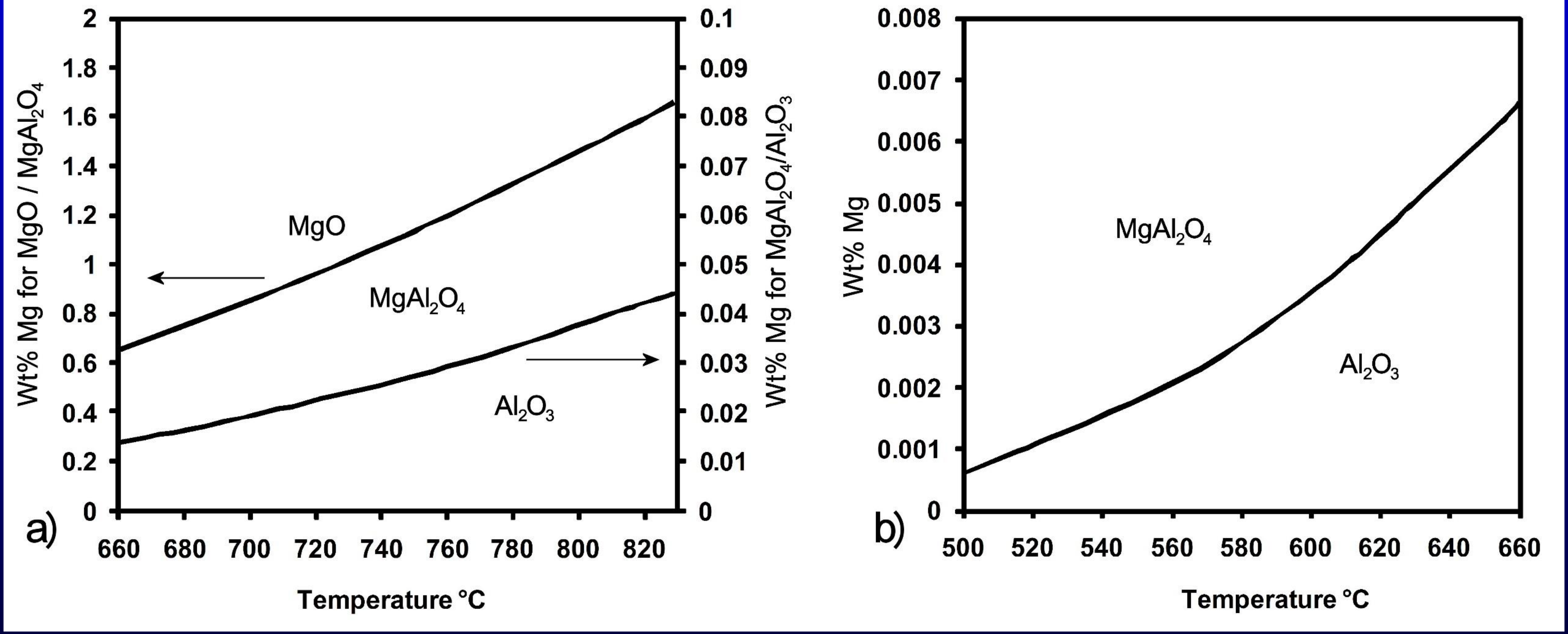


R. Lumley et.al 1999

Mg reacts with Al_20_3 to partially reduce the oxide

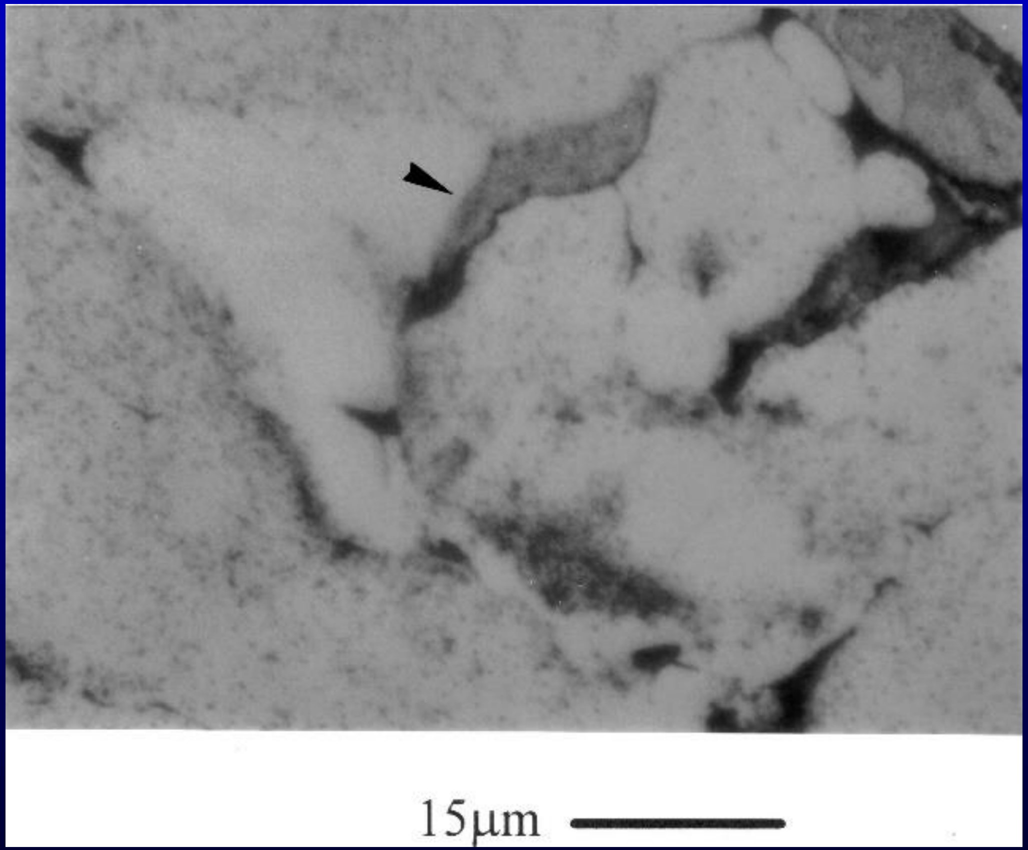
-
- $3Mg + 4Al_2O_3 \rightarrow 3MgAl_2O_4 + 2Al$ (more favourable at <2%Mg)
- Or
- $3Mg + Al_2O_3 \rightarrow 3\ MgO + 2Al$ (More favourable above 4%Mg)

Stability of Oxides in Al-Mg Alloys.



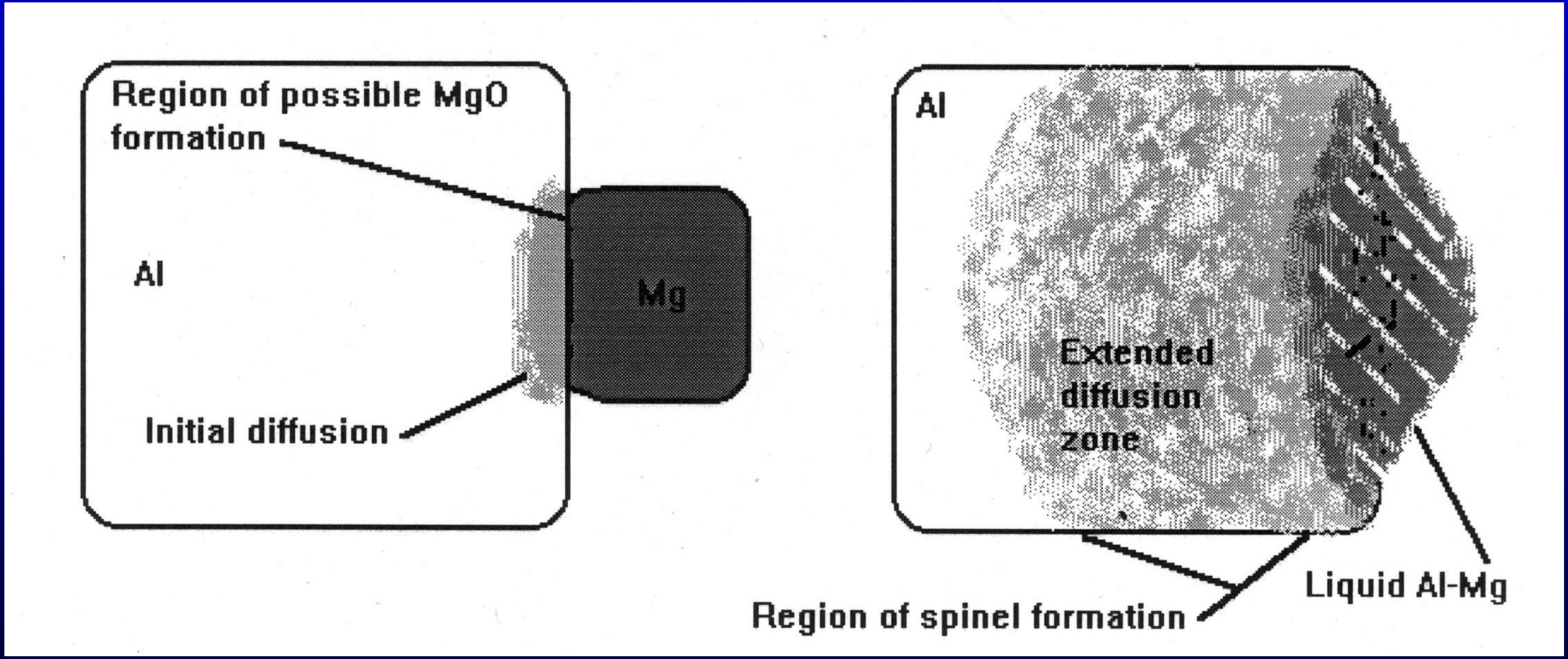
Thermodynamic stability of Al-Mg oxides in Al-Mg alloys; (a) liquid alloys, (b) solid state.
(From Mc Leod and Gabryel).

Magnesium diffuses rapidly below 500°C and reacts with oxides.



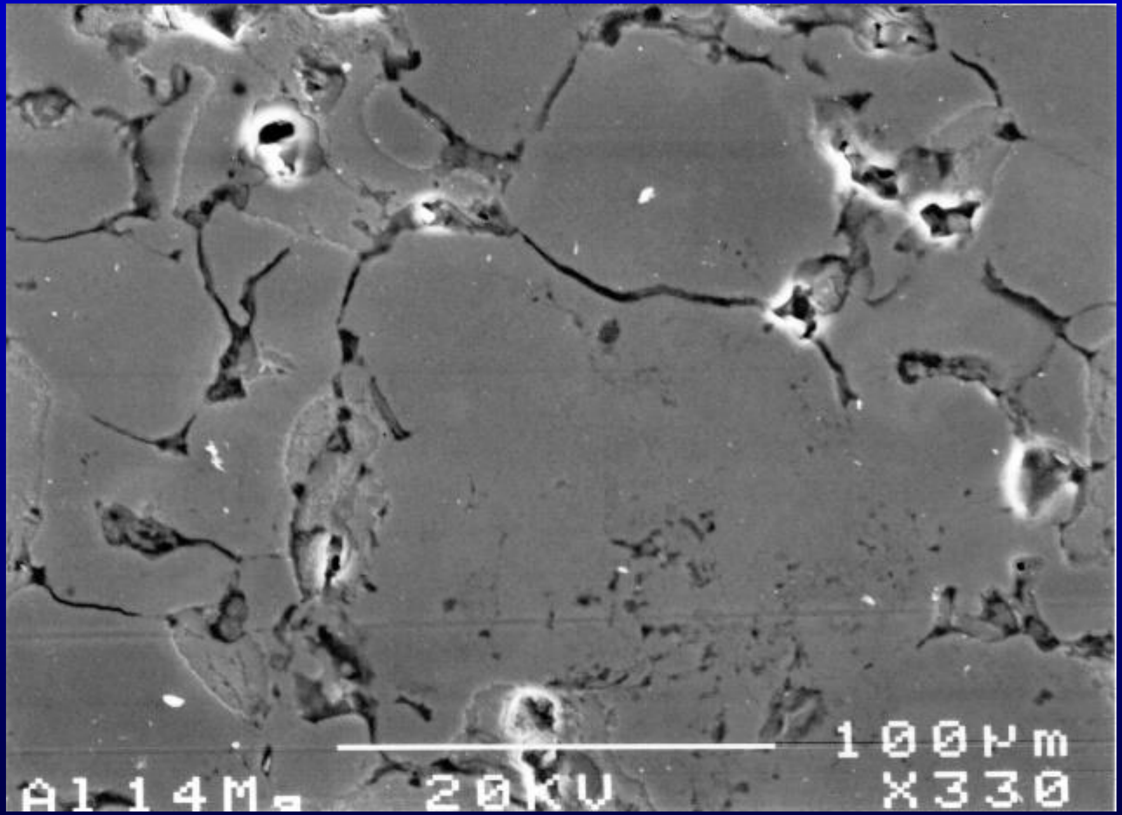
Diffusivity of Mg in Al is 1.2cm^2/sec at between 300 and 550°C

Mechanism of spinel formation in the presence of a liquid



Al-Mg Eutectic temperature 437 / 450°C

Magnesium diffuses extremely quickly



10°C to 465°C Al-14Mg

Diffusivity of Mg in Al is 1.2cm^2/sec at between 300 and 550°C

Mechanism of spinel formation in the solid state:

1. Diffusion of magnesium is so fast it can interact with nearly all of the Al_2O_3 present within a few (e.g. 1-2) minutes where there is intimate contact with at least one metal oxide interface.

2. In the presence of Mg, the Al_2O_3 undergoes an energetically favourable reduction reaction to form fine spinel crystals and aluminium. The product is discontinuous.

Consequences to thermal processing

- When cooling from casting, how mobile are the Mg atoms and for how long?
- (Remember diffusivity > 1.2cm^2/sec at between 300 and 550°C.)
- It appears very likely most oxide with one intimate interface might be converted.

- Anything left is likely influenced during solution heat treatment.
- (e.g. solution treatment 540°C 8h.)
- What is the probability oxides are <u>not</u> converted to spinel?

Conclusion.

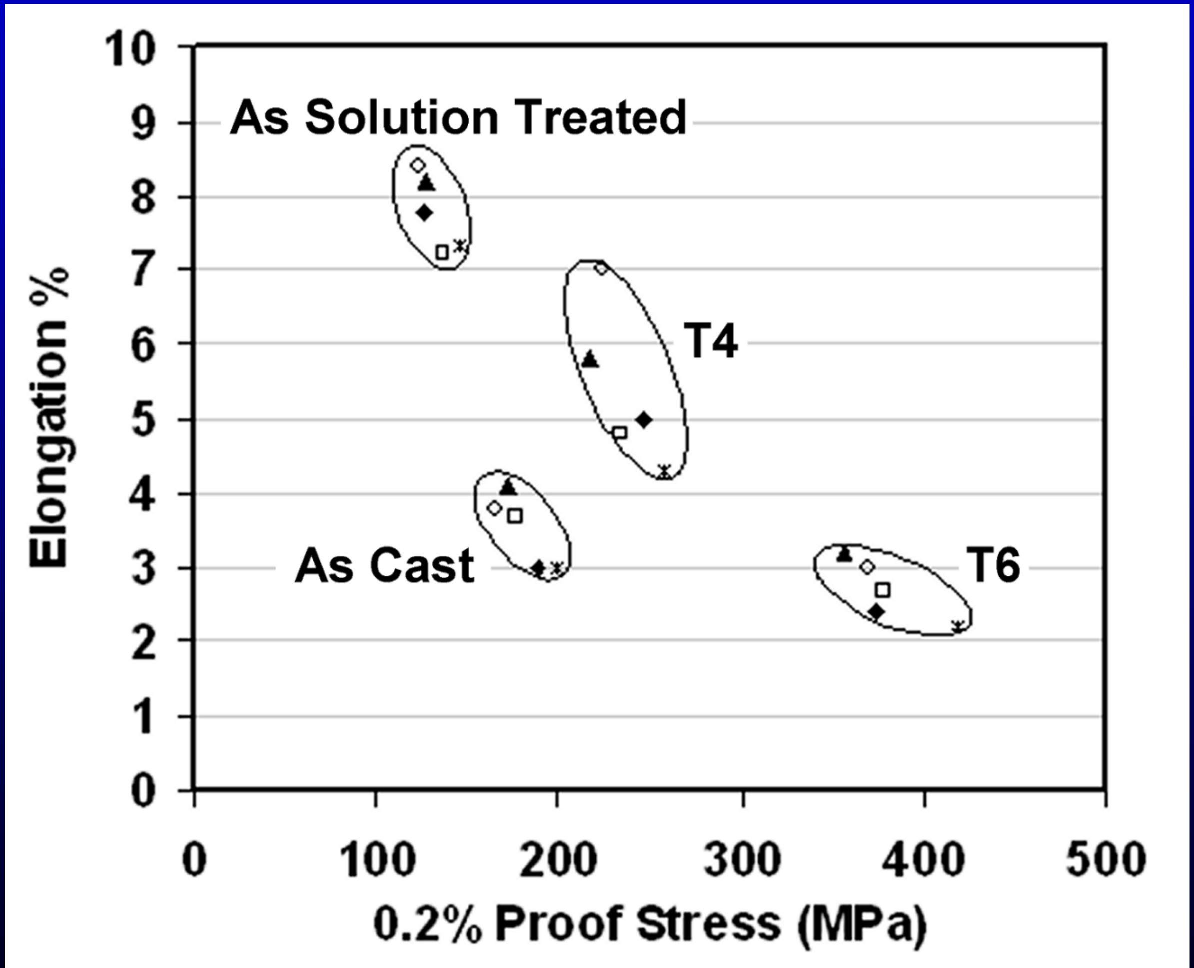
- Magnesium plays a critical role in the disruption of the alumina layer present on all aluminium. This occurs due to the solid state (partial) reduction of the γ-alumina to spinel.

- $3Mg + 4Al_2O_3 \rightarrow 3MgAl_2O_4 + 2Al$

- Most oxides present in molten aluminium where Mg is present are spinel types.
- In the solid state, alumina can also be transformed to fine spinel crystals within a discontinuous matrix via a partial reduction reaction. This also occurs at temperatures suitable for solution treatment.

Studies of Heat Treatment of High Pressure Diecastings

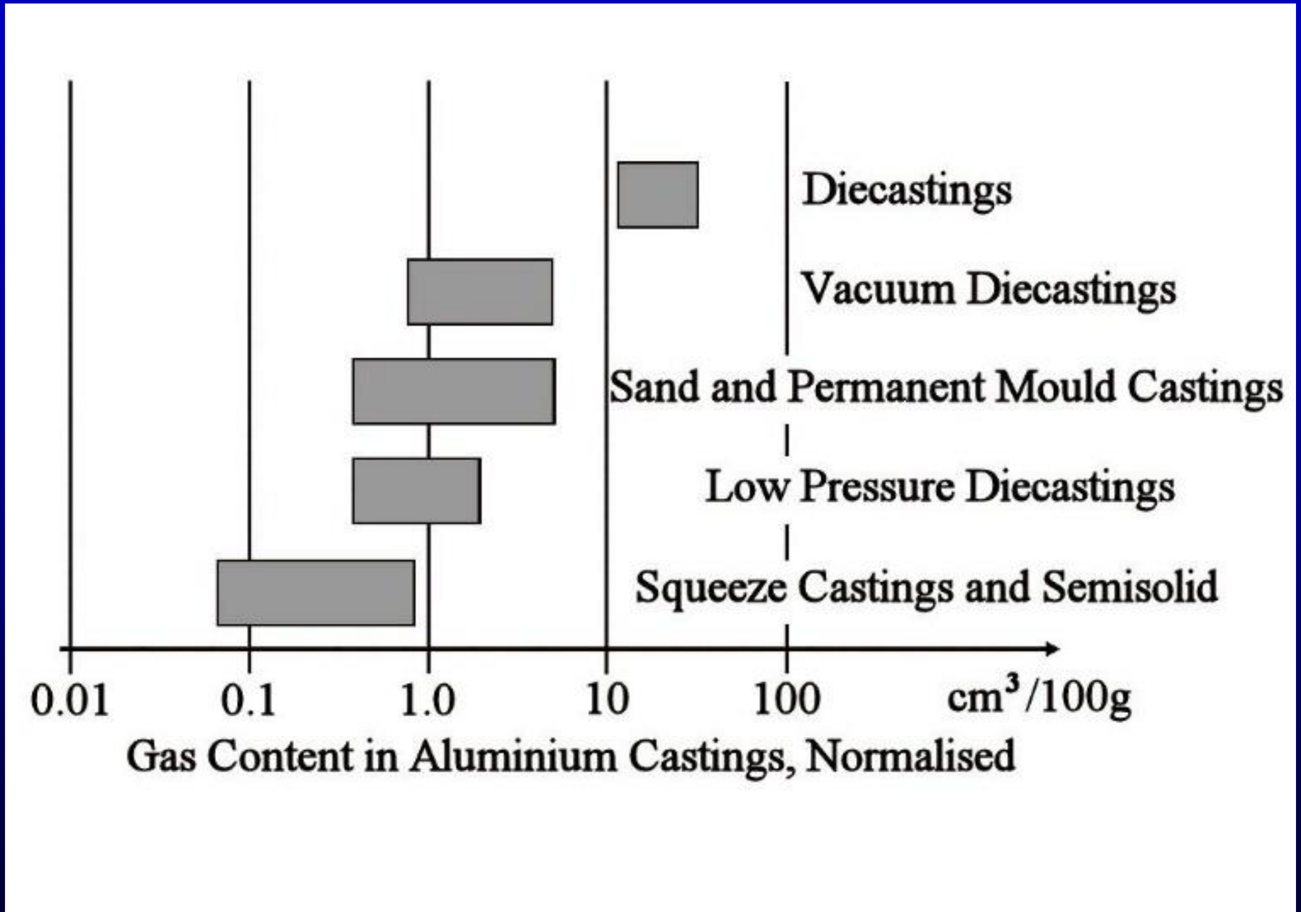
Properties of heat treated HPDC's may be excellent



A very short solution treatment is sufficient to produce major property enhancements without blistering.

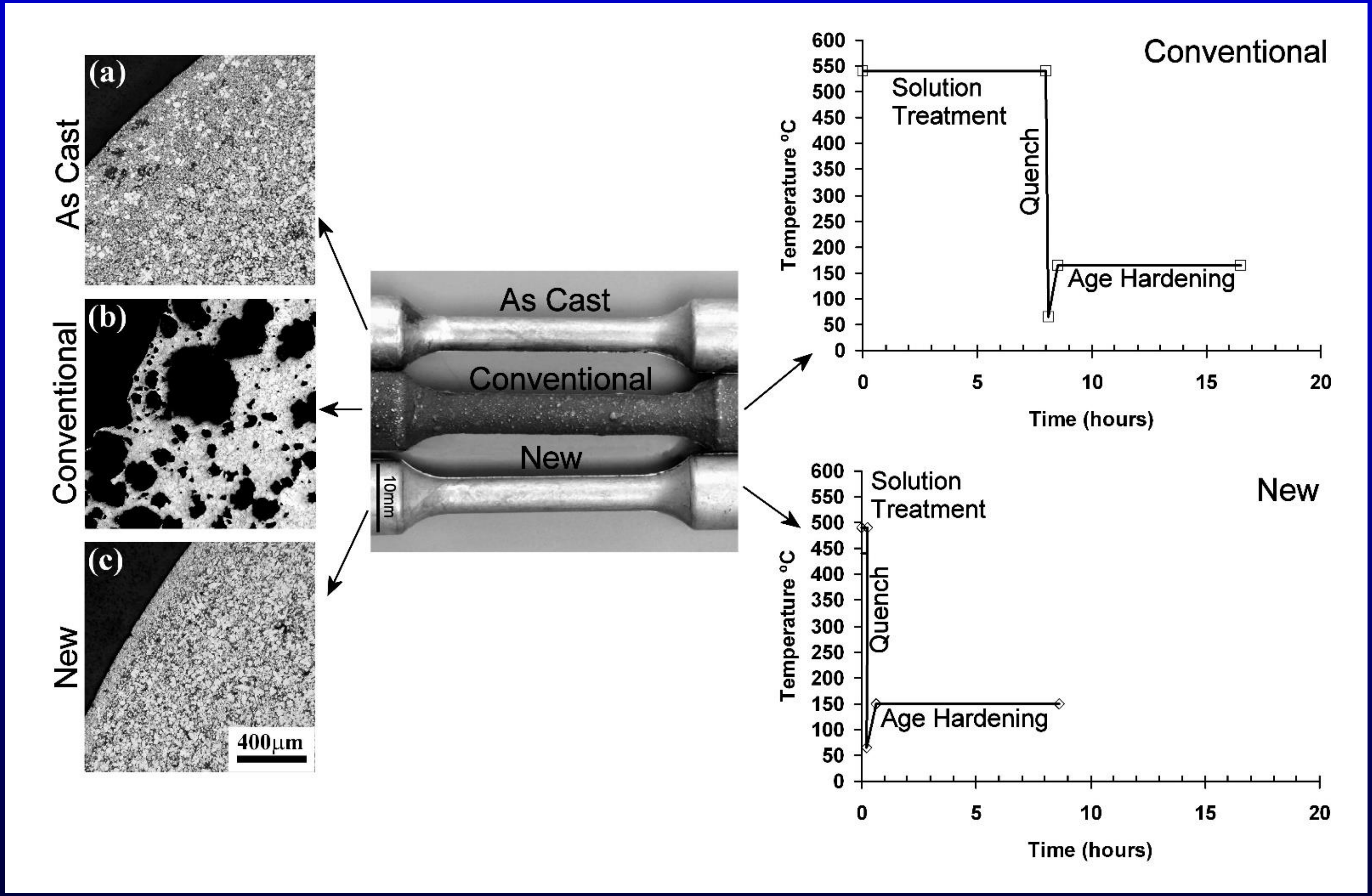
Lumley et.al. 2006

Diecastings have lots of gas!



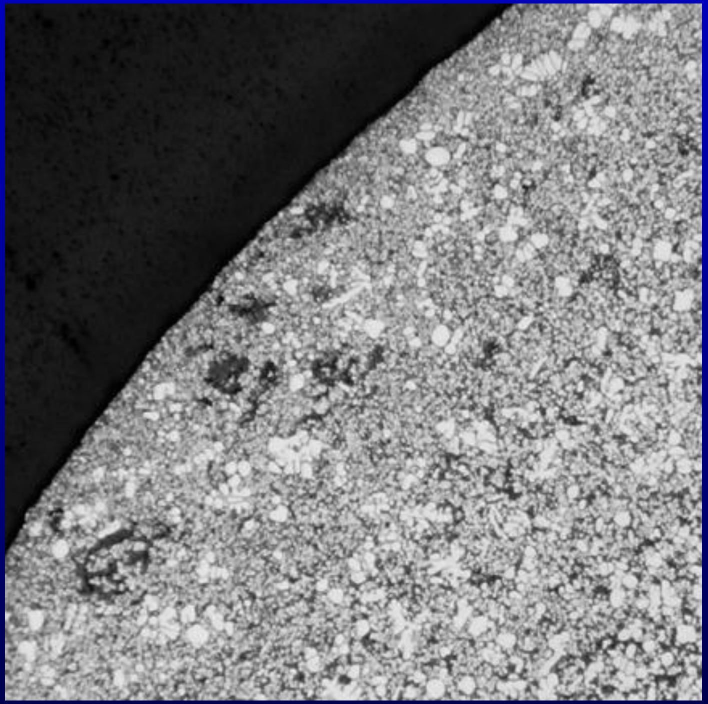
Bonollo et.al, 2002

The Process



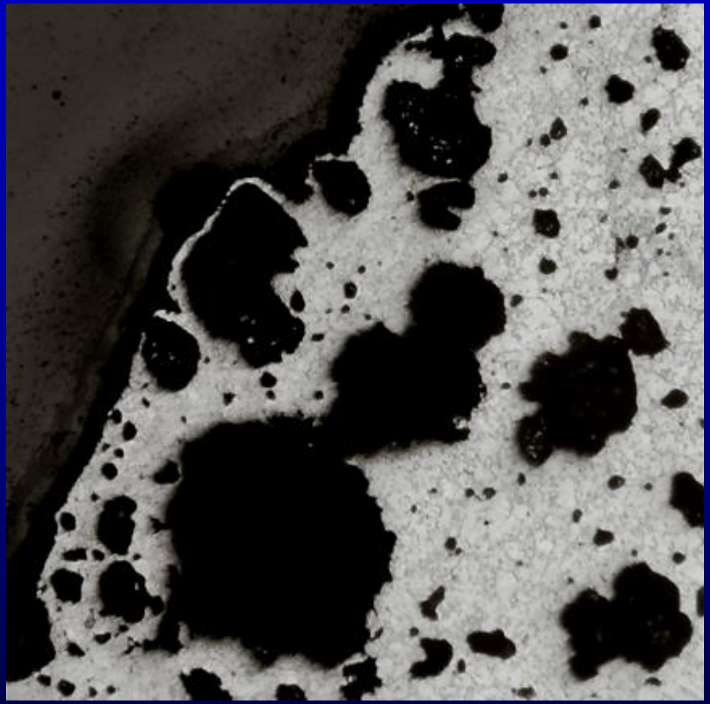
R.N. Lumley et.al 2005-2010

Blister Formation



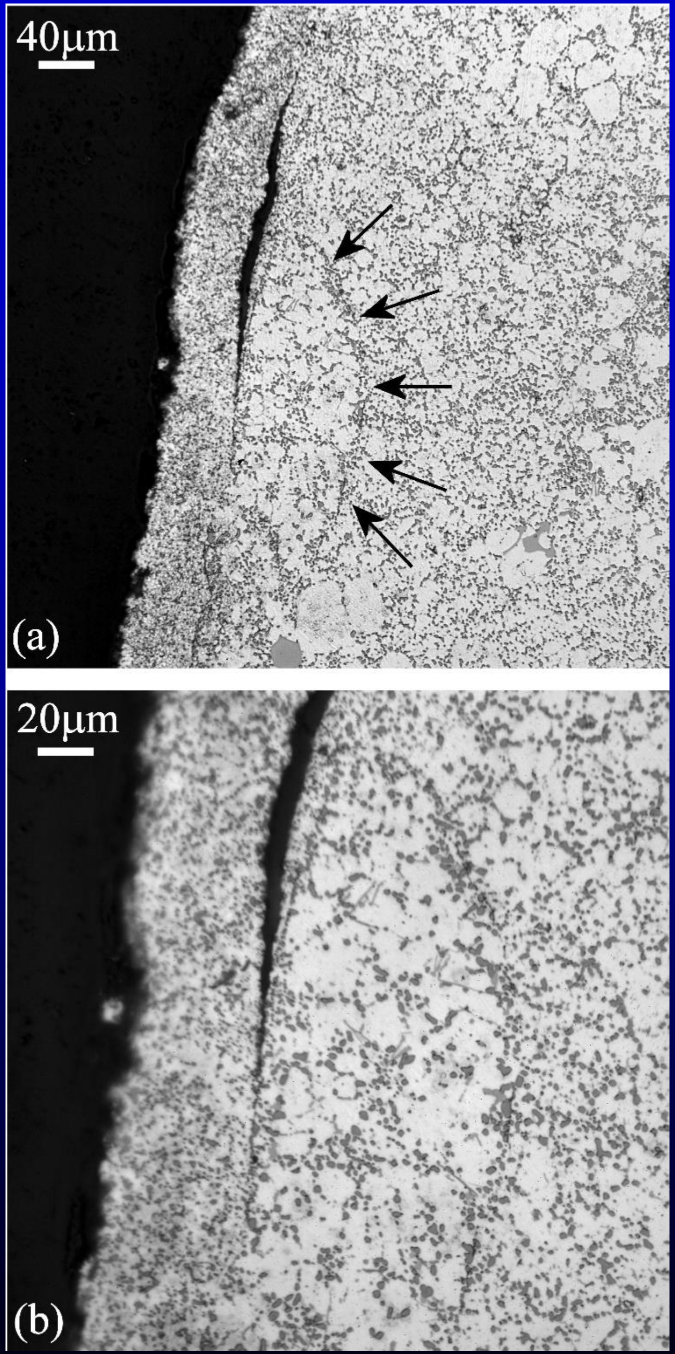
As Cast

No Spherical Pores as cast.

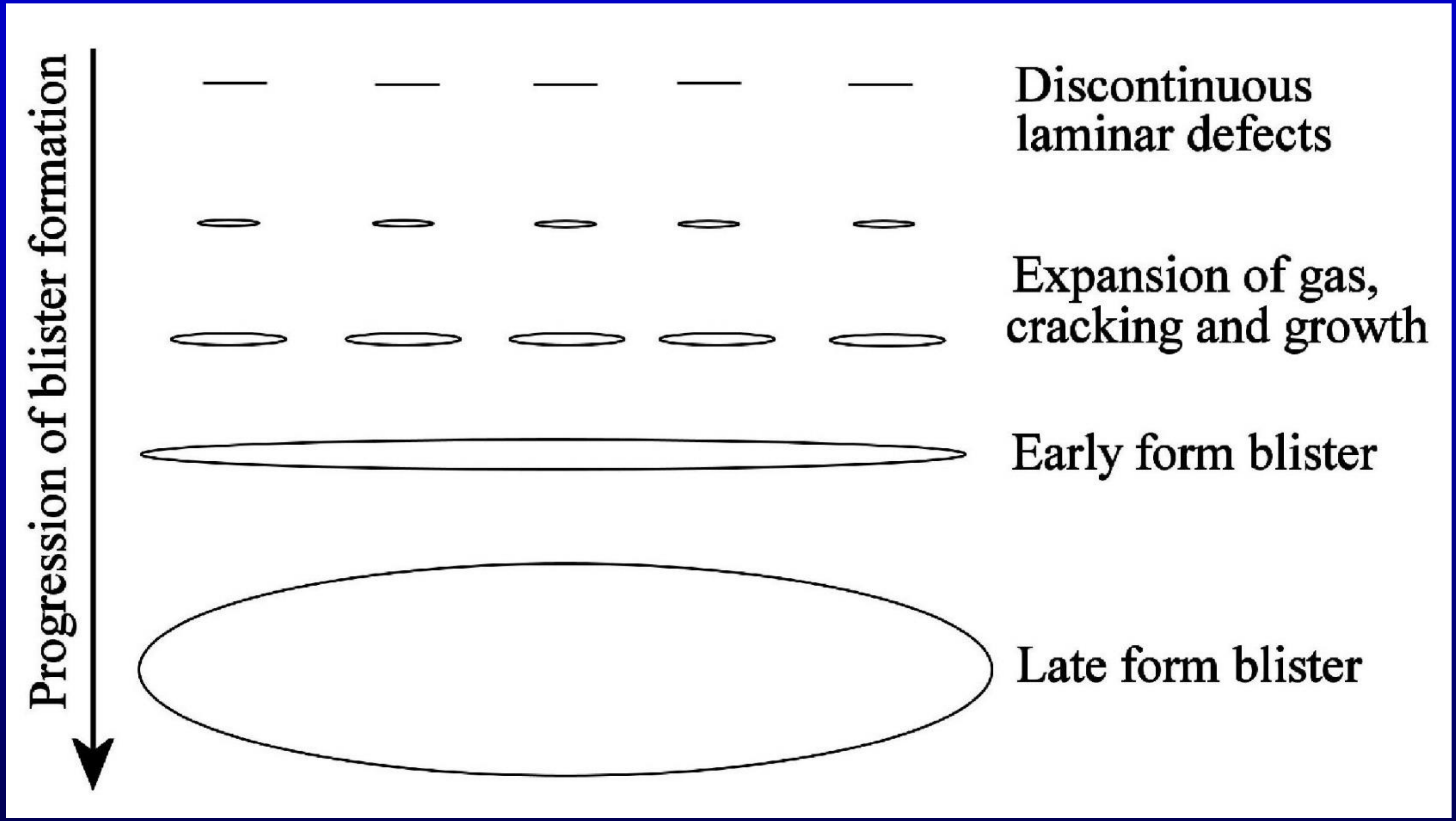


545°C 16h

Gas is clearly present in large quantities!



How do Blisters Form?



It is important to consider that in HPDC that the entrapped gases will co-segregate with or on oxides, especially bifilms.
Time of solidification and cooling is so fast there is no time for other reactions.

R.N. Lumley et.al 2010

Conclusion

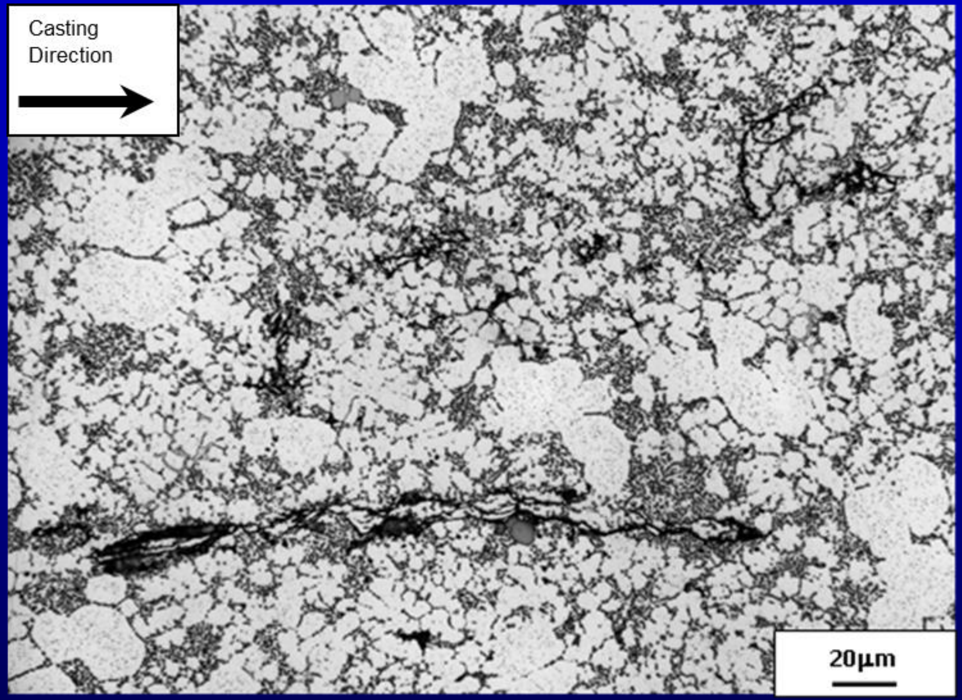
- **Oxides are present in great quantities in HPDC's due to extreme turbulence and their presence can be directly observed. They are present in conjunction with gases trapped under pressure. Blister formation and oxides such as bifilms are critically interrelated.**

Defect structures in HPDC's are extremely complex.

- If the oxide defects etc. are as detrimental as believed, this should show in directionality of mechanical properties, especially if perpendicular to the tensile direction.

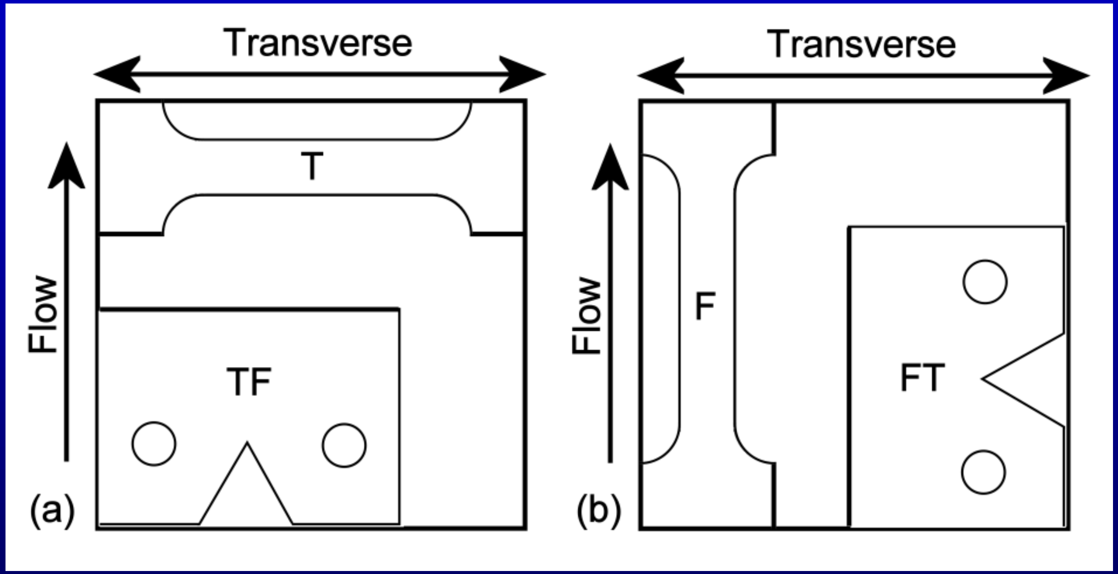
- If you know the flow direction, you know their alignment.
- Fracture will tend to "find" the defects.

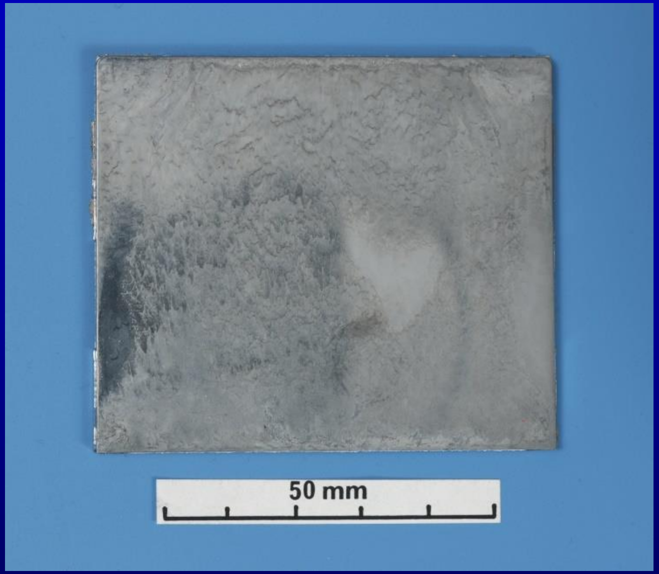
Examples of Laminar Defects



These would be classic oxide bifilms according to literature.

Test Pieces & Notation





Notation	Relates to	Stress axis	Crack axis
TF	Tear test	Perpendicular to flow direction	Parallel to flow direction
T	Tensile test	Perpendicular to flow direction	Parallel to flow direction
FT	Tear test	Parallel to flow direction	Perpendicular to flow direction
F	Tensile test	Parallel to flow direction	Perpendicular to flow direction

Results

Tensile properties for the tested conditions in each orientation

Temper and (Orientation)	0.2% Proof Stress, MPa	Tensile Strength, MPa	Elongation, %
As Cast (T)	158 MPa	302 MPa	3.2
As Cast (F)	156 MPa	333 MPa	4.9
T4 (T)	213 MPa	357 MPa	5.1
T4 (F)	213 MPa	381 MPa	7.3
T6 (T)	331 MPa	392 MPa	2.2
T6 (F)	315 MPa	420 MPa	4.4

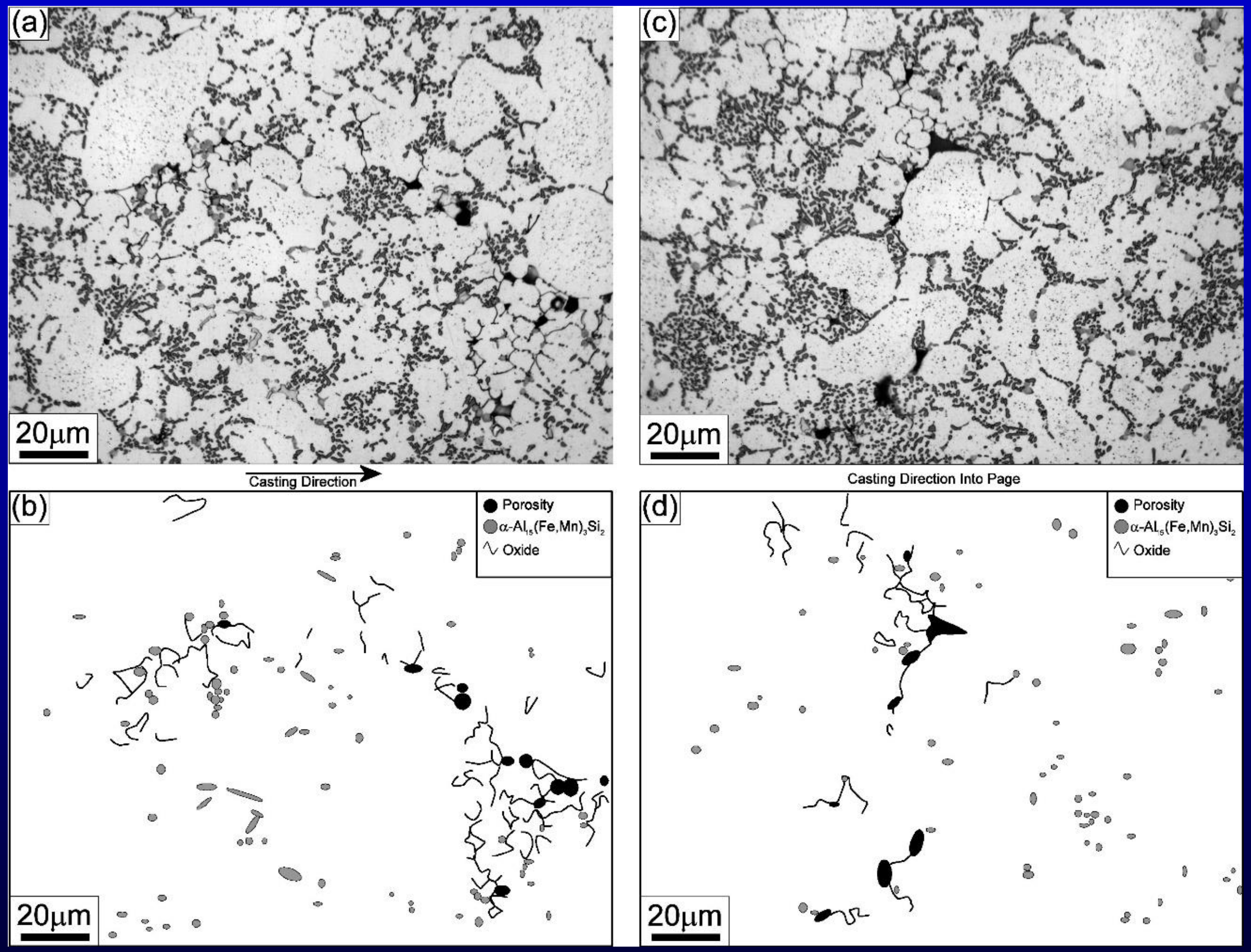
(5 samples per condition)

Tear test properties for the tested conditions in each orientation.

Temper and (Orientation)	Tear Strength (MPa)	Notch Sensitivity	UIE (KJ/m^2)	UPE (KJ/m^2)	UTE (KJ/m^2)
As Cast (TF)	242	1.55	15.9	16.9	32.8
As Cast (FT)	247	1.58	17.7	18	35.7
T4 (TF)	340	1.6	29.2	33.5	62.7
T4 (FT)	341	1.6	32.5	37.5	70
T6 (TF)	288	0.87	14.1	6.3	20.4
T6 (FT)	295	0.92	14.6	8.4	23

F&FT (Fracture perpendicular to flow)   T&TF (fracture parallel to flow)

Defect Maps (2D)

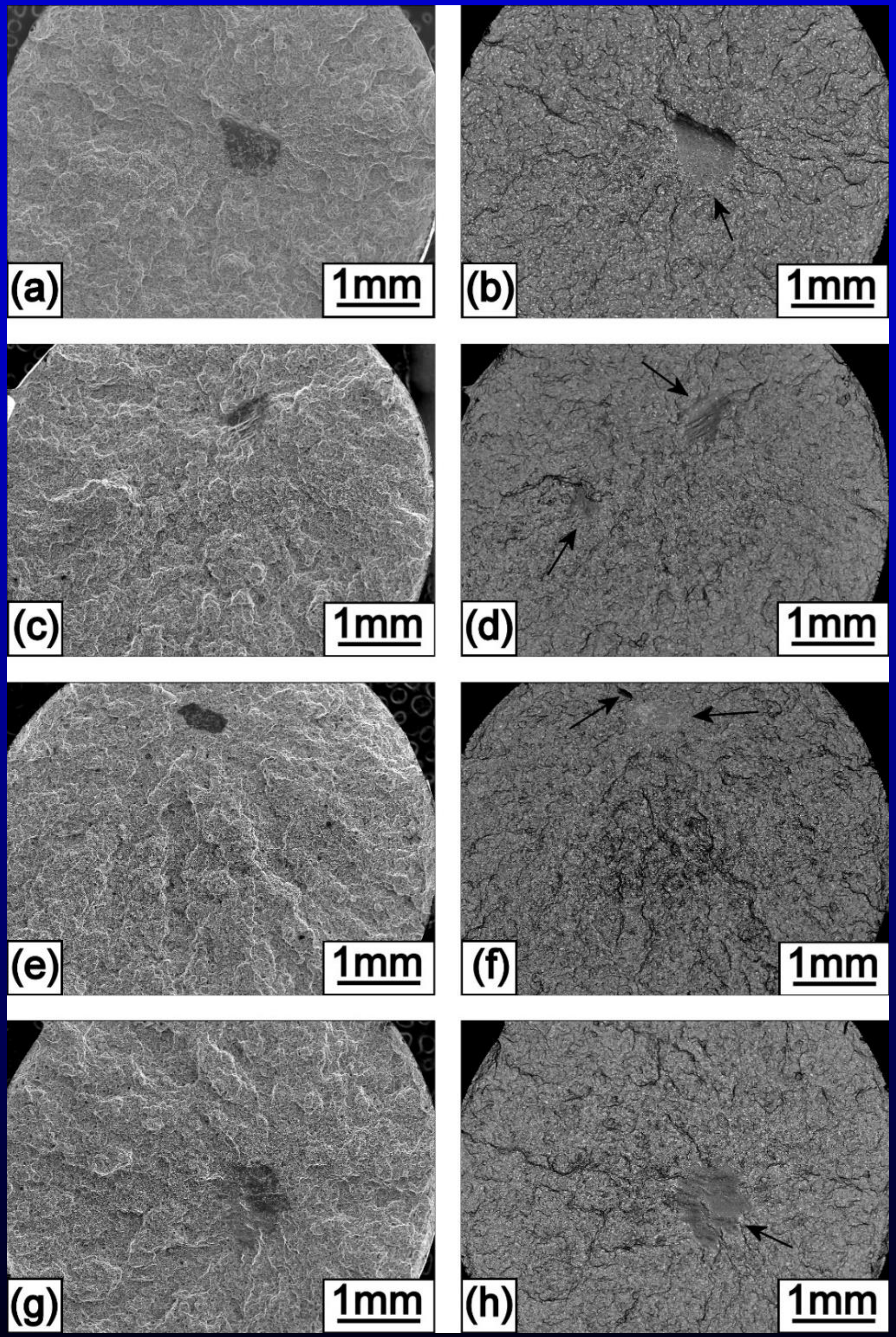


Far more complex than might be thought

Lumley 2016.

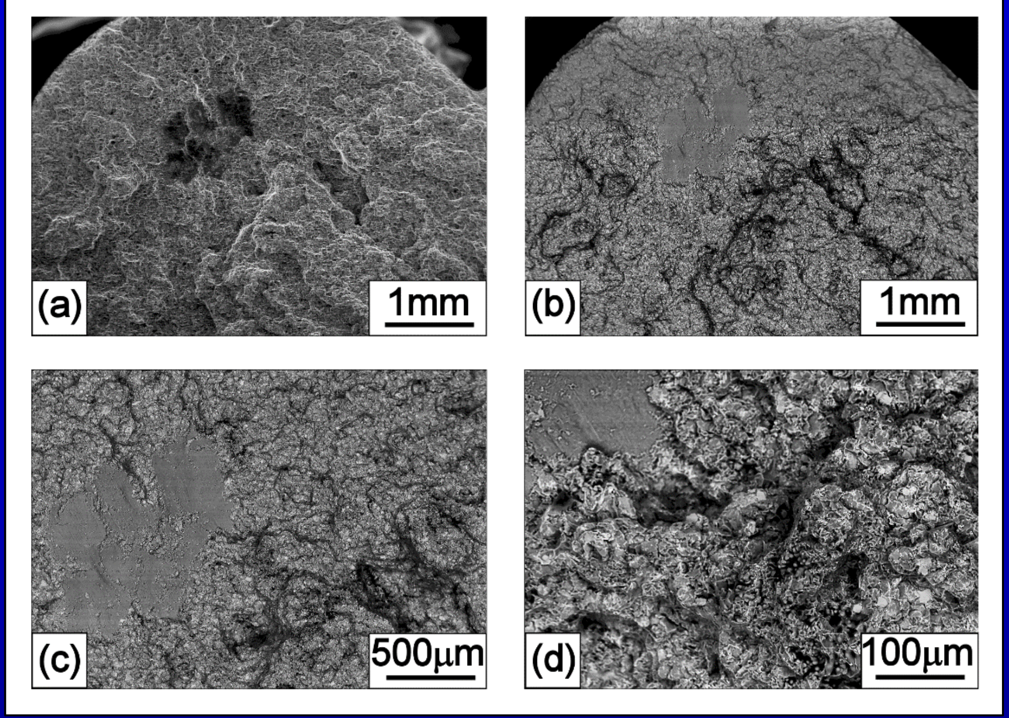
Evaluations of Quality

It is common to find oxide on the fracture surfaces of high pressure diecastings. Actually almost every fracture surface and often in conjunction with other defects.

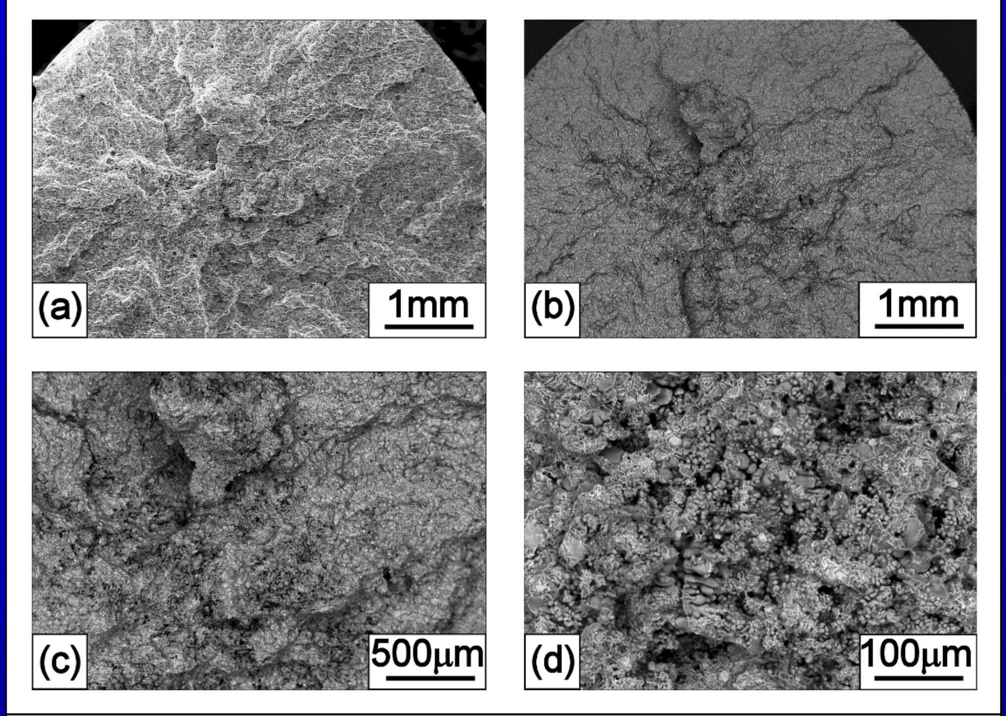


Lumley, 2011

(1)



(2)



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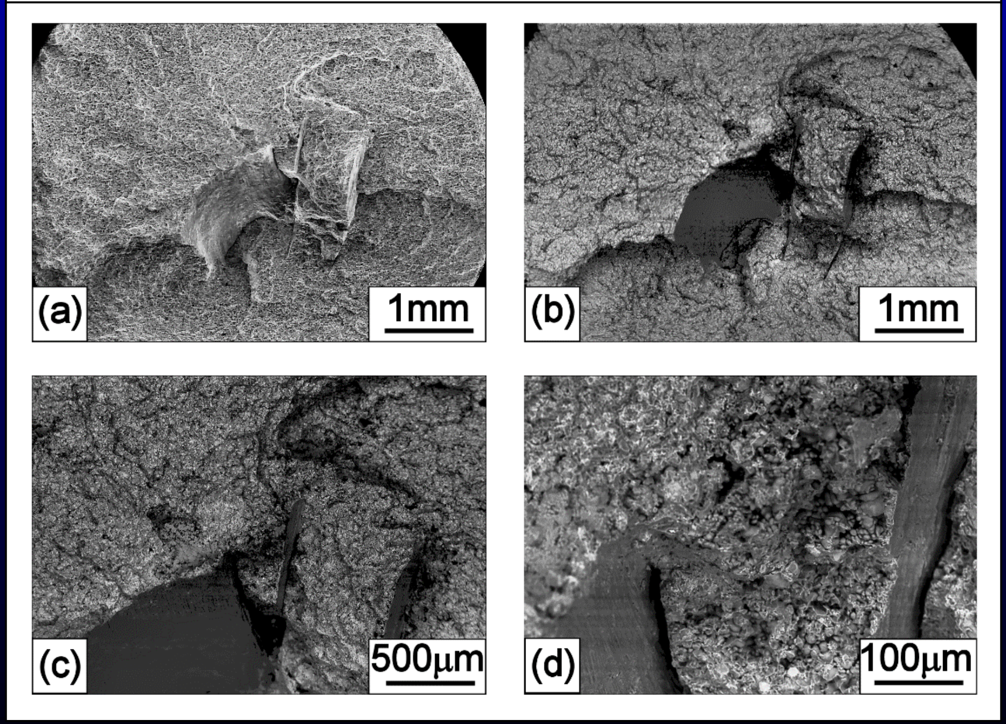


Fracture surface of three different tensile samples.

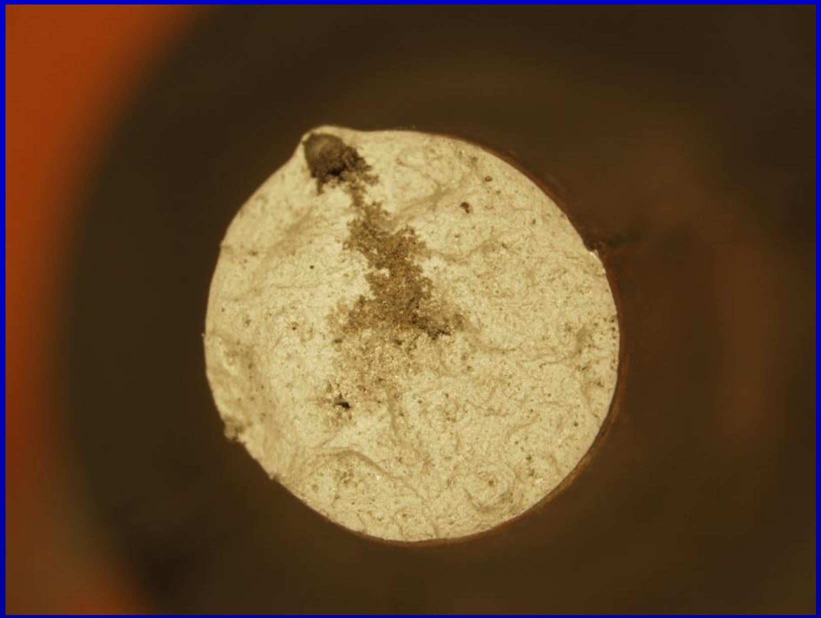
1. Oxides + Shrinkage+ intermetallics
2. Shrinkage + intermetallics
3. Massive Oxides+ intermetallics

Which is worst?

(All displayed virtually identical tensile properties!)

Lumley 2011

Which is the worst defects?

Oxides?
Gas?
Carbonaceous?
Shrinkage?


How about dimensional inaccuracy?

Defect Hierarchies for Aluminium

- **Developed using statistical methods for high pressure diecastings.**
- **Establish the sequence of remedial actions for improvement from most important to least important.**

- 1. MASSIVE POROSITY;
- 2. LARGE OXIDES;
- 3. FOAMY POROSITY CLUSTERS;
- 4. SMALL OXIDES;
- 5. IRON (&MANGANESE) BEARING PARTICLES;
- 6. HOMOGENEITY OF MICROSTRUCTURE (SCALE & COMPOSITION);
- 7. SI MORPHOLOGY;
- 8. DISTRIBUTION OF CU;
- 9. SMALL, ISOLATED POROSITY;
- 10. HYDROGEN CONTENT

R.Lumley, 2011

Conclusion

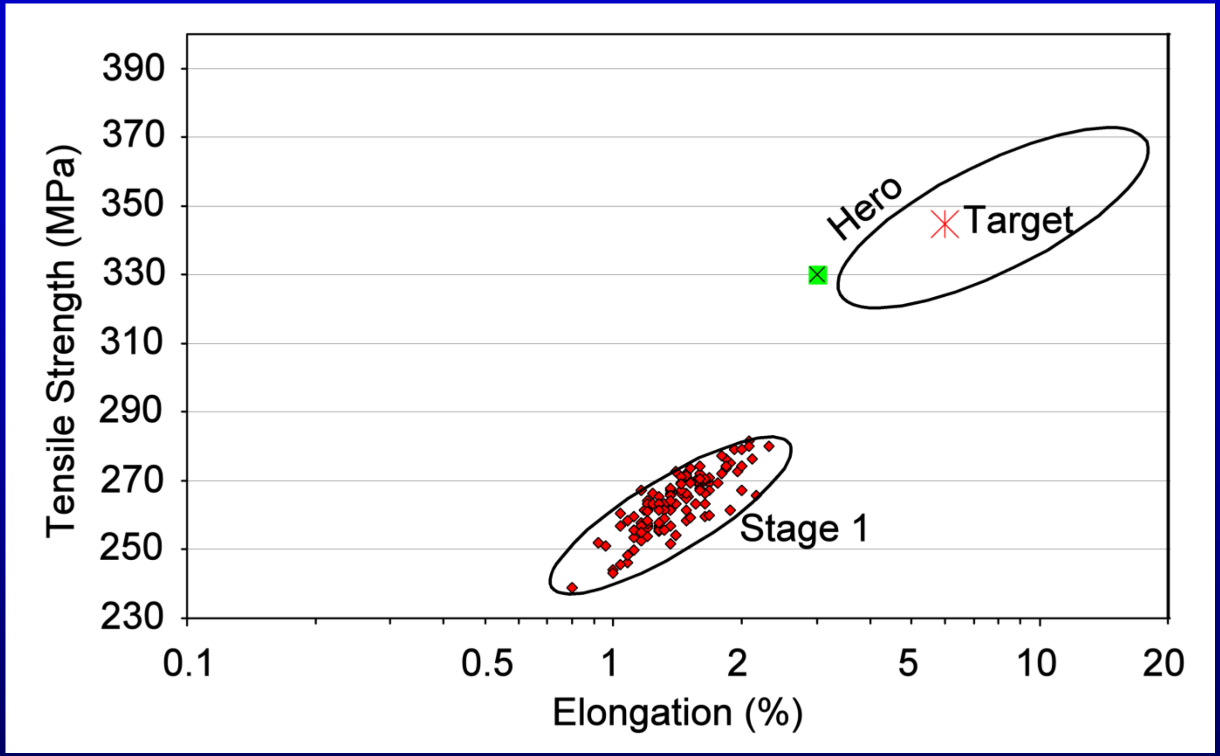
- Oxides are important but they are no worse than other defect types.
- A defect hierarchy can be established which lays a framework for which discontinuities to address first.
- An oxide may have an equivalent effect on mechanical properties to any other kind of defect, but they may be of different sizes.

Investment Cast Aluminium

- Development of the Aluminium Billet Equivalent Process (2011-2015)

- Using the defect hierarchy approach to fast track improvement.

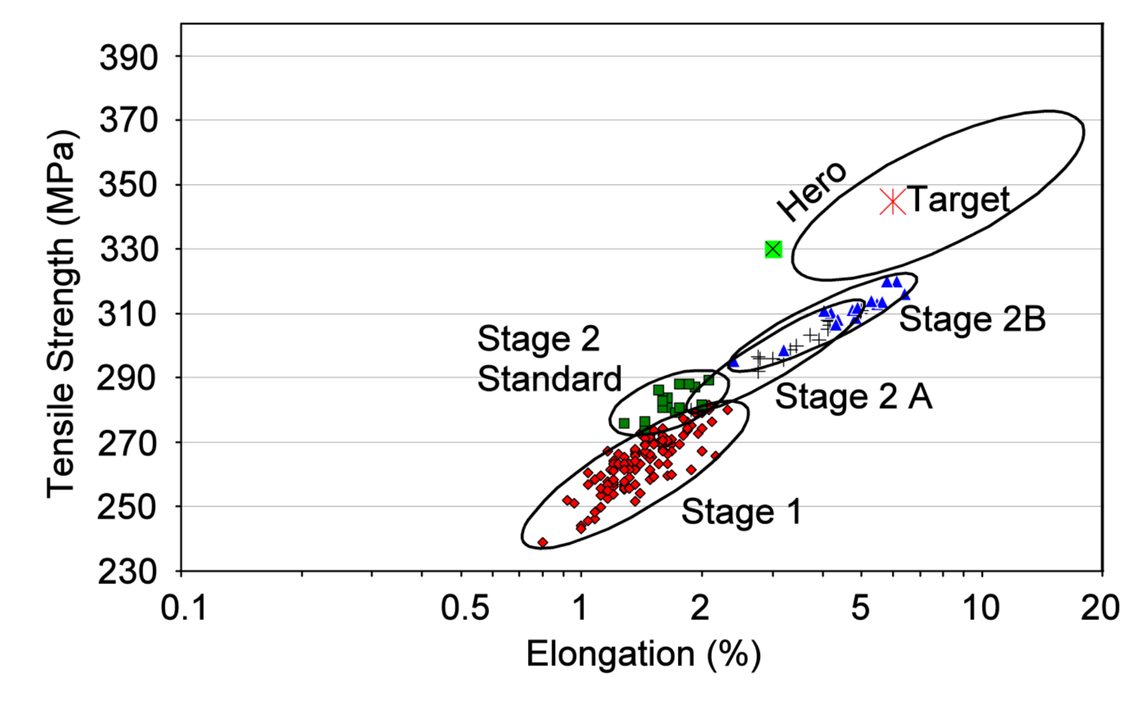
Benchmarked Properties

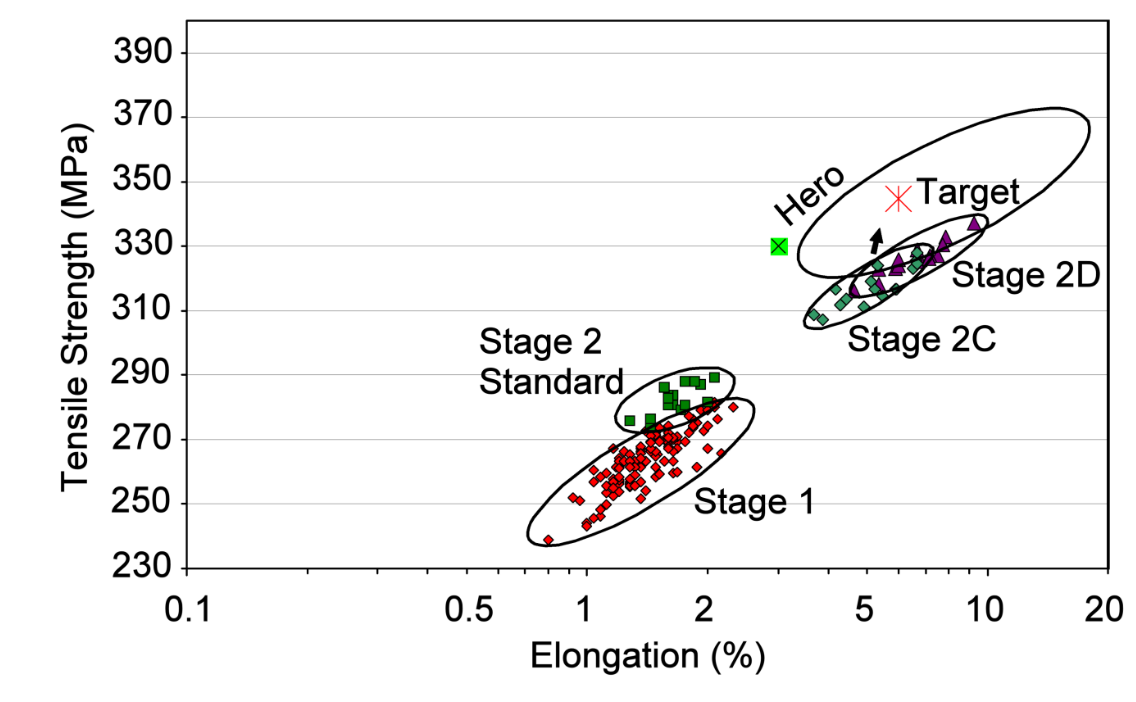


Averages: 227 MPa Y.S; 264 MPa UTS; 1.4% Elongation

Benchmarked properties typical for standard thick wall A357 investment castings

Properties Development as Defect Hierarchies Addressed

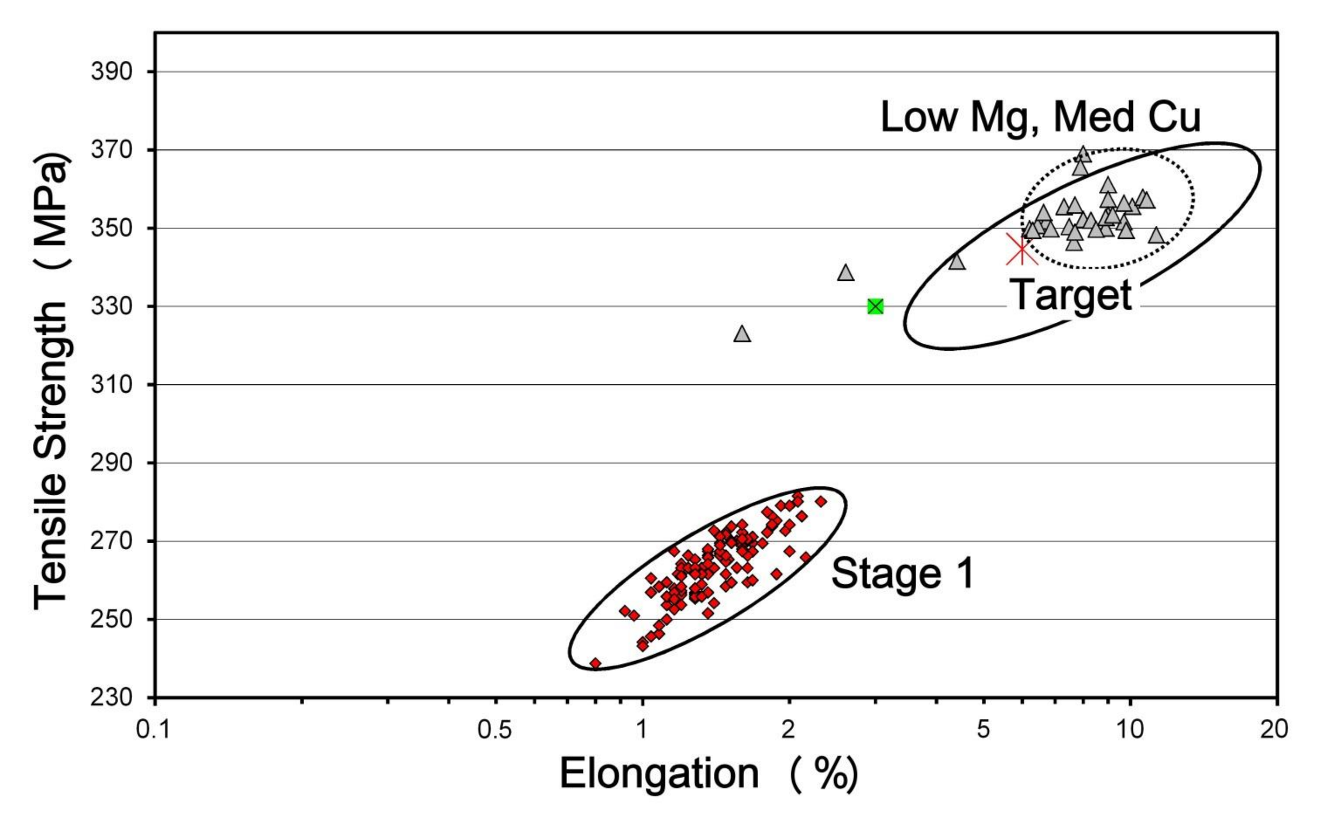




Addressing shrinkage, composition, microstructure, heat treatment

Improved A.B.E process

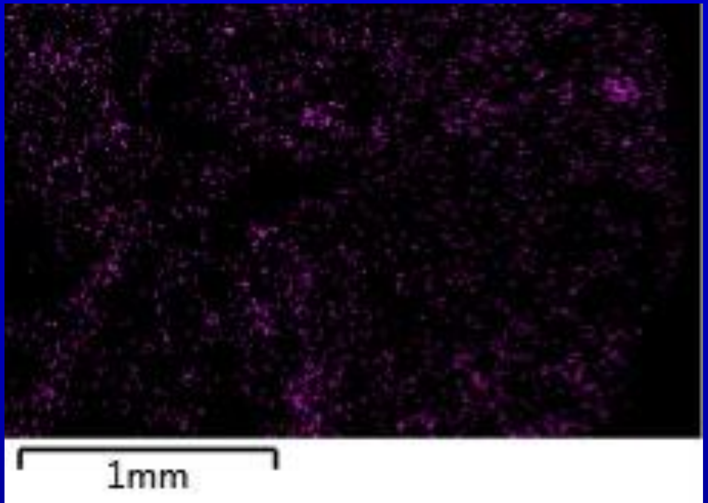
Remnant low values due to a single defect type



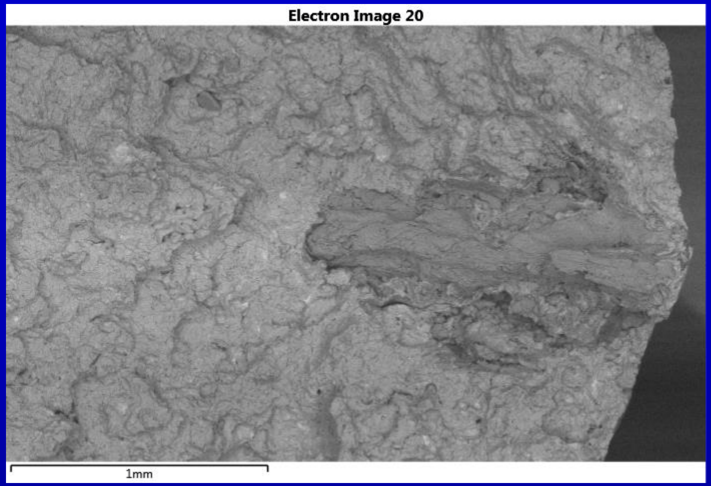
91% meet or exceed target

Addressing Iron, Copper, Strontium, Cooling rate / Homogeneity

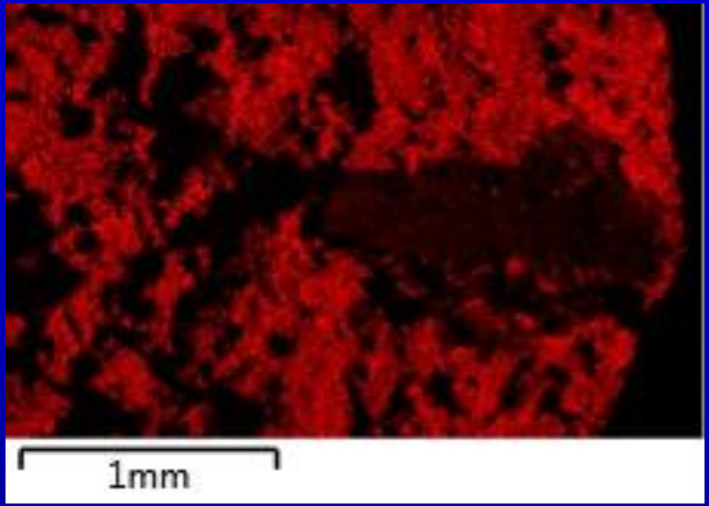
So what were the causes of the low results?



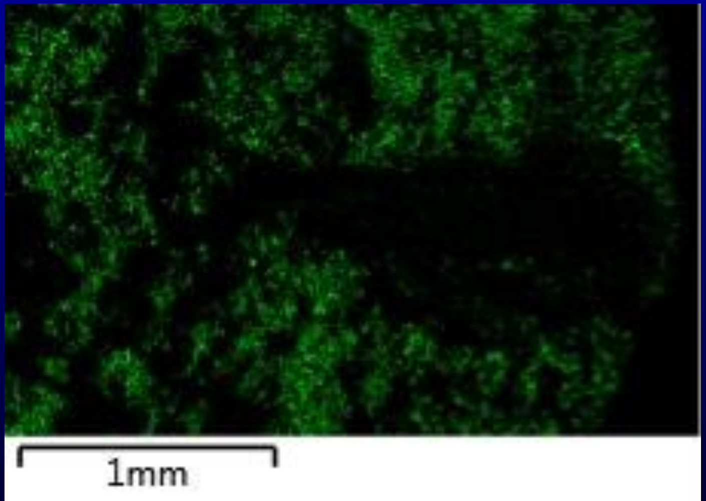
Fe



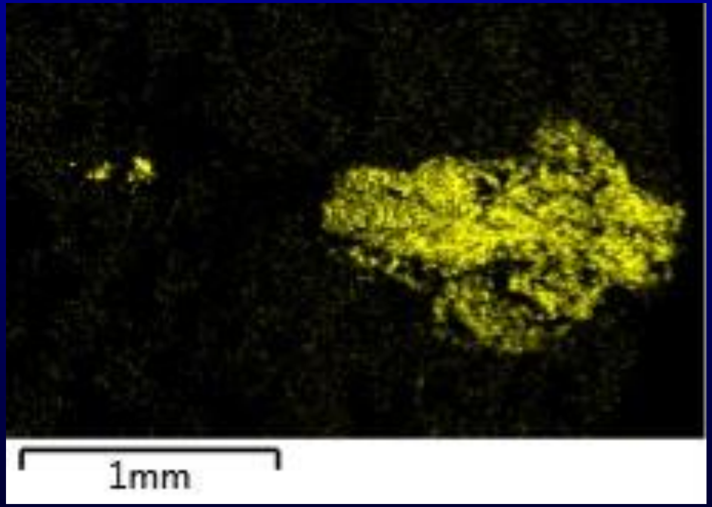
BSE



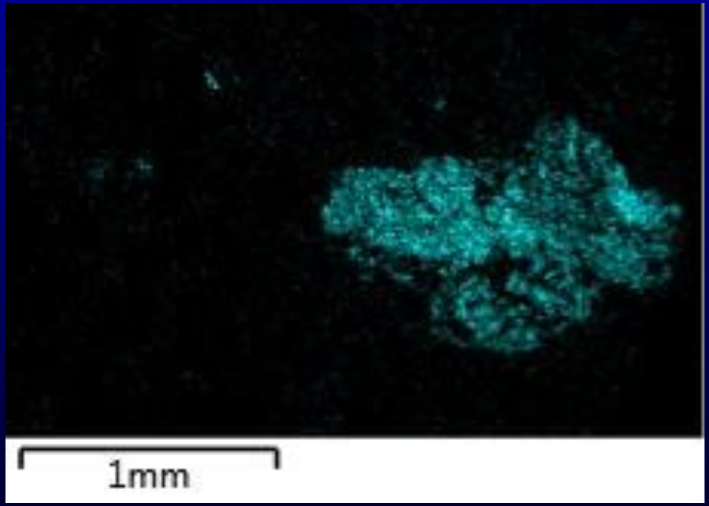
Al



Si



Mg

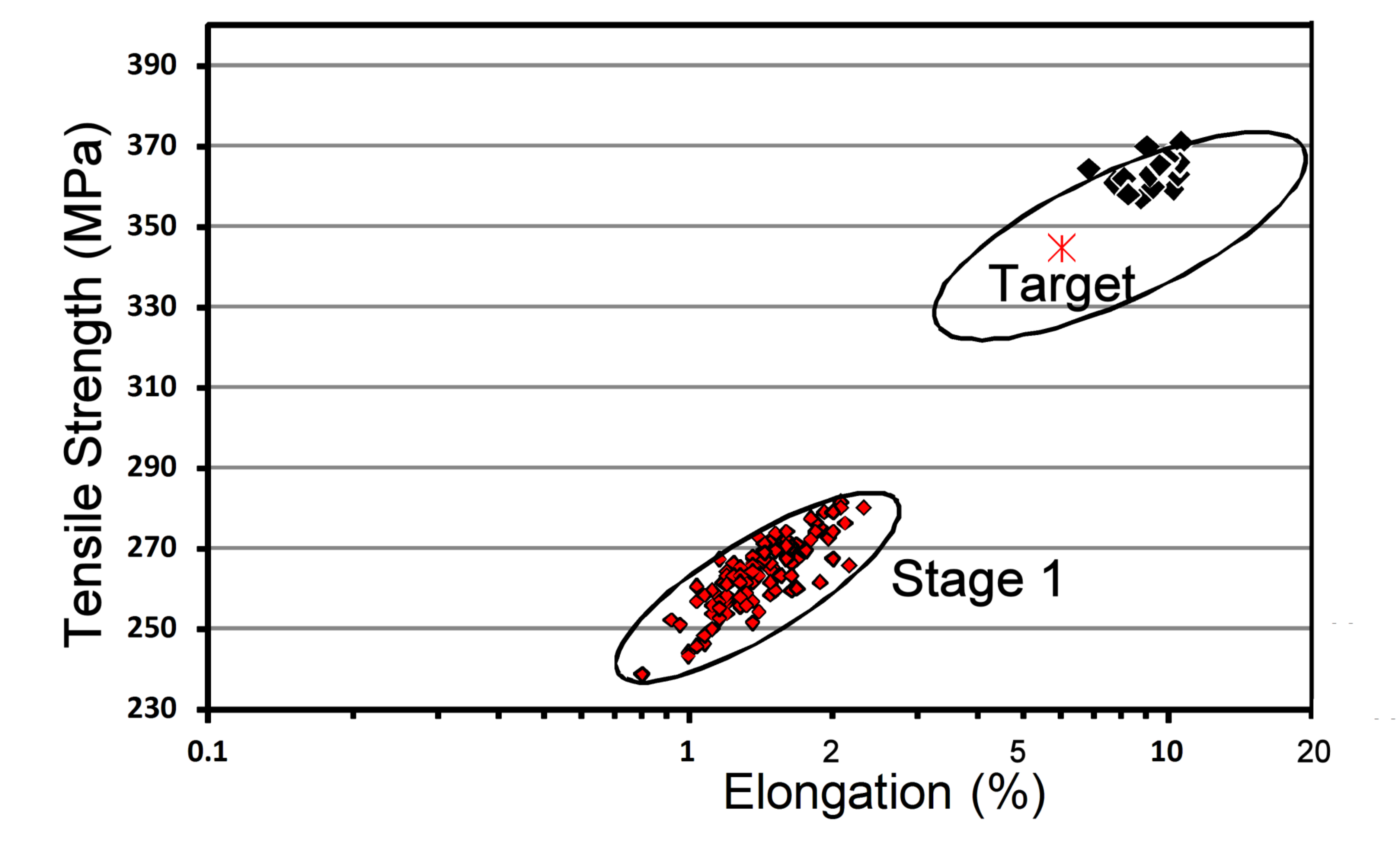


O

Oxides likely to be $MgAl_2O_4$

Courtesy Terri Kittel, CSIRO

Final trials; optimized ABE process



The last step was the recognition and removal of the identified oxides.

Conclusion.

- The defects in aluminium alloys must be addressed in the correct sequence, following the defect hierarchy established for the given alloy.

Aluminium Bronze (& Manganese Bronze)

- Probably the most notorious material in history for oxide bifilms;
- Contains a lot of aluminium by volume and cast at high temperature.
- Historically cast in fatigue limited applications (e.g. boat propellers).
- Gating methods for preventing or minimizing oxides & bifilms published widely since the 1910's.
- Durville Process (tilt casting);
- Meigh Process (modified Durville process for making castings).
- Avoid turbulence and promote directional solidification.

- Read "Casting Brass" by C.W. Ammen
- CDA publication 31: The Aluminium Bronzes by Macken and Smith.
- "Cast and Wrought Aluminium Bronzes" by Harry Meigh.
- Also papers by Geoff Meredith on AlBr.

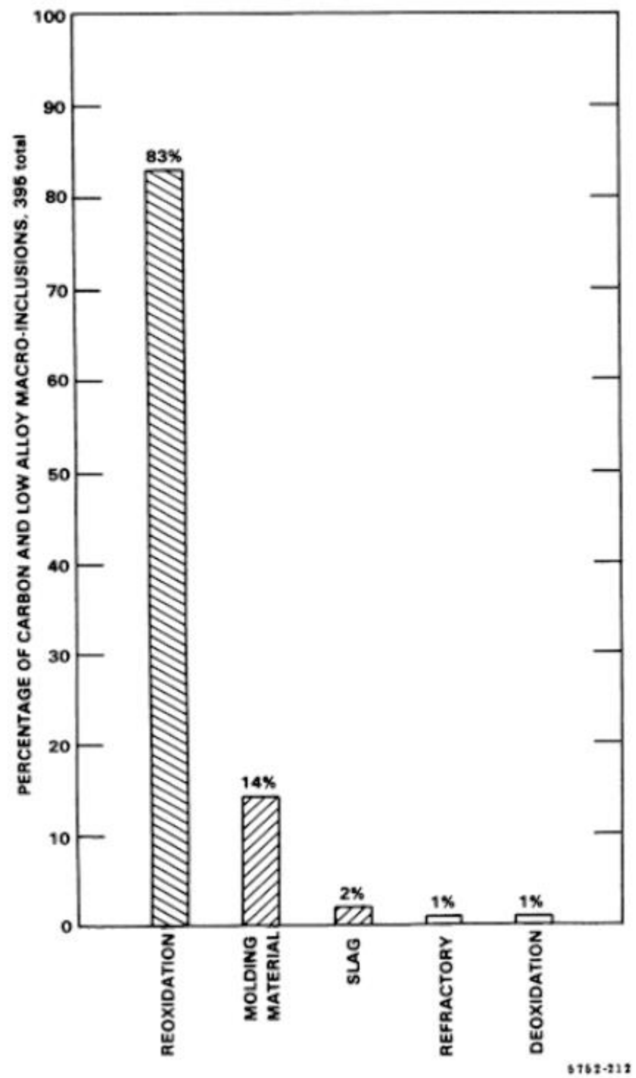
Some Problems with Magnesium Additions in Investment Cast Ductile Iron

←Mg = 0.048%

- Strong tendency to form oxide bifilms at ≥0.04%Mg and when gating is not optimized. These oxides do not segregate to slag.
- Influences tensile properties when present internally. No evidence of Mg reaction with ceramic shell.
- Surface breaking oxides cause NDT failure for Penetrant, Visual inspection or cast tolerances cannot be maintained.

Steel, Cobalt, Nickel

- **Oxides present in the microstructure are almost always fine, spherical and formed as re-oxidation inclusions caused by pour height.**
- **Can be misidentified as gas porosity after shot blast.**
- **Mechanistically, the same causes as bifilms but an entirely different morphology.**



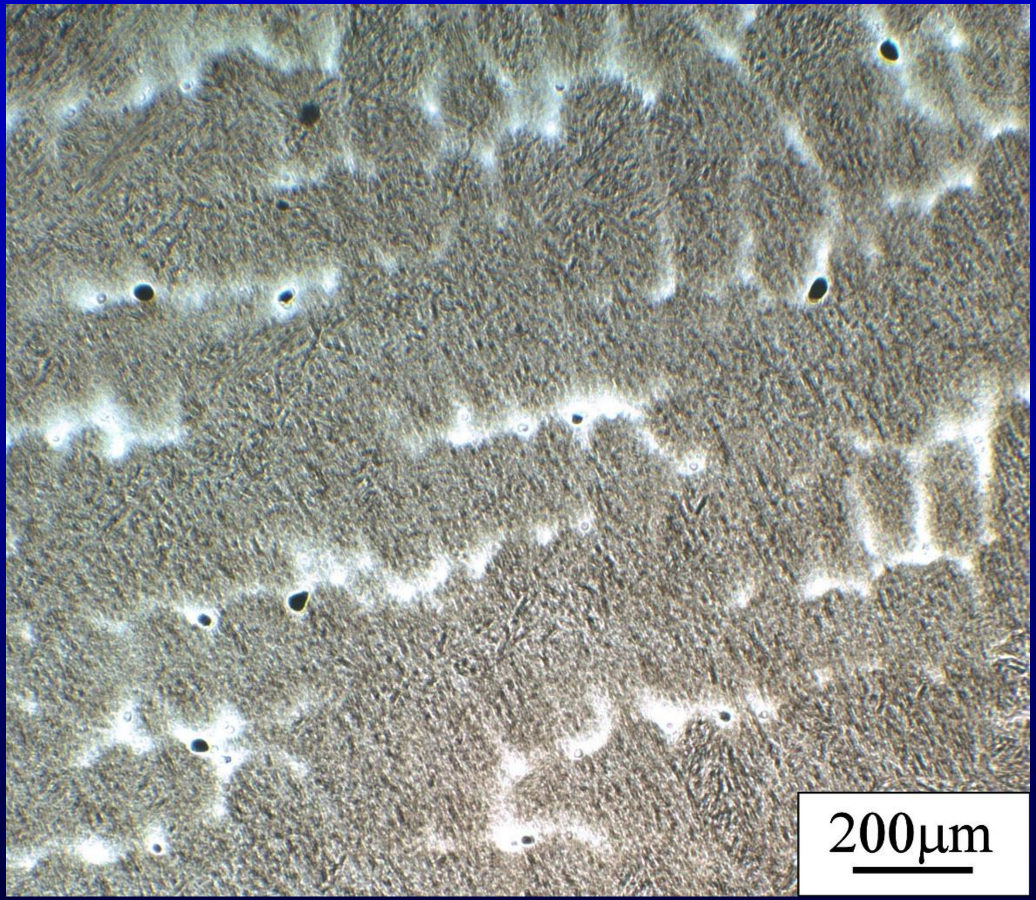
Distribution of macroinclusion sources in carbon and low alloy steel castings

R. Monroe, SFSA

LC2-1 Steel As Cast

Deoxidized with Al.

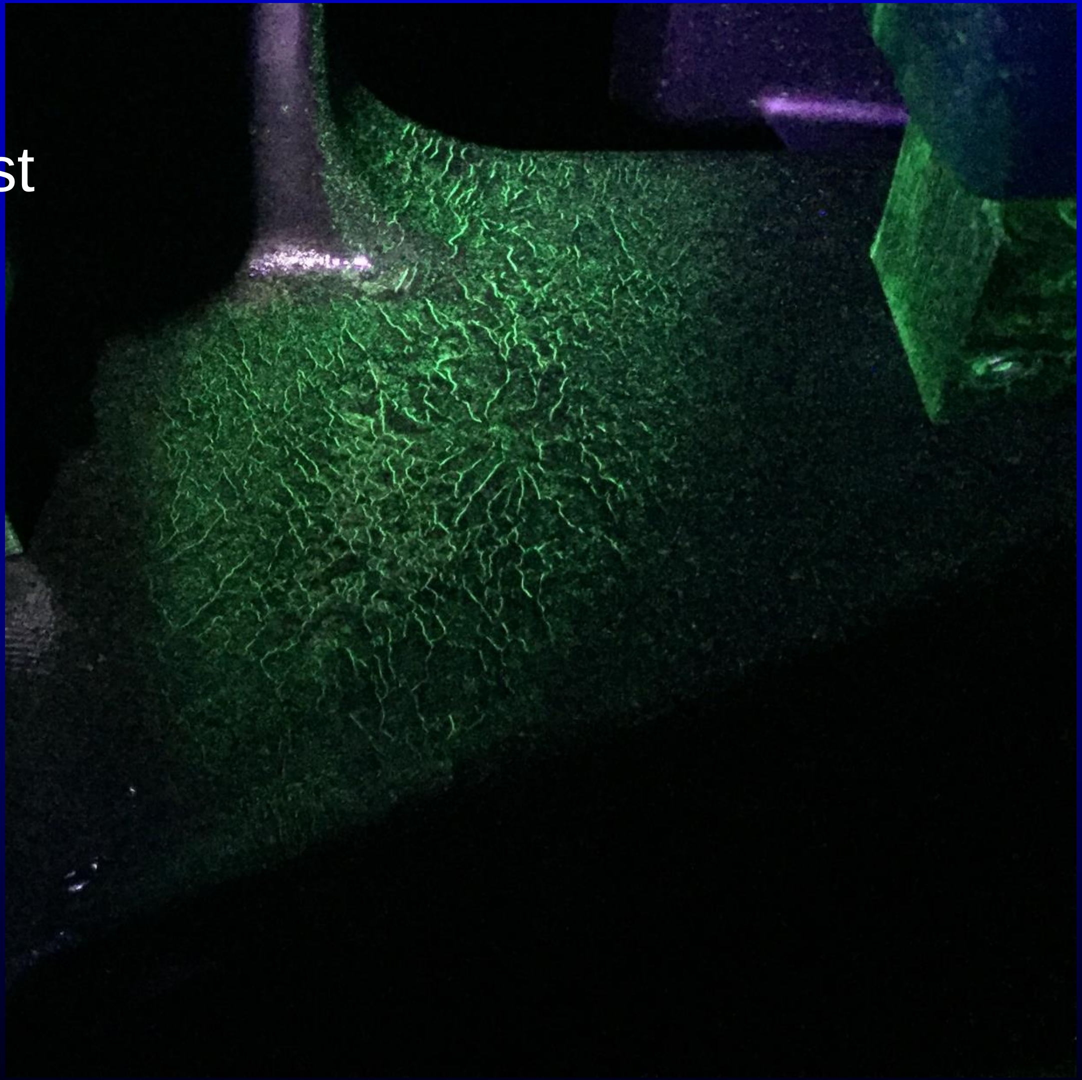
Cryogenic low alloy steel ASTM A352



Oxides are common but innocuous

There are however bigger problems with steel that look a lot like bifilms!

LC2-1 Steel As Cast



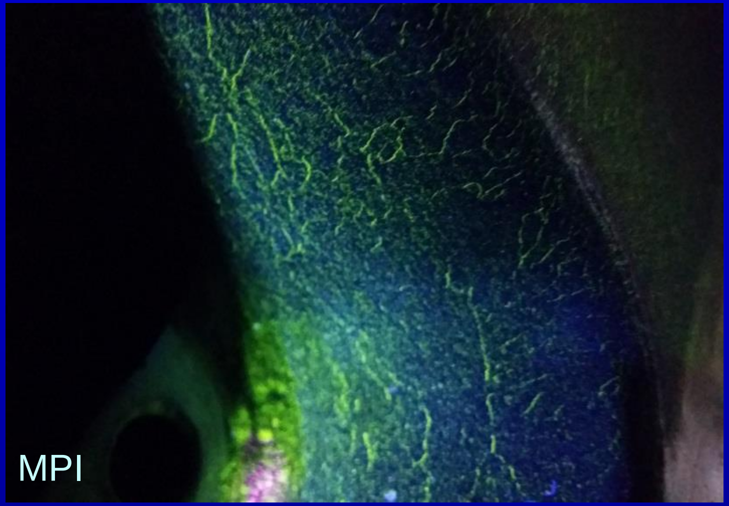
Magnetic Particle Inspection DNC.

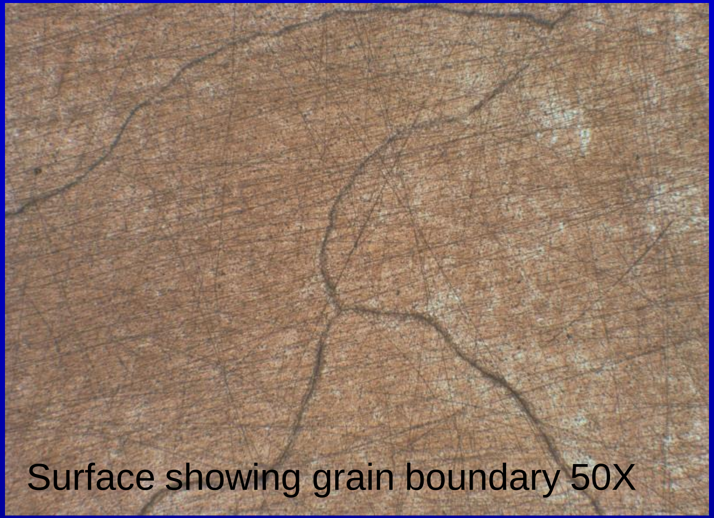
Some penetrate as much as 0.5mm and classify as cracks.

Cannot be detected by Dye Penetrant

Sometimes called “Chicken Wire Defect”

LC2-1 Steel As Cast (Investment Casting)

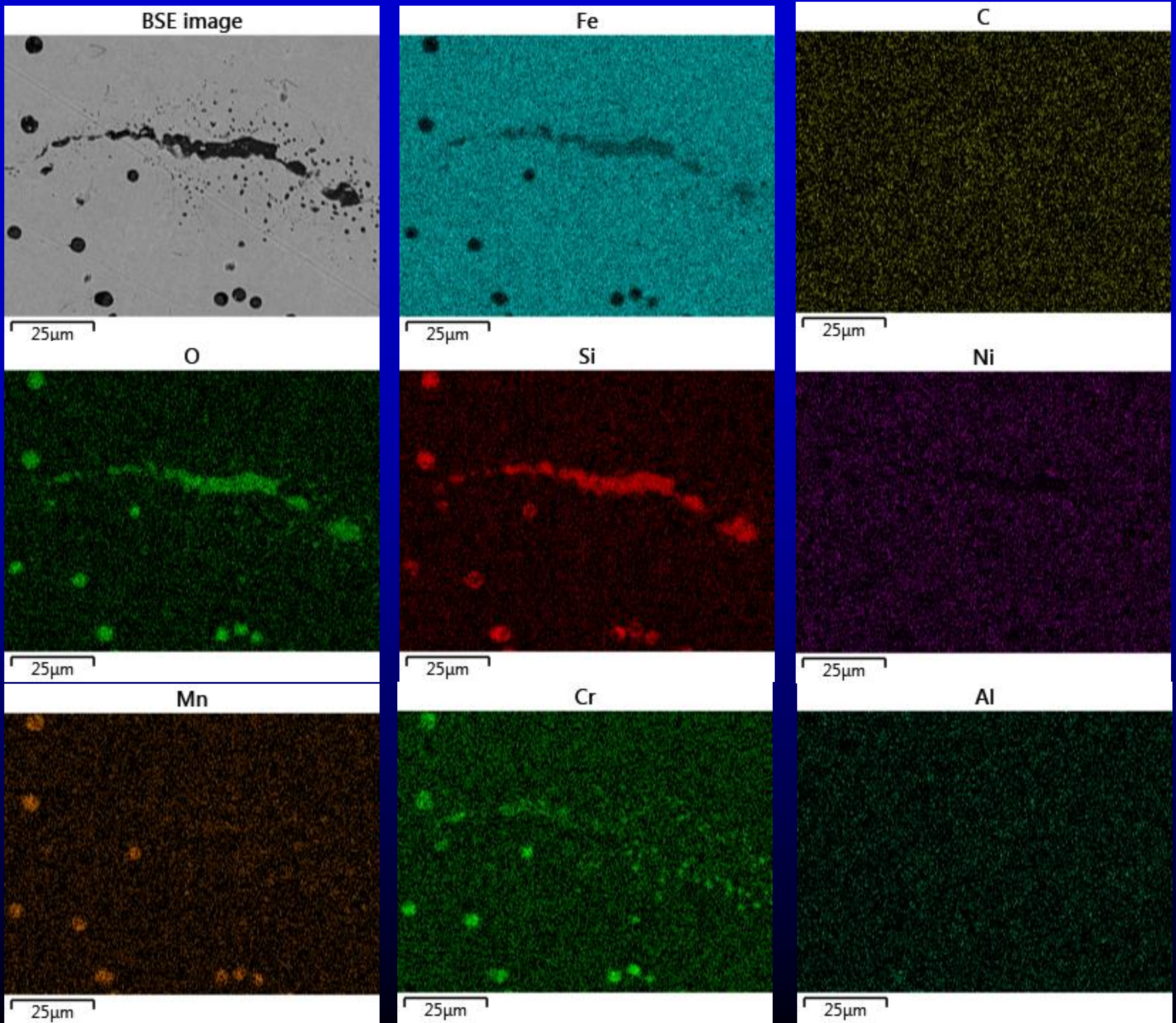




- Linear phase that appears at the casting surface, possibly associated with grain boundaries.

Complex oxides containing Si,Mn,Cr,O

(i.e. fine reoxidation, slag, etc.)



XRAY MAPS

Courtesy Terri Kittel
CSIRO

Summary and Conclusions

- In cast alloys, oxides are extremely complex.
- In Aluminium casting alloys it seems likely the Al_2O_3 may be reduced by a partial reduction reaction with Mg to form spinel, $MgAl_2O_4$. This also facilitates sintering of aluminium powder. Small oxides should be rendered innocuous.

- Defect structures in HPDC's are extremely complex. Oxides and gases appear to co exist and give rise to blisters. It is likely both may segregate to the last areas solidified.

- Establishing a defect hierarchy allows for the identification and elimination of defects. The defects must be addressed in the correct order, following the defect hierarchy for the given alloy.

- Some materials such as ductile iron and aluminium bronze, are especially impacted by oxide films.

- Not all cast materials display oxide bifilms. In particular, steel, cobalt and nickel tend to be form small, spherical oxides, well distributed. These materials may have other kinds of linear oxide defects that require addressing in a different manner.

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